

INVESTIGATION OF THE  
SEDIMENTS AND POTENTIAL  
MANGANESE NODULE RESOURCES  
OF GREEN BAY, WISCONSIN

J.R. Moore, R.P. Meyer, and C.L. Morgan

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Sea Grant Laboratory

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J. R. MOORE, R. P. MEYER, AND C. L. MORGAN

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GEO-ENVIRONMENTAL AND MINERAL RESOURCES PROGRAM



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## FOREWORD

As the initial minerals resource investigation of the University of Wisconsin Sea Grant Program, this study of the sediments and manganese nodules of Green Bay, Wisconsin, has brought forceful attention to the resource potential of the Great Lakes. Moreover, the importance of also conducting a base-line geo-environmental survey, in addition to describing the sediment and manganese resources, cannot be overlooked. This is particularly so in the present period of awakening national concern for environmental safeguards in further use of the Great Lakes.

While the economic implications of the manganese deposits are not fully known --- they are complex and related to many factors --- the recognition and assessment of this modest resource suggests that other and perhaps more valuable mineral resources lie beneath the sovereign waters of the State of Wisconsin. Indeed, the potential for adding to this nation's mineral wealth by exploring all the Great Lake floors and sub-lake rocks is only now coming to the attention of mining companies and state and federal agencies. Such surveys as this also provide clues to pollution sources, to sites where underwater engineering and construction may be planned, and to new sources of sand and gravel.

It is our desire to see this technical report, with its wealth of scientific data, widely circulated through the industrial sector. Further, we solicit comments from the reader in regard to economic, scientific and regulatory matters which pertain, or may eventually pertain, to man's use of Green Bay, Wisconsin.





## ABSTRACT

During the period of June 1968, to August 1972, with Sea Grant support, staff personnel of the University of Wisconsin conducted a comprehensive survey of the sediments, sub-lake geologic structures, and manganese nodule resources of Green Bay, Wisconsin. The objectives of the investigation were largely confined to mapping and assessing the sediments and manganese mineral resources, to determining sub-lake structures of concern to engineering development or source of metals, to characterizing the polluted muds and their sources, and to providing an environmental base line. In meeting these objectives, the USCGC MESQUITE was used to make over 1,000 miles of seismic profiles, to obtain over 700 core and dredge samples, and to obtain selected bathymetric and water chemistry data. The shipboard work was confined to 1968 and 1969, and detailed laboratory investigations were subsequently conducted, terminating in August of 1972. A low grade manganese resource in the form of small nodules (1.5 to 10.0 mm in diameter) was identified and mapped. While the manganese content is reported to vary from 4.4% to 16.0% by weight, the nodules in themselves are of potential economic value due to their high specific surface area and possible use in catalysis and chemical absorption applications. The overall manganese deposits cover approximately  $1.3 \times 10^3 \text{ km}^2$  of lake floor. However, the Mn-rich nodules are largely confined to two sites in the middle bay area, and the largest nodules --- potentially useful in absorption processes --- are confined to the area around Sturgeon Bay. Correlation studies indicate a fairly strong correlation between Mn and the group IIA cations Mg, Sr, and Ba. Comparisons between nodule com-

position and associated sediment composition reveal no apparent relation between nodule and associated sediment composition, though a correlation between nodule size and mean sediment size is likely.

X ray diffraction analyses of several bulk surficial sediment samples and microscopic point counts of selected samples show that the Green Bay sands are predominately quartzose and feldspathic with an unexpectedly low concentration of carbonate minerals. Orientated diffractograms of the silt and clay fraction suggest the presence of Kaolinite, chlorites, and several micas, but no expandable layered clays were detected.

The study has not been concerned with explaining complex geochemical processes, although some conclusions regarding sediment and manganese origin are presented. While the ferromanganese deposits have been, and continue to be, the subject of economic interest by several companies, exploration and extraction permits are presently being held in abeyance until legal and operational guidelines are prepared by the state. To aid in effective utilization of the manganese nodules, we recommend that mining guidelines be established, and in order that industry may further research other uses of the nodules, we recommend that substantial bulk sampling be made, particularly of the large nodules near Sturgeon Bay.

## ACKNOWLEDGMENTS

Our study of Green Bay sediments and manganese nodules has been made possible through the cooperation and indefatigable effort of many people. Accordingly, we extend our thanks to the officers and crew of the Coast Guard Cutter MESQUITE who made shipboard operations possible; to Carol Anne Hall, James Kosalos, Thomas Meyer, and Lee Powell for their able assistance in dredging and in geophysical surveying, and to Richard Cashwell for many of the early analyses. Laboratory investigations including data processing and charting, chemical and petrographic analyses have been conducted by David Henry, Morton Wakeland, and Carol Anne Hall. We are also appreciative of the interest of many citizens of Sturgeon Bay, Wisconsin, who provided services and supplies during two summer surveys. Most of the shallow samples were collected by Dennis Van Buskirk, who also served as chief diver on the project, and to whom we are indebted for working under demanding conditions of rough seas and cold water. During the course of the study we benefitted from counsel and exchange of ideas with our fellow scientists at the University of Michigan, particularly Dr. Ted Callender. Lastly, we gratefully acknowledge the financial support given us through the Sea Grant Program, and the supplementary support of Mobil Oil Corporation. While all of the above have contributed to the success of this investigation, the authors alone assume responsibility for the interpretations, conclusions, and the limitations of the research.

## CHAPTER 1

### INTRODUCTION



## I, A. Purpose of Study

The purpose of our investigation has been four-fold:

- (1) - to map and characterize the sediments flooring Green Bay in terms of their texture, mineral content, chemical content, and origin
- (2) - to map and assess the economic potential of the manganese deposits covering much of the bay
- (3) - to determine the sub-bottom geologic structures and bay floor physical conditions as they relate to engineering development, and, in part, to possible sources of metals
- (4) - to characterize and chart the source and dispersal patterns of polluted muds entering the bay from the Fox River

While these were the stated objectives made early in the survey, in accomplishing our survey tasks we have also provided --- through detailed field and laboratory work --- a modern environmental baseline for future reference by others. The intensive sampling and geophysical profiling has never been conducted on such a scale for any other body of water in the Great Lakes, and such detail makes Green Bay unique among the studied fresh water bays in the Great Lakes.

We would also point out that the manganese deposits in Green Bay have been known for many years, although they had never been scientifically surveyed, mapped, nor characterized as a specific mineral resource. Interestingly, Mr. Peter Renfro, a former student in Professor Twenkofel's sedimentation class at the University of Wisconsin, informed one of us (JRM) that Twenkofel mentioned Green Bay manganese-rich sediments (and other Wisconsin lakes with manganese) in his lectures during the 1940s. Moreover, a few samples of Green Bay manganese deposits had been collected prior to our investigation (Callender, 1969), although these were obtained for geochemical study and not to assess the resource. Thus, our investigation has been pragmatic in nature as far as the manganese is concerned: map, identify and assess the deposits as a mineral resource. To this end, our efforts have been directed, and, in fact, this is the substance of our purpose and our present report.

Philosophically, the principal investigators have approached the problem of conflict between extraction and preservation using the concept of multiple use of the environment. While such a concept is not one with precise definition, it seems to us that it does provide for an avenue of cooperation leading to wise use. We, too, are concerned that the environment not be further spoiled; we also believe that preferred extraction, with realistic guidelines, can be conducted for the benefit of all sectors.

This attitude has clearly influenced our approach to this study, and we feel that any shortcomings inherent in the concept are balanced in total consideration.



## I. B. 1 & 2. DESCRIPTION OF THE AREA

### GEOLOGY, REGIONAL SETTING, AND HYDROLOGY

Green Bay is located in the northeastern part of Wisconsin with southern and northernmost boundaries at the city of Green Bay, 44°31' N, and Big Bay de Noc, 45°54' N respectively. It is bounded to the west by portions of Michigan and Wisconsin and to the east by the Door Peninsula, Wisconsin. The Door Peninsula, along with Washington, Rock, and St. Martin's Island, separate Green Bay from Lake Michigan. The general trend of the elongated body of water is from southwest to northeast. Generally, depths of the bay are less than 100 feet. The deepest point is only 176 feet, occurring four miles west of Washington Island. Green Bay is very shallow in the southern portion (less than 40 feet) with increasing depths to the north toward the middle of the bay. The bathymetric contour lines roughly parallel the bay. (Fig. 1)

The approximate length of the bay is 120 miles, and it averages 12 miles in width. The area of the bay is estimated to be approximately 1,500 square miles. The surrounding topography ranges in elevation from 580 feet above sea level along the shore of Green Bay to 900 feet above sea level along the northwestern side of the Green Bay valley.

The regional geology consists of several sedimentary units ranging in age from Cambrian to Silurian which dip to the southeast with a slope of less than one degree. The strike of these units roughly parallels the trend of the bay. These sediments were laid down during the Paleozoic era over the subsiding Precambrian Canadian Shield. They are typically shallow marine deposits of

dolomite and sandstones. The various units along with their age and average thickness are as follows:

UNIT	AGE	THICKNESS
Niagara Dolomite	Silurian	300'-700'
Richmond Shale	Ordovician	200'-350'
Galena-Black River Dolomite	Ordovician	200'-350'
St. Peter Sandstone	Ordovician	0 -330'
Prairie du Chien Dolomite	Ordovician	200'
St. Croixan Sandstone (Potsdam)	Cambrian	500'-1000'

The resistant Silurian Dolomite of the Door Peninsula causes the eastern shores of Green Bay to have either cobbly beaches or steep rock cliffs with fine grain muds offshore. The gently shoaling water on the western shore reflects the soft Ordovician shale geology. It is the erosion of these soft sandstones and shales that produces the low gradient beaches along the western shore.

A complex of crystalline igneous and metamorphic rock occurs to the west of these sedimentary units. This 600 million year old bed-rock represents roots of ancient mountains. One is referred to the geologic map of the area (Fig. 2 Geo.) for a better understanding.

The major water input of the bay is from the drainage of two river basins --- the Fox-Wolf and Menominee-Oconto-Peshtigo River Basins. A general description of these two basins follows.

#### FOX-WOLF RIVER BASIN

Draining this basin is the largest river which empties into Green Bay --- the Fox River. This river flows into Green Bay from the largest inland lake in Wisconsin --- Lake Winnebago. The river actually enters the bay at the city of Green Bay in the southernmost portion of the bay.

The basin itself is located in two geographical provinces, the Eastern Ridge and Lowlands and the Northern Highlands. The Eastern Ridge and Highlands is a continuation of the depression occupied by Green Bay. The drainage area of the Fox-Wolf River Basin is approximately 6,520 square miles. It has been estimated that the Fox River contributes to the bay 40 tons of sediment per square mile per year.

The drainage pattern of the basin is controlled by the topography of bedrock surfaces. The region may be described as having relatively broad flat plains with several north-south ridges dominating the topography. The most significant of these ridges is the Niagara Cuesta which forms a high escarpment east of Lake Winnebago. The escarpment is due to the differential erosion of the Niagara Dolomite and Richmond Shale. The escarpment is not discernible everywhere because of glacial drift covers.

The Prairie du Chien Group and St. Peter Sandstone form the principal bedrock aquifers in the basin. The Niagara Dolomite, although not in the basin, forms an important aquifer to the east of the basin. Where thick, permeable, extensive aquifers underlie the basin, base runoff to streams is large and the streams have a consistently high sustained flow. Conversely, where aquifers are impermeable and very thin, base runoff is low and the stream flow is highly irregular.

#### MENOMINEE-OCONTO-PESHTIGO RIVER BASIN

The location of this basin is adjacent to and north of the Fox-Wolf River Basin, and west of Green Bay. The two major rivers that drain this basin are the Oconto and Menominee rivers. The entire basin covers approximately 4,300 square miles. It is bounded by the

Brule River (Michigan) to the north, the Wisconsin, Wolf, and Fox rivers to the south, and Green Bay to the east. The general topography of the basin may be described as an irregular rolling landscape with uneven glacial till overlying the eroded bedrock.

In the northern part of the basin the bedrock is part of a Precambrian igneous and metamorphic crystalline dome. This resistant metamorphic complex forms the highlands of northern Wisconsin. The southern portion of the basin is dominated by sedimentary bedrock overlying the crystalline bedrock. (see geologic cross-section of area, Fig. 3.)

The profiles of the streams often reflect the underlying bedrock and to some extent the glacial till. An example of this is the Oconto and Wolf rivers which flow essentially parallel and then change abruptly to follow the softer sandstone and limestone formations along the face of the contacts. The Oconto, upon encountering the resisting Lower Magnesian Limestone, turns east and flows along this contact until it breaks through to Green Bay, while the Wolf flows to the south.

The Menominee and Brule rivers flow over Precambrian crystalline bedrock at their headwaters. In the last 40 miles before reaching Green Bay, the Menominee flows over essentially the same units but in its lower reaches it flows across ground moraines and glacial lake deposits which overlie the Paleozoic sedimentary rock.

Aquifers provide water to many wells and springs in the basin. They also furnish a perennial base to stream flow. The principal aquifers in this basin are the Prairie du Chien Group and the St. Peter Sandstone. The Galena-Platteville unit is another important aquifer. The median values for dissolved solids of all these aquifers are 264 mg/l for the sand and gravel type and 5,084 mg/l for the

crystalline type.

The reason for the importance of dissolved solids in the aquifers is that the streamflow is derived from surface runoff and ground water discharge from these aquifers.

It is estimated that 1,400 billion gallons of streamflow leave the basin yearly, of which 43 percent originate in Michigan.

Streamflow is more mineralized in the southern and southeastern portions of the basin due to the slow movement of ground water through moraine and clayey lake deposits.

The estimated input of sediment to the bay from this basin is approximately 20 tons per square mile per year.

### I. B. 3. PLEISTOCENE TO MODERN TIMES

The Pleistocene to recent history of Green Bay is primarily one of advancing and retreating continental glacial ice sheets. In most cases, each stage of advancing ice obliterated or at best left only vague clues of former glacial and interglacial events within the area. However, workers such as Hough (1958) determined and described the complex glacial history of the Great Lakes area. From their work it appears that, depending on the water level in the Lake Michigan basin, Green Bay alternately formed either a large fresh water estuary not unlike its present form, or a broad river valley. The following summary pertinent to this study comes mainly from Hough (1958).

The events pertinent to surficial sediments and detailed morphology start during the Toleston stage of Lake Chicago, approximately 10,000 years ago. At this time Lake Chicago in the Lake Michigan Basin and Lake Duluth in the Lake Superior Basin both stood at higher levels than at present. Lake Chicago was approximately 20 feet higher than the present Lake Michigan (580 ft.), and Lake Duluth was nearly 500 feet above its present 600 foot level. Both lakes drained south into the Mississippi River. Lake Chicago flowed through the Chicago outlet, and Lake Duluth drained first into an outlet near Brule, Wisconsin, then into the St. Croix River which emptied into the Mississippi. The Toleston stage of Lake Chicago ended as the retreating Mankato ice opened the Lake Michigan Basin to the Huron Basin through the Little Travers Bay Lowlands or the Straits of Mackinac. Because water in the Huron Basin also stood at 605 feet and the Chicago outlet was already cut of bedrock, no change occurred in the level of Lake Michigan and Lake Huron. These combined lakes are known as Lake Algonquin.

Though drainage was still to the south, a connection with the Huron Basin permitted drainage to the east, and subsequent lower stages were caused when channels further east were cleared of ice. Lake Algonquin maintained a fairly constant level at 605 feet for nearly 3,000 years. As a result, distinct shoreline features developed, many of which are still evident (see Thwaites, 1943).

Near the end of the Lake Algonquin stage, a new drainage channel opened on the northern side of what is now Georgian Bay. The withdrawal of ice coupled with insufficient time for isostatic readjustment allowed the lakes to drain to lower levels, with the Michigan Basin draining into the Huron Basin via the Straits of Mackinac. As a consequence of this drop in lake level, Green Bay was drastically reduced in size and eventually totally drained. Drainage took place in steps, not as a steady fall in lake level, and when a new level persisted, beaches formed. Stanley (1936 and 1937) suggests that four prominent "lower Algonquin" beaches exist in the Georgian Bay area and all are parallel. Hough (1958) concludes that these same beaches existed in the Lake Michigan Basin. One of these, the Wyebridge beach, was approximately 90 feet below the present lake level and may be evident in Green Bay (See Fig. 5). The beach appears in several high resolution profiles (see textural analysis for discussion). Textural characteristics also indicate possible beach sands coinciding with topographic expression.

The next reduction in lake level, approximately 6,700 years ago, drained Green Bay completely. The Fox, Menominee and Oconto rivers probably all joined somewhere south of what is now Chambers Island and formed one large northward flowing river which emptied into the Lake Michigan Basin between Washington Island and the northern end of the Door Peninsula. Evidence of this river is seen in high

resolution profiles which show dissected sediments west of Chambers Island (Fig. 4, Profile 6). The morphological expression of the bottom also suggests a channel in this area.

During the time of the low stand of water in the Lake Michigan Basin, Lake Duluth in the Superior Basin stood at over 1,000 feet. Ice blocked the northern outlets which now connect these basins, and drainage was to the south. However, when the ice front retreated far enough to expose the Au Train Valley, a new, much lower drainage channel opened. This channel allowed flow down the Au Train Valley into Green Bay through Little Bay de Noc then out into the Lake Michigan Basin. This new outlet resulted in a rapid lowering of material in Green Bay by this draining. This canyon, up to 2 miles wide and 100 feet deep, extends completely across Green Bay. Large well-rounded boulders up to 3 feet across are found in various parts of the canyon indicating rapid movement of water. Steep walls, indicated by high resolution profiles and observed by divers, also point to rapid downcutting. Preservation of these steep banks indicates filling of the bay by a rapid rise in lake level. Hough (1958) indicates that such an event did in fact occur; lake level in the Michigan Basin rose rapidly to 605 feet approximately 4,500 years ago. Retreating ice then exposed lower drainage channels further north and the Au Train Valley was abandoned.

Apparently little sediment was deposited in Green Bay from the Au Train Drainage. Divers report sediment (sand) only a few inches thick on the terrace above the canyon. However, large amounts of material may have been deposited in the Lake Michigan Basin. Bathymetric contours give the appearance of a delta-like protrusion east of the channel connecting Green Bay to Lake Michigan.



## CHAPTER 11

### METHODS



## II. A. SURVEYING TECHNIQUES

There were two main cruises for sample collection aboard the USCGC MESQUITE --- the summers of 1968 and 1969. Different surveying techniques were used on each of these cruises.

Navigation for the 1968 cruise was accomplished by a combination of triangulation (angles from visual sightings) and trilateration (radar distance measurements).

Fixes were made and recorded at five minute intervals on U.S. Lake Survey Charts. In addition to the "normal" radar targets, four reflector buoys were moored in the bay and three active radar transponders were located at known positions on shore to augment the accuracy of the fixes.

For the 1969 cruise, a new navigational system was employed. It included a Motorola RPS-1 Range Positioning System which consisted of radar transponders placed on towers and lighthouses, dual channel multiplex receivers (in series with ship's radar), and a two channel range console providing visual readouts of range from the transponders.

Ranges were automatically recorded at two minute intervals on punched paper tape and magnetic tape. One inherent difficulty existing with this system was the necessity for an unobstructed "line of sight" between the ship's radar antenna and the transponders. Any encountered obstruction would cause a "blind spot" on the radar screen. It was found the mast of the ship hampered reception for several degrees aft of the ship on each rotation of the antenna.

Rough weather caused sporadic rather than continuous reception. On several occasions other ships of the same radar frequency triggered the transponders or receivers to cause a false range readout.

Upon arrival at a pre-selected sampling station, bottom profiles were taken to give some indication of the type of sediment(s) present on the bottom. This, along with the suspected bottom types, was used in determining the type of sampler or corer to be used. Even with these methods for estimating bottom types, it was often necessary to use the other sampler because of an insufficient sample.

There were two types of bottom samplers and piston corers used for sample collection in Green Bay. The two types of surficial sediment samplers were the "Shipek" and the "Van Veen." The Shipek was used for most sampling except in areas with very large cobbles. The Van Veen was used in unconsolidated sediments except where high currents or large cobbles existed.

Some cores were taken with a short Alpine Geophysical Associated Model 210 corer, one and one-half inches in diameter. A plastic liner in a protective brass core tube was used to obtain the short cores. Other cores were obtained by use of a Benthos Model 2170, 300 pounds, four inches in diameter.

The length of an average core was six to eight feet. The major problem that existed with obtaining a good core was the difficulty in estimating the bottom sediment type and sub-surface constituents. Oftentimes, a surficial sample of sand would give no indication of the stiff red-gray clay that existed one to two feet below the sediment-water interface. The sudden jolt of the corer impacting with the clays caused the coring tube to be either bent or snapped off completely.

Because of the shallow draft of the USCGC MESQUITE (less than 25 feet), samples were not collected near shore. Samples were collected, however, by Dennis van Buskirk in these shallow areas by use of a specially weighted bucket and SCUBA (summer, 1969).

Distinctions were made between samples taken aboard the USCGC MESQUITE and van Buskirk's samples by attaching a prefix to the sample number -- GBA and DVB respectively.

Samples brought aboard the MESQUITE were washed into a large baker's pan. After a qualitative inspection and labeling, the samples were placed in one quart jars and stored aboard ship until they could be transported to the Marine Laboratory for further analysis. Cores were bled, capped, and stored in an upright position.

Samples taken by van Buskirk were also placed in quart jars for transportation to the Marine Laboratory.

No preservatives or chemicals were added to any of the samples by either van Buskirk or on board the MESQUITE.

For the summer of 1968, 208 surficial samples and 13 cores were taken. In the summer of 1969, 178 surficial samples and 12 cores were taken. There were 270 samples taken in the shallow regions by van Buskirk (see sample stations, Fig. 9).

II. A. 3. HIGH RESOLUTION PROFILING (From 1969 Technical Report  
by J.R. Moore & R.P. Meyer)

Equipment and Technique

A. High-Resolution Profiling System

The heart of this system is an Edo Corporation transducer and fish, model 415-7 .0, and a modified Edo Corporation sonic transceiver, model 248A/TVG. A Hewlett-Packard oscilloscope, model 141A, is the return pulse monitor. The dual drum recorder and all interfacing equipment are Wisconsin design and construction. The recorder uses components for Times Facsimile Corporation wire photo machines. The principal departure in technique centers on the use of short sonic pulse of high power. In the Green Bay research, we used a single cycle of a 7kc oscillation with instantaneous input power to the transducer of up to 1,400 watts.

B. Bathymetric Measuring System

The basic component of the system is an elapsed time interval counter, Hewlett-Packard model 521A. Interfacing and decision-making units are of Wisconsin design and construction. The taking of this measurement in digital form insures accurate and speedy processing with the elimination of human error and drudgery. An independent high-frequency back-up fathometer, a modified Raytheon model E 721A, was also integrated into the system as a field modification.

A functional block diagram of the 1968 instrumentation system is shown in Fig. 6 along with the over-the-side configuration of the transducers, Fig. 7. Several design features important to the reliability and accuracy of the data are:

- (1) The independence of record time marks from recorder operation in this case drum rotation. Each tenth second,

for a ten-microsecond duration, timing pulses from the master chronometer are recorded, thus providing a continuing check on recorder performance and the necessary scale for the measurement reflection times.

(2) The essentially simultaneous recording of both the 40 kc and the 7 kc bathymetric data on the same chart, with one transducer tied to the ship (40 kc) and one transducer supported by elastic shock cord. In a first-order approximation, this ties the lower frequency transducer to the water to remove ship roll and pitch while the 40 kc unit was rigidly mounted to a frame of reference which could not change during the course of the survey.

(3) The automatic taking and logging of digital bathymetric data at selected regular intervals, and in addition, at the time of input of navigational data. These data are, of course, also recorded continuously on the profiler records.

(4) The profile recorder's rotational or time stability was better than 400 micro-seconds peak to peak.(about one foot water depth equivalent), the average rms value being about 1/3 foot.

## Analysis

### A. Bathymetry

Figure 8 is a new bathymetric chart for southern Green Bay. Depths less than 15 feet were not surveyed, due to vessel drift. The bathymetry near the Oconto River is incomplete, due to lack of sufficient data for an area of this complexity.

Bathymetric data for the southern bay are taken from 7 kc profiler records, read to the nearest 0.0003 seconds (0.5 feet depth) or

0.04 inches on the profiler record. The digital bathymetric data and computer navigation will both be checked against these profiler records when the digital data analysis system is operational. Corrections for datum and transducer depth have been applied. Lake level for July 1968 was established at 1.7 feet above mean low water level from measurements furnished by the Lake Survey Division, Corps of Engineers. Fish depth, estimated from a scale taped to the side of the support cable, recorded at the beginning of each profile record as part of the teletype comments, was checked using bottom reflections between the fixed 40 kc transducer, at two feet below the surface, and the recorded depth of the 7 kc transducer. These show agreement within one foot for southern recordings. Further checks of the 7 kc fish depth are being made, using the multiple reflections. Crossings of the 1968 profile lines are planned in 1969.

At present, we know the 7 kc fish depth to 0.5 feet on 90 percent of the profiles. Finally, the bottom reflection times have been reduced to water depth on the basis of 4,800 feet per second for the velocity of sound in water. Considering the shallowness of the water, this cannot be an important source of error.

In planning the experiment, bathymetry was not the highest priority consideration, the highest scientific priority being penetration and identification of sediment by its "acoustic signature." The 40 kc fathometer, which we now find useful for verifying the position of the 7 kc transducer, was installed for quite another reason -- as it provided additional acoustic data from a source almost three octaves higher in frequency to aid in



differentiating unconsolidated sediment types.

#### B. Sub-bottom Profiling

From the outset of the field work, which first covered southern Green Bay, dramatic differences in the type of reflections received from the immediate sub-bottom were evident from location to location. In some areas only a surface sediment reflection was found; the largest of these areas are (1) that area south of the Green Bay entrance light, and (2) that area east of the Peshtigo River.

In most areas of southern Green Bay, good penetration of the bottom was attained and two types of sediment delineated. The first, present almost everywhere on the bottom, represents a grey black organic-rich mud, and its acoustic signature was easily recognized by its very weak return and poorly developed internal structure. In no cases where this material was acoustically predicted was it not found. The correlary was not true, for the material was found in areas where we did not predict it. The areas of non-prediction were areas in which the only reflection seen was the immediate bottom, i.e., no sub-bottom penetration. The only possibility for this type of acoustic response so far thought plausible is that these effects characterize areas where a gas is being generated in these sediments. Almost all the profiles, however, were characterized by intermittent opacity of this type.

The second and deeper type of sediment recognizable on profiler records has been poorly sampled. We can only imagine that this sediment, which appears to have much internal structure, represents finely-layered older lake beds. At this time, it is

difficult to separate multiple reflections from what appear as thinly bedded strata. One thing is clear, however. The soft sediments are discordant as they lie on what appears to be an ancient erosion surface terminating these bedded sediments.

#### SUB-BOTTOM PROFILING

One of the major objectives of the sub-bottom profiling in Green Bay was the identification of surficial sediments by their "acoustic signature."

From the profiles obtained, there were five major distinctions made of bottom types -- glaciolacustrine clays, glacial till, sand, post glacial muds, and bedrock.

The various "signatures" may be observed on several of the profiles (see Fig. 4). One may observe on profile eight of Figure 4 that bedrock occurs on the left hand side while glaciolacustrine clay is observed in the adjacent trough, overlain by postglacial muds. Sand is distinguished on the same profile from muds by the lack of penetration of the seismic reflection.

Glacial till is difficult to differentiate from bedrock but is characterized by having a less irregular surface than bedrock.

Glaciolacustrine clays are identifiable because they are readily penetrated acoustically and show a number of closely spaced reflecting horizons which are often contorted into slump-like structures (Fig. 4, profile 10).

Postglacial muds are identifiable on the sub-bottom profiles because of the high intensity of the sub-surface reflection. Most postglacial muds are also characterized by a smooth surface relief. Bedrock is distinguishable because of its high irregularity and good reflectivity.

## II. B. 1 TEXTURAL DATA

### LABORATORY PROCEDURES

In the laboratory, samples were desiccated to remove excess water. They were then divided into three parts for drying. Two sets were dried in an oven at 70° C for twenty-four hours while the other was dried at room temperature. Each of the three sets was used for a specific analysis: (1) clay analysis, (2) thin section analysis, and (3) textural analysis, neutron activation, and emission spectroscopy.

Size analysis was conducted by sieving thirty grams of the sample for fifteen minutes on a Ro-Tap shaker using U.S. Standard Sieves at one phi intervals. The range of sieves used was from -1.0 phi to +4.5 phi.

If, after sieving, the cumulative weight of the individual sizes varied more than one gram from the original weight, the sample was sieved again.

## II. B. 2. COMPOSITIONAL DATA

### Green Bay Compositional Data

Analytical techniques: Five gram cuts from selected DVB samples and the ferromanganese nodules from the GBA samples were dried, ground, and submitted to the Wisconsin Alumni Research Foundation in Madison for emission spectroscopy elemental analysis. Each sample was analyzed according to the following procedure:

Approximately 0.1 gram was weighed to within  $\pm 1\%$  in a

platinum crucible, then heated to 500°C for two hours. The sample was cooled, and dissolved completely in 5 ml. of 48% HF. After drying, the sample was again dissolved (in concentrated HCl), and dried once more. Final preparation consisted of taking the sample up in 10% HNO<sub>3</sub> and adding Li<sub>2</sub>CO<sub>3</sub> as both a buffer and internal standard.

The precision of this method was within a few percent for all of the elemental percentages determined by WARF. Specifications for the spectrometer used as well as precision estimated for individual elements can be found in Christensen (1968). Phosphorus could not be accurately determined with this method and wet chemical techniques had to be used. The Standard Methods Molybdate Yellow Method was chosen because of its relative insensitivity to Fe. Several controls and standard additions were run, and the results are accurate to within 1 part per thousand. (Table C ).

The bulk elemental analysis for the GBA samples was done by neutron activation techniques. Samples were ground to a fine powder, weighed, and submitted to the University of Wisconsin Nuclear Engineering Department for neutron activation analysis (Hall, 1969). The ground sediments were irradiated with thermal neutrons.

Gamma ray spectra were then recorded at varying intervals depending on the half-life of the element under scrutiny and compared to control spectra for the elements Mn, Fe, Cu, Zr, Ag, Ni, Ti, and Co. The sensitivities of these elemental determinations varied between 100 mg for Fe and  $5 \times 10^{-5}$  mg for Mn.

## II. B. 3. MICROSCOPE WORK

Mineral analysis microscope I.D. method samples selected for mineral content analysis were first dried then impregnated with polymethyl methacrylate as described by Moore (1963). Hardened plugs were then sent out for commercial thin sectioning. Mineral identification was made using a petrographic microscope, while counting and spacing was accomplished with the aid of a stage micrometer. The average reported in table A represents 200 grains counted per sample.

Manganese nodules were hand picked from bulk samples then prepared for thin sectioning using the same process as used on the bulk sediment samples. Nodule core mineralogy was determined using a petrographic microscope.

## Green Bay Clay Study

## I. Analytical Techniques

Fifty-eight samples were selected from the GBA and DVD samples such that the bay was covered as uniformly as possible without regard to sediment type. A procedure similar to that described in Carroll (1970) was used to separate the clay and silt sized particles from the sands. A longer settling time was substituted for centrifugation (10 - 15 minutes / 5 cm.). The clay-water slurry was then deposited on glass slides and allowed to dry at room temperature to permit orientation of the clay particles. Duplicates of seven of the slides were made in order to determine the reproducibility of this procedure.

The slides were then x-rayed with a Norelco diffractometer using Cu-K $\alpha$  radiation under the following conditions:

Filter	graphite monochromator
Scan Speed	1° / minute
Full Scale	500 cps
Divergence slit	1°
Receiving slit	1°
Range	4°-40° (two theta)
Time Constant	1 sec.

Ten slides of the fifty-eight were then glycolated for two hours and baked for one hour at 300° C; each slide was x-rayed after each of these treatments. These procedures were abandoned after significant changes were not detected in any of the resultant patterns.

In order to distinguish between the chlorites and kaolinities present, the 7 Å and 3.5 Å peaks of these minerals were x-rayed under slow-scan conditions similar to those used by Biscaye (1965). The following instrument settings were used:

Scan Speed	1/8° per minute
Full Scale	100 cps
Divergence slit	1°
Receiving slit	0.1°
Range	12.1°-13.1° and 24.4°-25.6°
Time Constant	10 sec.

The slow scan method is quite effective in resolving the two peaks, and relative peak heights are easily obtainable.

X ray examination of the entire sample was also carried out for twenty selected samples using standard powder methods. The sample was ground, dried at 100° C for two hours, and then ground again by hand. The samples were x-rayed under the following conditions:

Scan Speed	1°/min.
Full Scale	1000 cps
Divergence slit	1°
Receiving Slit	1°
Range	5°-60° (2θ)
Time Constant	2

The purpose of this examination was to seek supporting data for the microscope point count determinations and to check for any obvious irregularities in the mineralogy of the sediments.

## II. B. 5 ORGANIC CONTENT OF SELECTED SAMPLES

A determination of readily oxidized organic carbon was run on 20 sediment samples, 19 from the bay itself and one from the Fox River within the city limits of Green Bay, Wisconsin. The figures given in Table B represent the total dry weight loss of samples treated with 30% H<sub>2</sub>O<sub>2</sub>. It is assumed all of this weight loss is due to the oxidation of organic carbon.

Each sample was dried at 100° C for 48 hours and then weighed. The samples were then placed in 400 ml beakers and covered with 50 ml of 30% H<sub>2</sub>O<sub>2</sub> and allowed to react at room temperature. Additional H<sub>2</sub>O<sub>2</sub> was added every 24 hours until no further reaction was noted. All samples remained covered with 30% H<sub>2</sub>O<sub>2</sub> for two weeks. Each sample was then filtered, washed, dried, and weighed. Total weight loss was converted to a percentage of the original sample weight.

## II. B. 6. FERROMANGANESE NODULES

The total reserves of Fe, Mn, and Cu in the ferromanganese nodules of Green Bay were estimated using the volume distribution map from Hall (1969) (Fig.10 ). Average values for the Fe, Mn, and Cu were calculated from emission spectroscopy data (Table C).

Areas were determined by tracing the map onto uniformly thick (Dietzgen) graph paper and then carefully cutting out and weighing the graph paper representing different areas. The volumes of nodules were determined by assuming a depth of 10 cm. for every bed and then multiplying the resultant volume by the middle percentage for each range. For example, the area in the bay which has 10-30% nodules was 373 km<sup>2</sup> in extent. The volume of nodules in this area was calculated as:

$$(373 \text{ km}^2) \times (10^{-4} \text{ km}) \times (.15) = 7.46 \times 10^6 \text{ m}^3$$

From these volumes and a knowledge of the average density of the nodules (determined at 2.39g/cm<sup>3</sup>) the total weights of the nodules and the amounts of Fe, Mn, and Cu were calculated. The results of these calculations are given in Table D.



## II. C. 1. TEXTURAL DATA

### GRAPHICAL ANALYSIS

Cumulative curves were drawn to derive Inman's moments (1953) for the modal class, median, mean, dispersion, skewness, and kurtosis of the individual sediment samples. The graphs were drawn on arithmetic probability paper where the independent variable was the logarithm (or phi equivalent) of the measured sample, and the dependent variable of frequency was the cumulative weight percent. Inman's moment formulas are as follows:

Mode,  $M_o$  = read directly as the highest frequency

Median,  $M_d = \phi_{50}$

Mean,  $M_z = \frac{\phi_{84} + \phi_{16}}{2}$

Dispersion,  $s_\phi = \frac{\phi_{84} - \phi_{16}}{2}$

Skewness,  $Sk = \frac{M_z - M_d}{s_\phi}$

Kurtosis,  $K = \frac{1/2 (\phi_{95} - \phi_5) - s_\phi}{s_\phi}$

The interpretation of size frequency distributions expressed as cumulative curves, as unique frequency curves, or as probability curves is likely to remain qualitative and largely subjective unless an appropriate change in analytical technique is adopted which results in a simple curve (Griffiths, 1967)

The inherent difficulty with the above procedure lies in the fact that grain-size distributions, e.g., the cumulative curve

obtained from the sieve analysis, possesses an open end, usually occurring in the finer sizes. This sometimes leads to ambiguous results.

## II C. 2. CORRELATION COEFFICIENT

### GREEN BAY PAPER - ELEMENTAL DATA

Data Analysis: To more effectively interpret the elemental and textural data from the GBA and DVB samples, correlation coefficients were calculated for many pairs of parameters (Tables E and F). A correlation coefficient is a statistical quantity which tests for possible functional relationships between two parameters. With the Green Bay data, a correlation coefficient for a linear relation was sought. A linear correlation coefficient ( $r$ ) can be defined as follows:

$$r = \frac{m S_x}{S_y}$$

where  $m$  = the slope of the linear least squares fit to the data

$S_x$  = the standard deviation of the x data set

$S_y$  = the standard deviation of the y data set

If the x and y data sets form a perfectly linear relationship, the  $x/y$  term would be equal to the reciprocal of the absolute value of the slope of the line. The correlation coefficient would then be equal to either +1 or -1, depending on the sign of  $m$ . In the general case, the correlation coefficient must be between -1 and +1, and the closer it is to either extreme, the closer the data points fit a least squares line. For ease in computation, correlation coefficients for this study were calculated from the following equivalent formula:

$$r = \frac{\left( n \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i \right)}{\left[ n \sum_{i=1}^n x_i^2 - \left( \sum_{i=1}^n x_i \right)^2 \right] \left[ n \sum_{i=1}^n y_i^2 - \left( \sum_{i=1}^n y_i \right)^2 \right]}$$

All correlation coefficients were calculated using the University of Wisconsin Univac 1108 computer.

Another way to understand the significance of a correlation coefficient is to consider its square. The quantity  $r^2$  represents the approximate fraction of one data set which statistically correlates with another data set. Thus a correlation coefficient of .50 implies that 25% of the values from the x data set may be related to the y parameter.

It is important to realize that there are some potential problems in interpretation of correlation coefficients. When dealing with fractional quantities (percentages, ppm, etc.) there is always a negative correlation operating among all parameters, for they must always have a constant sum. This is particularly significant when one is analyzing parameters which constitute major percentages of a sample (e.g., see Chayes, 1960). When the variances of the parameters being tested are well below the sum of all the variances (as is the case with trace metals), then this anomalously negative correlation is insignificant.

The elements under consideration in the bulk sediment analyses averaged approximately 1.5% of the total sediment sample, and varied between less than 1% and 16%; the individual variances were less than 1% of the total variance in all cases. The elemental percentages which were determined for the nodules averaged 34% of the total sample, and had a total variance of only 2.01%. Most of this total variance was in the Fe and Mn variances (Fe - 1.6% and Mn - 0.34%), and correlations involving these two elements had to be considered with this fact in mind.

Another important aspect to consider is the number of data points which are used. A correlation coefficient calculated from a finite set of number pairs is only an estimate of the population correlation coefficient, and as such represents a potential range for the values of the population coefficient ( $\rho$ ). The width of this range is approximately inversely proportional to the number of data points used in the calculation and is directly proportional to the difference between the correlation coefficient and the extremes (1 or -1). Tables are available which convert calculated correlation coefficients into potential ranges for fixed confidence coefficients and with given numbers of pairs (Guenther, 1965, p. 340-41). In this study, if the absolute values of the range limits are between .5 and 1, then the two parameters are said to be correlated. If the range limits are between -.3 and +.3, then the two parameters are considered to be independent of each other, and with given numbers of pairs (Guenther, 1965, pp. 340-1). In this study, if the absolute values of the range limits are between .5 and 1, then the two parameters are said to be correlated. If the range limits are between -.3 and +.3, then the two parameters are considered to be independent of each other.

For the purposes of the correlation study, the sample stations were divided into four separate regimes: the deep water (GBA) stations, and the northern, eastern, and southern, shallow water (DVB) stations. (Figure 11). Separate correlation coefficients were calculated for each regime. The elemental data from the nodules was included in the correlation calculations for the deep water stations because nodules were found only in this regime.

## II C. 3. X-RAY STUDIES

### GREEN BAY CLAY STUDY

#### Data Analysis

The only clays considered were the 7 Å, 14 Å, and 10 Å clays. No 15 Å clays were detected either in the first examination or after glycolation. For the purposes of this study, the 7 Å, 14 Å, and 10 Å clays are called kaolinites, chlorites, and 2M<sub>1</sub> micas respectively. Further detailed categorization was not attempted. Mixed layer clays were not considered due to the negative results of the glycolation and heating procedures.

Peak intensities were approximated by peak heights for all measurements. This was necessary because the peak widths of kaolinite and chlorite were not resolvable from each other. The errors introduced through this approximation are not believed to be large, because the degree of crystallinity of the three clays remained essentially constant throughout the study, and the resulting peak intensities were generally proportional to the peak heights.

The reproducibility of peak intensities from different slides of the same sample was surprisingly good. Two slides each were prepared from seven randomly chosen samples, and the resultant pairs of diffraction patterns (slow scan) were examined for consistent relative intensities (Table G). The different ratios showed an average error of less than ten percent, well within the expectations of the study.

The peak-height intensities derived above were then

compared in a relative manner by taking simple ratios of the peak heights. Biscaye (1965) has defined a method for comparing more than two clays at a time, but this method depends upon the assumption that the clays under consideration comprise a constant proportion of the total sample. This condition was not met by the Green Bay sediments, and thus the three possible pairs of clays were analyzed separately.

## CHAPTER 111

### RESULTS





### III. A. & B. TEXTURAL ANALYSIS & MINERALOGY OF THE SEDIMENTS

#### BOTTOM SEDIMENTS

Figure 12 shows the basic sediment distribution for Green Bay. Five basic sediment types, mud, sandy mud, sand, clay, and rock, are grouped by field note descriptions and megascopic laboratory examination. The five classes described consist of: (1) Dark gray to black muds; organic rich muds with extremely high water content. Clay and silt size detritus, with wood chips and sewage are locally common near river mouths. (2) Sandy-muds (and muddy-sands) -- usually dark gray to light brown depending on the amount of organic mud or clay. These are apparently transition sediments between the sands and finer sediments; many would be classified as sands by exacting terminology based on sieving. (3) Buff to very light brown sands are coarse to very fine-grained but mainly medium to fine-grained, fairly well sorted, chiefly quartzose. (4) Brick red, stiff Pleistocene glacial deposits, which are probably tills or layered clays. (5) Rocks and gravel -- chiefly large fragments of dolomite and sandstone, some metamorphic and granitic material, 3 to 6 inches in diameter, blocky to subrounded, manganese stains common on most, patchy distribution.

Sand, mud, and muddy sand ( or sandy mud) are by far the most common sediment types; rock or gravel and clay are restricted to smaller areas. There seems to be a direct relation between sediment type and bottom topography, with the finer sediments found in deep water, and the coarser types in shallower water. Such a distribution probably results from a combination of ancient shorelines, supply of clastics, and bottom topography.

Medium to fine-grained quartzose sands dominate the northern end and western side of Green Bay. Geology seems to control the

absence of sands on the eastern side. It is generally assumed that the sands are derived from glacial drift and weathered sandstone and shale.

Mineral content of the sands varies, but the overall composition is predominately quartz with feldspars being second in abundance in most cases. Average composition is 70% quartz and 15% feldspars; varying amounts of carbonates, amphiboles, micas, and zircon occur without a significant pattern. Quartz content tends to increase as size decreases, with most silt size material being almost pure quartz. Murray (1953) reports similar trends in the Cary and Valders tills which are found not only surrounding the bay but cover most of its drainage basin.

Using the mean size ( $\phi$ Mz measure, a contoured chart was drawn for the Green Bay Deposits (Fig. 13). The most notable thing about the pattern of size distribution is its randomness. There is a trend towards finer grained sands in the southern half of the bay, but by and large mean grain size does not define depth. Any particular mean size class can be found at any depth. Medium grained sands may lag at intermediate depths.

Several large bodies of medium grained sand along the west side of the bay seem to be related to adjacent rivers. These areas are off the Menominee and Oconto rivers. Bathymetric contours which indicate the channels of both rivers, extend into the bay, probably as the result of lowered lake levels within the last 7,000 years. Slightly coarser material supplied by the rivers formed these sand bodies. However, a third medium grained sand body located north of Menominee in the Rocherem Point - Arthur Bay area shows no connection with a river, indicating that the differences in grain size may only indicate a difference in source areas.

Dispersion, sigma, a statistically derived measure based on a cumulative curve, was plotted to determine the degree of sorting. Sigma is not necessarily related to the textural size measures and is therefore useful in determining changes within a given mean size range. Values of sigma for the sediments in Green Bay range from very well sorted at .35 to very poorly sorted at 3.0 (Fig. 14).

While mean size distribution is seemingly independent of depth, sigma is, in the case of Green Bay, quite depth dependent. Well sorted sediments are limited to waters 60 feet deep or less, and moderately well sorted sediments occur only in water less than 85 feet in depth. Such relationships do not hold for less well sorted sediments which appear at all depths.

One thing implied by figure 14 is the gradational contact between sorting provinces. Although this may be substantiated in some parts of the bay, it cannot be proven in all areas. Sorting trends between Washington Island and the mouth of Little Bay De Noc, for example, are interrupted by a very sharp change in depth. In this case intermediate sorting values appearing on the map have no basis and are only placed between well sorted and poorly sorted sands for the sake of a continuity which may not even exist. Divers report an extremely sharp break in slope with very little sediment mixing other than an occasional slump. On the other hand, most areas of gradual shoaling show a definite, gradual change in sorting with depth.

Intra-measure relationships, designed to show relationships between grain size and sorting, show a slight tendency for medium grained sands to be better sorted than fine grained sands. Such a relationship is the inverse of the generally accepted norm (Folk, 1968)

and probably results from a combination of factors. One possible explanation is the presence of submerged beaches. Beach sediments would be better sorted than open lake sediments, having had the more mobile fine sand removed. This fine sand would be deposited in deeper water where the energy available is too low for sorting to take place.

The possibility of submerged beaches accounting for at least some of the textural variations seemed quite likely. Green Bay's history of rising and falling water levels, combined with what appears to be terraces on some high resolution profiles, lead to the plotting of certain textural parameters which can indicate the environment of deposition. Friedman (1961) contends that sorting, when plotted against skewness, will separate river deposited sands from beach sands. Because Green Bay was dry for a 2,000 year period ending about 5,000 years ago, the sedimentary environment would be one of river and stream deposits. Such deposits would be found toward the center of the valley rather than on the steeper valley sides. The postulated beach would have been created during one of the stands as the lake level dropped. Survival of the beach terrace and deposits seem likely, because many older beaches cut at high stands still remain. One further assumption is made, that the rate of clastic deposition is very low in the northern part of the bay. This last assumption seems reasonable because the three major rivers draining into Green Bay -- the Fox, Menominee, and Oconto, are all at the southern end of the bay. Further, many of the suspected beach areas are on slightly elevated topography many miles from shore.

Samples having textural characteristics indicative of a beach depositional environment are shown in Figure 15. Also plotted is

the proposed drowned shoreline based on present day depths.

Muds, consisting of silt and clay size mineral grains mixed with varying amounts of organic material, constitute a sizeable portion of the sediments found in Green Bay. Most muds are mixed with at least a little fine-grained, poorly sorted quartz sand. An extremely high water content, up to 80%, points to very recent deposition. Such sediments would either be compacted or washed away if they had been there long.

Muddy sediments tend to increase in abundance and thickness toward the central or long axis of the bay. Thickness varies from several inches, as reported by divers off Little Bay De Noc, to over 30 feet (Moore and Meyer, 1968) 2 miles northwest of Little Sturgeon Bay. Muddy sediments are generally more abundant in the southern half of the bay. In this area mud, sandy mud, and muddy sands are by far the dominant sediments.

Sands and mud usually do not make sharp contact; there is a gradation from sand to muddy sand, to sandy mud, to mud in most cases. This points to mixing which is likely in view of the mobility of the mud. The sand fraction shows a decrease in grain size and sorting combined with increased angularity as the mud fraction increases. These conditions suggest that mixing occurs in low energy zones intermediate between conditions providing for moderately sorted, shallow water sands and quiet, very low energy zones where pure muds settle out.

Muddy sediments present in shallow waters, where sands are usually found, are restricted to more or less sheltered areas. These include the head of Little Bay De Noc, the east side of Big Bay De Noc, and the shallow waters in and around Sturgeon Bay. In each case, the area is either sheltered or restricted, suggesting

low energy conditions suitable for the accumulation of muds.

Composition of the mud itself is best described as very fine, partly reduced organic material with lesser and varying amounts of silt and clay size silicate mineral fragments. Occasionally wood chips and/or sewage are observed in a sample. The bulk volume of this sediment, in situ, is water, up to 80% in some cases. In some areas gas, perhaps generated from the organic content of the mud, may account for a considerable volume of the sediment. This gas is probably responsible for the complete lack of penetration noted in some areas with regard to sub-bottom profiling (Fig. 4, Profile 8).

Minerals, as identified by x-ray techniques, include quartz, feldspars, 7Å, 10Å, 14 Å layer silicates and occasional traces of hornblende and carbonates. Quartz and feldspars seem to show no pattern of distribution. A discussion of clays and their distribution is included below.

The organic content of the muds ranges between 5.8% and 15.6% organic carbon by dry weight (Table B). These numbers probably do not represent the total organic content as they were derived by treating the sediment with 30% H<sub>2</sub>O<sub>2</sub> until all reaction ceased. The highest percentages of organic material seem to follow the long axis of the bay with lesser amounts occurring toward shallow water. One particular exception is sample D115, taken from the Fox River directly north of the Chicago and Northwestern railroad bridge in the city of Green Bay. Water depth is 20 feet in mid-river where the sample was taken. Such a high organic content from sediments taken from a flowing river indicates that large quantities of organic material such as sewage or nutrients are being introduced into the river.

The organic content then falls off as the amount of mud decreases. About 15 miles north of the mouth of the Fox River the organic content and amount of mud both increase. The organic content remains approximately the same throughout the entire mud facies in the southern half of the bay.

A characteristic acoustic response verified by physical samples allowed for accurate and confident mapping of the mud facies. The muds are acoustically transparent provided there is no gas content, at which point they become opaque; this is, no sub-bottom penetration occurs, and only the surface reflection is recorded. The largest areas of "opaque" muds are (1) the area south of the Green Bay entrance light, and (2) a larger area east of the Peshtigo River.

The thickness of unconsolidated muds ranges up to 30 feet. The mud accumulates in depressions on the old subareal erosion surfaces. It is probable that the fine sediments, other than the stiff red clays, have such a low shear strength that they cannot persist in any great thickness on even gentle slopes. As a result, they move down slope by flowing, probably helped by water movement and possible slumping. It is interesting to note that the greatest concentrations of Fe and Mn, excluding the pellets, are found in association with the thickest deposits of mud.

The pattern presented by infilled areas suggests some connection to the Fox and Peshtigo rivers. The largest changes in depth occur off these rivers. In addition the sediments off the Peshtigo River are "seismically opaque" suggesting gas production from organic decomposition within the sediments (Fig. 4, Profile 8).

Howmiller and Beeton (1971) report changes in the bottom fauna of southern Green Bay between 1952 and 1969. They cite the increase

in oligochaete (sludge worm) and chironomidea, the larvae of midges, which are both pollution resistant animals. There is also a sharp decline in the abundance of snails, leeches, fingernail clams, and amphipods -- all less tolerant to pollution. They conclude these major changes are the direct result of pollution.

Rocks and gravel make up a small but distinct sediment type confined for the most part to the northern part of the bay and beaches on the Door Peninsula. Rocks and gravel, other than the beach deposits, may indicate strong currents. Such high energy deposits occur in the channels north of Washington Island. Other deposits, such as those around Big Bay De Noc are most likely lag deposits from gently washed till.

Occasionally Pleistocene glacial deposits, tills or glacial lake clays, crop out on the floor of the bay. These "clays" occur infrequently as true surficial sediments. They are usually covered with several inches of sand or mud. Similar deposits occur in Lake Michigan (Hough 1953, Moore 1961) where they are also interpreted as glacial till.

#### GREEN BAY CLAY STUDY

The semi-quantitative x-ray analysis of the clay mineralogy of the Green Bay sediments yielded the following distributions of kaolinite/mica ratios and chlorite/mica ratios (Fig. 16). One trend is apparent; both the kaolinite/mica and the chlorite/mica ratios show distinctly higher values in the south of the bay than they do in the north. This is true even though the kaolinite/chlorite ratio appears to be independent of location. Kaolinite/mica and chlorite/mica average 1.47 and 1.42 respectively, south of Sturgeon



Bay and 0.77 and 0.86 to the north of this point. The mica peak has roughly the same intensity throughout the bay, and thus can be considered the baseline by which the other variations can be evaluated.

Of some interest is the fact that the ratios are not related noticeably to sediment type. Though the fine-grained sediments naturally have stronger overall intensities for the clay minerals, the ratios between the intensities are quite independent of grain size.

### III. C. ELEMENTAL TRENDS IN BULK SEDIMENT

#### Bulk Sediment Composition

Elemental compositions of the GBA and DVB samples of the Green Bay surficial sediments can be found in Tables I and J. Emmission spectroscopy was used for shallow water (DVB) samples, and each sample was analysed for Mg, Ca, Ba, Sr, Cr, Mn, Fe, Cu, Zn, and Al. The GBA samples were analysed using neutron activation, and concentrations of the elements Mn, Zr, Cu, Fe, Ag, Ni, and Ti were determined.

Average elemental compositions of four separate areas in Green Bay (Fig. 11) were calculated and are assembled in Table C. Standard deviations were also calculated and are presented in order to demonstrate the large amount of variation which can be found in each area.

Several significant correlations were discovered between various elemental concentrations in the GBA and DVB samples. These correlations are listed in Table K for the GBA bulk samples and ferromanganese nodules and in Table L for the DVB samples. The

possible implications which can be derived from correlation study and the various elemental distributions in the four sedimentary regimes are presented in the discussion section below.

### III. D. 1 & 2 FERROMANGANESE NODULES

The volume distribution of the ferromanganese nodules of Green Bay is presented in Figure 10. The nodules are generally associated with the sands and muddy sands in the northern part of the bay and are almost always found in water deeper than forty feet.

The nodules range from <1 mm. to over 1 cm. in diameter, with the largest nodules occurring mostly in a small, highly concentrated area just outside the mouth of Sturgeon Bay. The size of the nodules appears, from a megascopic examination, to be larger than the sediments in which they are found.

From impregnated thin sections studied under the petrographic microscope (Fig. 17), it is possible to make some generalizations. About half of the pellets contain a small nucleus, usually a small grain of quartz or feldspar. Two general growth types are present: (1) a round pellet, sometimes conforming to nucleus grain geometry, and (2) an aggregate growth pattern type with uneven outline. Generally, the smaller rounded pellets contain a proportionally smaller amount of manganese, in part because of a high nucleus--to  $MnO_2$  ratio, while the irregular shaped or aggregate type pellets contain proportionately larger amounts of manganese. The majority of the pellets are of B-B shot size and vary in manganese content relative to iron with geographic distribution (Moore, 1969). Also quite distinct in some nodules are the alternating concentric bands of Mn rich and Fe rich zones which are so characteristic of marine nodules. The detailed structure of these features has been explored using electron probe by Rossman et al (1972).

Elemental compositions of the nodules can be found in Table M. Emission spectroscopy was used to determine concentrations of Mg, Fe, Cu, Zn, Mn, Cr, Al, Ba, and Sr, and in the nodules. Average values for these concentrations can be found in Table C.

Table N compares the elemental composition of Green Bay nodules with compositions of other ferromanganese nodules. The values given are averages, and there is a considerable variation from station to station. It is believed, however, that these averages accurately reflect the overall compositional trends in the Green Bay nodules, and that useful comparisons with other fresh water and with salt water nodules can be made.

The most noticeable difference between the Green Bay nodules and other fresh water deposits is the relatively low percentage of manganese in the Green Bay nodules. The results of this survey show that the manganese percentage in freshwater deposits is not generally lower than the percentage in marine deposits. It appears instead that the lower Mn/Fe ratio in fresh water nodules is caused by an increased percentage of Fe. Green Bay nodules, however, appear to contain less than half as much manganese as other fresh water deposits.

Also evident in this table is the scarcity of trace elements in fresh water nodules. Marine deposits contain ten to a hundred times the concentrations of economically important elements such as Co, Ni, and Cu.

The surficial sediments associated with fresh water ferromanganese nodules are noticeably lower in trace element

concentrations than the associated sediments of marine nodules (Table O). Oceanic sediments are appreciably higher in Mn, Fe, Cu, Ni, and Co; though sediment elemental composition does not seem to correlate generally to nodule composition, it is possible that this relative scarcity of trace elements in the fresh water sediments could be part of the reason for the low trace element concentrations in fresh water nodules. Also important is the fact that fresh water nodules generally form much more rapidly than marine types, allowing less time for trace element adsorption.

Several significant correlations were discovered among the compositional and textural parameters of the nodules and the bulk sediment samples. In general, it can be said that the correlations present in the nodules are not the same as those in the bulk samples; this is true for the deep water sediments as well as for the three shallow water regimes. In addition, the Fe, Mn, and Cu percentages in the nodules do not correlate with the percentages of these elements in the associated sediments of the same sample stations. Significant correlations are given in Table K for the deep water samples and in Table L for the other three areas.

Due to an incomplete record of sample station water depths, it was not possible to calculate correlation coefficients between water depth and various elemental percentages. It was discovered, however, that the Fe percentage map in the nodules shows a great deal of similarity to the bathymetric map of the bay (Figs. 18 & 19). Fe appears to have a strong inverse relationship to water depth. Mn concentration in the nodules displays

the reverse relationship (Fig. 19) but this trend is not nearly as pronounced, and is likely to be caused by the imposed negative correlation between Fe and Mn (see Data analysis).

Average elemental compositions of the four separate regimes of Green Bay (Fig. 11) and of the ferromanganese nodules have been assembled in Table C. Standard deviations for each average are also presented in this table. These averages were used in conjunction with Figure 10 to estimate the total reserves of Fe, Mn, and Cu in the nodules of Green Bay; the resulting estimates are given in Table D.

Obvious contrasts among the four separate regimes are rare, and almost all of the elements are equally abundant in all four populations. The exception to this is the nodules, which vary considerably from the bulk samples in their concentrations of Fe, Mn, and Cu. The implications of these results will be considered in the discussion section.



## CHAPTER IV

### DISCUSSION





#### IV. A. TEXTURAL ANALYSIS

The Carry and Valders tills of Wisconsin age are the primary sources of clastic sediments in Green Bay. These tills are found not only adjacent to the bay but also cover large portions of its drainage basin. Additional clastics may be derived from exposures of sandstone and shale to the northwest. Door and Eschman (1970) suggest that sands are delivered to the bay from these weathered outcrops by the Escanaba River.

Murray (1953), in a study of the petrology of the Carry and Valders tills, computed the following average size distributions:

	GRAVEL >1.0mm	SAND 1 to 1/10mm	SILT 1/10 to 1/256	CLAY <1/256	MEAN SIZE	MEAN SIZE OF SANDSTONE
VALDERS	5%	25%	45%	20%	.06mm	.32mm
CARRY	10%	63%	25%	2%	.14mm	.34mm

Both tills are apparently capable of supplying the .4 to .2mm sands which are the predominant clastics found in the bay. Weathered shale and sandstone may account for the slight increase in well rounded and frosted grains in the northwest quarter of the bay. These grains, however, may also be derived from the till having been originally derived from sedimentary rocks eroded by glacial action.

Wave and ice erosion probably account for most of the sediment with river and stream runoff supplying the rest. Such processes act to improve sorting, and the repetition of these processes of delivery with shallow water deposition improve sorting even more. Repetition of delivery and deposition is likely in view of the numerous changes in lake level since the retreat of the last glacial ice. Abandoned beaches, left by drops in water level, are subject to erosion and redeposition at the new beach. Conversely, a drowned

beach results in moderately well sorted material in deep water surrounded by less well sorted sediments.

Complete drainage about 7,000 years ago probably resulted in the formation of river deposits near the central part of the bay. These river deposits were reworked somewhat as Lake Michigan re-filled. Because the water level was rising at a steady rate, beaches did not have time to form. The overall environment in Green Bay with regard to energy is rather quiet compared to an ocean environment. This means that it takes some time for prominent beaches to form or for river-laid deposits to be reworked sufficiently to lose their characteristic textural properties.

The mineral composition of bay deposits and the tills are quite similar. Dominant heavy minerals in both are amphiboles with lesser and varying amounts of garnet and opaque minerals. Traces of apatite, sphene, staurolite, and zircon also appear.

Moore (1961) concludes that the red clay till found in north-eastern Lake Michigan is either the Valders till or reworked Valders till. He bases this conclusion on texture, color, and heavy mineral content. Similar sediments in Green Bay are probably from same till. High resolution profiles taken in Lake Michigan (Lineback, Gross, Meyer and Unger, 1971) show this till overlain by lake sediments. Identical sequences are observed in profiles taken in Green Bay. The tills in Green Bay are presumably the same as those in Lake Michigan and are probably either of Carry or Valders age.

The bottom sediments of the western and northern portions of the bay are sands, while thick unconsolidated organic rich muds dominate the eastern side. The sands extend 6 to 10 miles from shore before becoming covered with mud. No sharp contact occurs between the two facies, indicating at least some mixing or contemporaneous deposition.

High content of water and organic matter generally indicate recent, rapid deposition. The muds are being deposited over a pre-existing sandy bottom, filling in deeper parts with highly unconsolidated material. This westward decrease in grain size with depth might indicate an adjustment to energy conditions coupled with high rates of fine sediment deposition. However, the high depositional rate probably results from human influences. The sands themselves show no general decrease in grain size away from shore but rather a "patchy" nature in their distribution. Sand size distribution is probably controlled by source and reworking with changes in lake level, and seems adjusted to the present energy conditions.

Further indication of adjustment consists of continuous trends in sorting. Deeper water deposits are almost always less well sorted than their shallow water counterparts, even for continuous sand bodies of the same grain size extending from shallow to deep areas. Exceptions to this generalization are those areas receiving large amounts of sediment such as the mouth of the Menominee River.

Based on sorting and grain size alone, it appears that Green Bay is adjusted to its energy environment and for the most part one finds fine grained sediments in deeper waters with improved sorting toward shore. However, the extremely rapid rates of deposition, not only in small areas of enhanced supply but over the entire western half of the southern end of the bay, indicate that conditions are other than normal. These sedimentation rates occur only in muddy sediments and are highest near sources of pollution such as Menominee-Marquette, Oconto, and Green Bay. The composition of

these sediments also indicates conditions other than those naturally supplying fine material. These factors include the presence of sewage and wood chips, the high organic content and increased concentrations of certain elements such as Cr, Cu, and Zn with increased organic content. Sedimentation rates for clastic material is much lower than for the muds, especially in the northern part of the bay. There, erosion surfaces cut by the drainage of the Superior basin 7,000 to 8,000 years ago are covered with only 3 or 4 inches of sand.

The organic muds should and do conform to the energy conditions within the bay. The primary force acting on these sediments is gravity, and the results are as expected; the muds being highly mobile flow into lows on the bottom thereby smoothing out the topography. The only other force acting on these sediments is that imposed by water movement.

Johnson (1963) concludes that the tidal range in Green Bay is small; spring tides range from 0.55 to 0.73 feet while neap tides have a range of 0.4 to 0.5 feet. He concludes that winds play a greater role in altering water level than tides. Ahrnsbrak and Ragotzkie (1970) calculate a mathematical model of seich-induced and wind driven circulation. Near the mouth of the Red River, some 15 miles north of the mouth of the Fox River, the Fox River water moves out into the bay and loses its identity as a water mass. Although these are surface circulation patterns, they must affect the sediments. Muds become dominant where the water mass loses its identity in southern Green Bay. This model agrees with circulation patterns arrived at by synoptic surveys taken by those authors and by Modlin and Beeton (1970). In both cases, Fox River water was traced and a circulation pattern deduced. Water moves north out of

the Fox River and along the eastern shore of the bay. The mean size map shows the relation quite clearly. Fine grained sands can be found near shore directly below the path of the Fox River water. Once this water moves out into the bay and mixes, muds predominate the bottom sediments.

Conductivity measurements (Modlin and Beeton, 1970) indicate circulation may take the form of water moving southward near shore on both sides of the bay between the tip of the Door Peninsula to as far south as Sturgeon Bay and Oconto. The return flow is then up the center of the bay and to the west of Chambers Island. Local residents are familiar with currents moving south between Chambers Island and the eastern shore, then along shore through Strawberry Channel (J.E. Gilson personal communication).

From drift bottle studies by Ayers et al (1958), currents were found to be moving eastward through the passages into Lake Michigan north of the Door Peninsula. The dominant circulation in Lake Michigan is counterclockwise. Ayers et al (1958) report low transparency, warm water off Washington Island; and this seems to indicate movement into Lake Michigan from Green Bay since the bay water normally has a higher suspended sediment load, the result of several rivers flowing into the bay. Also the water from the bay should be warmer than Lake Michigan water as it is in a shallower basin and can more readily be warmed by the sun.

## GREEN BAY CLAY STUDY

### Discussion

The clay minerals in Green Bay are distributed in a pattern similar to that followed by other chemical, textural, and mineralogical parameters, and again draw attention to the contrasting depositional environments present in the northern and southern parts of the bay. The greater relative abundance of kaolinite in the south implies that these sediments have been exposed to a greater degree of chemical (especially acid) weathering than the northern sediments (Millot, Chapter 10). This corresponds quite well to the nature of the drainage basins which are represented by these sediments. The occurrence of chlorite is much more ambiguous; chlorite is found in several sedimentary environments, and is usually simply a detrital component from many rock types. Its predominance in the southern part of the bay, however, does indicate separate origins for the northern and southern fine-grained sediments.

#### IV. B. GEOCHEMISTRY OF SURFICIAL SEDIMENTS

##### DISCUSSION - COMPOSITIONAL DATA

Analysis of the compositional data from the Green Bay sediments, supported by textural data, microscope point counts, and x-ray diffraction data, has been quite valuable in the attempt to understand the overall mineralogy of the sediments and the distributions of trace elements in the muds, sands, and ferromanganese nodules.

The elemental composition of the recent sediments of Green Bay is, with a few exceptions, quite uniform, and the somewhat arbitrary division of the bay into four populations resolves only a few significant anomalies. The compositional data supports the microscopic point count to some degree, and agrees with the x-ray determination that the feldspar present in the sands is primarily K-feldspar.

Aside from some trace element concentrations in the southern part of the bay, only two elements, Ca and Mg, display any observable trends. These two elements are highly correlated with each other in the southern, eastern, and northern parts of the bay and are concentrated by a factor of two in the south (Tables L and C). The correlation is probably due to dolomite, which is abundant as a fine-grained flour in the many glacial tills through which the Menominee and Fox rivers flow. The dolomite which is present in the Green Bay sediments must be fairly fine-grained; it was commonly detected in the bulk x-ray analyses, but was found only occasionally in the point count examinations.

The enrichment of these elements in the south, however, is not as clear, for there is no reason to believe that the sediments derived from the southern rivers are any richer in dolomite than those from the northern rivers. It is possible that the observed

enrichment is due to the present low rate of deposition in the north and to the fine-grained nature of the dolomite.

It is believed that the sands to the north of Chambers Island are primarily beach sands which had been exposed to relatively high energy conditions before their recent submersion some few thousands of years ago (See Textural Analysis Results). If this is true, then the fine-grained dolomite which was in these older sediments would have been largely removed before the water level rose to its present height. The most recent sediments in the bay are derived chiefly from the Fox River and are concentrated in the southern portion of the bay. This explanation for the observed enrichment is possible, but a more detailed analysis of the size and concentration distributions of the dolomitic flour would be necessary before a firm conclusion could be made.

The elements Cr, Fe, Cu, and Zn show some interesting trends in the southern part of the bay. All of the elements (with the exception of Fe-Cr) are correlated with each other in the south but are not consistently associated in either the east or the north (Table F). Aluminum does not correlate with any of these elements. These correlations, together with the fact that Cu, Zn, and Cr are significantly more concentrated in the south than in any other area, strongly imply that the metals are associated to a major extent with the organic components of the southern Green Bay sediments. Organic extractions and hydrogen peroxide oxidations in this study, and numerous pieces of evidence from other studies (Sager, P.E., 15th Conf. on Great Lakes Res., 1972, p. 78 ; L. Vanderhoef, 1972, p. 116 ; A.M. Beeton, Annual Progress Report of Sea Grant Activities, Tech. Report #8, July, 1971, p. 13) all attest to the high organic content



in the southern waters and sediments. Transition elements are attracted to many sites on organic molecules, and complex readily with nucleophilic sites such as carbonyl groups, hydroxides, and amines (Riley and Skirrow, Chemical Oceanography, v. I, Academic Press, London, 1965, p. 17). Organic extractions of sediments and subsequent Infra-red Spectroscopy have shown that the appropriate organics (e.g. ketones, esters, and alcohols) are quite common in the sediments of the southern part of the bay.

Adsorption of these transition elements onto phyllosilicates does occur, and may be partially responsible for the observed enrichment; southern Green Bay does have a higher percentage of clay minerals than the north, and Cr and B in particular are known to be adsorbed by illites in marine sediments. Cr can also occupy the octahedral site of  $10 \text{ \AA}$  micas (Deer, Howie, and Zussman, 1967, p. 202 ; Moore, J.R., 1963). Adsorption onto clays may account for some of the enrichment of trace elements in Green Bay.

It is evident from an inspection of Table C that the ferromanganese nodules in Green Bay selectively concentrate several elements. Specifically, Fe is concentrated by a factor of 20, Mn by a factor of 200, Cu by a factor of 5 to 10. The mechanisms which cause these selective enrichments are intimately involved with the oxidation potential in the bottom and interstitial waters of the bay. It is known that the Eh in the southern part of the bay is quite low, due to the high organic content in the waters and sediments (Sridharan, 1971). This low redox potential causes dissolution of the Fe and Mn oxides present in the sediments, it is probable that an interstitial or bottom water flow could then carry the dissolved metals northward. Oxidation and precipitation could result when the  $\text{Fe}^{+2}$  and  $\text{Mn}^{+2}$  encounter the more oxidizing conditions which occur north of Sturgeon Bay (Callender, 1969).

Extensive work with the nodules themselves is necessary in order to establish any mechanism for the origin of the Green Bay nodules, but the compositional analyses and correlation studies of this project have uncovered some interesting trends which relate directly to the problem. The already noted correlation between Fe in the nodules and water depth is one such observation (Figures 18 and 19). It is reasonable from diffusion arguments alone to expect that the oxidation potential in Green Bay should decrease with depth, especially when averaged over a period of time. This average gradient will lead to an inversely related gradient of Fe solubility and thereby cause greater rates of accumulation of Fe in the shallow waters than in the deeper waters. Manganese is more soluble than Fe under the same conditions and would not be expected to follow the trend as closely. The observed positive correlation of Mn with depth is questionable at any rate, and is probably an imposed correlation caused by the large percentage of Fe. This marked vertical correlation of Fe with depth lends credence to the notion that interstitial transport is an important concern, but the south to north flow of the Fox River remains the most probable source path for the two metals. Another observation of this study which relates to the formation of the nodules is the possible correlation between mean sediment size and nodule diameter ( $r = .552$ ). It has been proposed that the spherical shape of the Green Bay nodules is caused by bottom currents which keep the nodules constantly in motion and prevent preferential growth on one side (Hall, 1969). It is true that large rocks in the bay have been found with Fe and Mn oxide concretion only on their upper faces (Callender, 1969), but these rocks are too large to have been affected by currents. The correlation analysis supports this explanation

of the nodule shape and suggests that nodules will be associated with sands which are their hydrological equivalents. Confirmation of this latter prediction would be strong evidence for the validity of the former.

The correlation coefficients calculated between the various elements of the nodules and the same elements in the bulk sediments make some general conclusions possible. The lack of correlation between the Fe, Mn, and Cu in the nodules with the same elements in the associated sediments (Table E) implies that the sources for these metals must be different than the immediate site of precipitation. The inconsistency between the correlation found in the nodule compositions and those found in the DVB populations (Tables E and F) also suggest that the nodule compositions are not directly related to the composition of the sediments in the bay.

The correlations found between different elemental concentrations in Green Bay agree quite well with the electron probe studies of Green Bay nodules done by Rossman, et al (1972). Rossman found a strong correlation between Mn and Ba in his examination of the nodules, and his findings are supported quite well by the correlation coefficient from this study ( $r = .780$ ). Other significant correlations in the nodules from this study are between Mn and Sr and Mn and Mg. It is interesting how the Group II cations (Mn, Sr, and Ba; Ca was not determined) all seem to be strongly correlated with the Mn phase of the nodules.

## C. Economic Potentials

### 1. Mn nodules - a. Elemental content

In the early stage of mapping these deposits much attention was given by the press and trade journals to the nodules as a source of elemental manganese. While such consideration is not unwarranted, particularly as the foreign sources of manganese become involved in politics and capricious pricing, we have always stressed the importance of the nodules per se. Nevertheless, given the favorable conditions of shallow mining, easy separation, local ore boat docks, and reasonably near iron and steel mills, there is some potential for using the richer Mn nodules as a "sweetening" manganese source in the upper Great Lakes mills. Should cheap foreign sources be cut off by political constraints or a changing defense posture, the Green Bay resource would become an alternative supply. To provide for such a contingency, we recommend full metallurgical testing of large (bulk) samples by industrial laboratories.

### b. Potential Use in Automobile

Perhaps the most fruitful use of the nodules would be as noxious fume scrubbers in the exhaust system of combustion engines. As we see greater demands for cleaning the environment, such use becomes more attractive. Independent analyses have shown that the nodules possess in excess of 200 square meters of specific surface area per dry gram of nodule material. Moreover, the nodules are of a size that permits them to be easily packed in disposable cylinders and inserted, periodically, in the exhaust piping of any automobile. With their relative cheapness --- we estimate

they can be produced in packaged form for 10 cents per pound --- this makes the nodules economically as well as technically desirable. Again, bulk samples are needed for extensive R and D testing in industrial laboratories.

A second use which relates to nodule surface area is that of catalysis material. Although little research has been done on this (Weisz, 1967), the nodules apparently do possess desirable catalytic properties. As in other potential applications, large pilot plants and samples will be needed to fully evaluate their catalytic properties.

## 2. Sand Reserves

Large-scale development of the Green Bay and Door Peninsula coastal zone for recreation and summer homes will continue to constrain using beach or even older glacial sands for construction and beach replenishment. However, our survey has confirmed a sand resource on the bottom of Green Bay, western side, that extends for about 40 miles along the shore and is at least 3 miles wide on the average. The sand is well sorted, medium grained, and essentially quartzose in composition. Because of its proximity, clean nature, and shallow mining depth, we suggest that local industry could soon start extracting this sand for use in the Green Bay area. The sand is amenable to clean hydraulic mining and there are numerous markets for barge-transported sand within 60 miles of the resource.

## 3. Legal Problems

The one constraint that has done more to hold back industrial extraction is that of the confused legal regime. Any entrepreneur

must be given legal protection in investing exploration and exploitation capital. We would suggest that early attention be given by regulatory agencies to this problem, and that legal offshore prospecting permits be issued to prospective miners. Such permits would allow the investor/explorer to protect his invested capital, while still allowing the state to regulate and monitor the exploration program. If the reserves warrant extraction, specific guidelines should be formulated to cover royalties, operations, safety practices, and anti-pollution measures. While full-scale mining would require full legal coverage, we would recommend that bulk sampling (for commercial testing) be allowed --- indeed, encouraged --- under a simple letter of agreement between the State Geologist and the company concerned.

In short, we can not over stress the need for early legal protection of both the explorer and the state in order to encourage orderly extraction which would benefit both the state and the local communities.

## CHAPTER V

### CONCLUSIONS





## V. CONCLUSIONS

Textural, mineralogical, and geochemical analyses of a large collection of Green Bay surficial sediment samples, correlated with high resolution acoustical profiling data, permit us to make the following conclusions about the Green Bay recent sediments:

1) Recent sedimentation in the bay is dominated to a large extent by the input from the Fox River which can be reasonably traced at least as far north as Chambers Island. The Menominee River provides a significant but more localized input.

2) High resolution profiles reveal several Pleistocene channel and beach relicts which are quite influential in determining the detailed morphology of the bay.

3) The maximum age of the bay at the current water level and thus the absolute limit for the age of the ferromanganese deposits is between 3,000 and 4,500 years.

4) X-ray analyses of clays, studies of organic content and structure, elemental analyses, and simple megascopic examination all support the contention that the fine-grained sediments in the southern third of the bay (see Figure 14) are high in reduced organic matter, adsorb and mobilize significant quantities of Fe, Mn, and other transition metals, and are generally characteristic of a highly eutrophic environment.

5) The complete lack of correlation between nodule elemental composition and adjacent sediment composition suggest that the metals in the nodules are not derived primarily from the immediate sites of precipitation.

6) An estimate of the total reserves of ferromanganese deposits in Green Bay (Table D) and a distribution map (Figure 10)

have been constructed from our data.

7) Lastly, we recommend that an effort be made at an early date to provide large, or bulk, samples of both the manganese nodules and the sand. Such samples are necessary in order for commercial firms to adequately test the various chemical, physical and metallurgical properties. Moreover, any process use of the nodules requires an initial pilot plan and test of relatively large samples in order to design full-scale systems and to ascertain the economic (i.e., profit-to-cost ratio) factors of commercial use.

To provide such samples, we recommend that industry be allowed to conduct such bulk dredging as would provide adequately for pilot plan and testing. Since such dredging would not be an economic venture as such, but only a prelude to possible mining, i.e., a decision making step, a simple agreement between the State Geologist and the company would suffice. Cooperative (applied) research between the company and the University's Underwater Minerals Program during bulk sampling would provide for independent monitoring of such sampling activities.

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TABULAR DATA



Table A  
 MICROSCOPIC IDENTIFICATION OF SELECTED MINERALS  
 (POINT COUNT --- 200 GRAINS)

<u>Sample Number</u>	<u>Quartz</u>	<u>Feldspar</u>	<u>CO<sub>3</sub></u>	<u>Amphiboles</u>	<u>Mica</u>	<u>Biotite</u>	<u>Chlorite</u>	<u>Opaque</u>	<u>Zircon</u>
GBA 52	70	13	5	4	2	5	0	1	-
GBA 57	63	15	12	3	1	0	7	-	-
GBA 79	61	23	5	2	0	0	2	7	-
GBA 80	78	12	4	3	0	0	0	4	-
GBA 84	79	8	2	2	0	0	0	4	5
GBA 85	76	14	4	6	0	0	0	0	-
GBA 88	66	8	10	2	0	1	1	13	1
GBA 94	77	5	6	5	0	0	0	5	3
GBA 95	80	6	2	3	0	1	0	7	2
GBA 102	86	2	0	1	0	0	0	1	0
GBA 103	71	19	3	1	0	0	1	5	0
GBA 115	63	18	15	2	0	0	1	0	0
GBA 118	82	13	4	0	0	1	0	0	0
GBA 131	48	9	42	1	0	0	0	0	0
GBA 135	21	6	72	1	0	0	0	0	0
GBA 139	79	16	3	1	0	0	0	1	0
GBA 145	72	8	20	0	0	0	0	0	0
GBA 156	69	6	4	1	0	0	0	20	0
GBA 164	52	12	28	4	0	0	0	4	0
GBA 172	60	21	3	6	0	3	0	6	0
GBA 176	75	15	2	0	0	0	1	6	1
GBA 183	46	20	16	6	0	6	0	2	4
GBA 193	58	24	4	4	0	0	0	8	2
GBA 196	64	23	1	1	0	0	0	6	5
GBA 205	48	26	12	4	0	0	0	10	0
GBA 220	61	21	6	5	0	0	0	6	1
GBA 238	63	15	18	0	0	0	1	3	0

MICROSCOPIC IDENTIFICATION (cont.)

<u>Sample Number</u>	<u>Quartz</u>	<u>Feldspar</u>	<u>CO<sub>3</sub></u>	<u>Amphiboles</u>	<u>Mica</u>	<u>Biotite</u>	<u>Chlorite</u>	<u>Opaque</u>	<u>Zircon</u>
GBA 258	70	5	16	4	0	0	1	0	4
GBA 290	77	10	4	3	0	0	1	5	0
GBA 291	57	22	5	2	0	0	0	14	0
GBA 294	48	37	3	2	0	0	0	10	0
GBA 307	84	14	0	1	0	0	0	1	0
GBA 309	60	23	5	5	0	0	0	6	0
GBA 314	75	15	3	2	0	0	0	4	1
GBA 315	48	17	25	2	0	0	0	6	1
GBA 319	57	21	11	6	0	1	0	3	1
GBA 333	80	9	1	0	0	0	0	3	3
GBA 342	38	6	45	0	0	0	0	11	0
GBA 344	48	10	32	4	0	1	0	3	0
GBA 354	84	9	1	5	0	0	0	1	0
GBA 357	63	10	21	2	0	0	0	3	1
GBA 368	74	8	17	0	0	0	0	0	1

Table B

## PERCENT ORGANIC CARBON IN SELECTED SEDIMENT SAMPLES

<u>Sample Number</u>	<u>% Organic Carbon</u>
D 115	15.61
6	5.84
5	8.06
253	13.19
248	13.60
209	6.12
73	3.12
150	11.12
271	5.87
149	2.70
206	2.97
132	6.88
306	2.56
164	9.52
318	2.09
357	2.58
100	3.88
114	6.17
112	5.11
113	6.59

Table C  
 AVERAGE COMPOSITION OF GREEN BAY SEDIMENTS  
 (PARTS PER THOUSAND)

	<u>Northern</u>		<u>Eastern</u>		<u>Southern</u>		<u>Nodules</u>		<u>Deep Water</u>	
	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.	Avg.	S.D.
Mg	7.1	7.4	8.4	4.4	17.0	16.0	2.1	1.1		
Sr	.031	.024	.028	.019	.029	.023	.27	.55		
Ba	.44	.18	.40	.15	.35	.12	12.23	47.07		
Cr	.013	.023	.030	.023	.040	.038	.16	.09		
Mn	.32	.22	.37	.13	.34	.20	86.0	58.0	3.1	5.7
Fe	8.4	4.5	9.8	4.5	9.5	5.3	230.0	130.0	9.6	4.8
Zn	.028	.026	.034	.015	.047	.69	.72			
Al	16.0	9.6	20.0	7.4	13.8	8.2	16.44	36.39		
Ca	17.0	19.0	17.0	9.1	35.0	33.0				

Avg. = Average

S.D. = Standard Deviation



Table D  
GREEN BAY FERROMANGANESE NODULES  
ESTIMATED RESERVES

	<u>0-10%</u>	<u>10-30%</u>	<u>30-50%</u>	<u>50-100%</u>
total area of sediment containing nodules (m <sup>2</sup> )	7.32 x 10 <sup>8</sup>	3.73 x 10 <sup>8</sup>	1.78 x 10 <sup>8</sup>	6.28 x 10 <sup>7</sup>
volume of sediment (m <sup>3</sup> ) [1]	7.32 x 10 <sup>7</sup>	3.73 x 10 <sup>7</sup>	1.78 x 10 <sup>7</sup>	6.28 x 10 <sup>6</sup>
volume of nodules (m <sup>3</sup> ) [2]	3.66 x 10 <sup>6</sup>	7.46 x 10 <sup>6</sup>	7.12 x 10 <sup>6</sup>	4.71 x 10 <sup>6</sup>
weight of nodules (gm.) [3]	8.42 x 10 <sup>12</sup>	1.72 x 10 <sup>13</sup>	1.64 x 10 <sup>13</sup>	1.08 x 10 <sup>13</sup>
weight of Mn (gm.) [4]	7.24 x 10 <sup>11</sup>	1.48 x 10 <sup>12</sup>	1.41 x 10 <sup>12</sup>	9.29 x 10 <sup>11</sup>
weight of Fe (gm.) [5]	1.94 x 10 <sup>12</sup>	3.97 x 10 <sup>12</sup>	3.79 x 10 <sup>12</sup>	2.50 x 10 <sup>12</sup>
total weight Mn (gm.)	4.54 x 10 <sup>12</sup>			
total weight Fe (gm.)	12.20 x 10 <sup>12</sup>			

[1] assume sample depth of 10 cm.

[2] multiply volume of sediment by median % of group

[3] multiply volume of nodules by density of 2.3 gm./cm.<sup>3</sup>

[4] 8.6% Mn in nodules (from previous results)

[5] 23.1% Fe in nodules (from previous results)

Table E

## CORRELATION COEFFICIENTS: GBA SAMPLES

	Mg <sub>n</sub>	Fe <sub>n</sub>	Zn <sub>n</sub>	Mn <sub>n</sub>	Cr <sub>n</sub>	Ba <sub>n</sub>	Sr <sub>n</sub>	Mean	Dspn.	Mn <sub>b</sub>	Cu <sub>b</sub>	Zr <sub>b</sub>	Fe <sub>b</sub>	Ag <sub>b</sub>	Ni <sub>b</sub>	Ti <sub>b</sub>
DIA <sub>n</sub>	-.086	.247	-.172	-.128	-.127	.056	-.061	-.548	.221	.230	-.125	.059	.312	-.195	.063	-.413
Mg <sub>n</sub>		-.270	.254	.867	-.139	.642	.739	-.085	.375	.423	-.230	-.404	.134	.350	.499	.371
Fe <sub>n</sub>			-.099	-.471	.287	-.179	-.304	-.194	-.335	-.054	-.065	.198	.112	-.051	-.385	-.378
Zn <sub>n</sub>				.231	.004	.053	.148	.116	.104	.142	-.193	-.185	-.053	.148	-.001	.002
Mn <sub>n</sub>					-.152	.780	.735	-.002	.407	.486	-.203	-.274	.224	.326	.423	.316
Cr <sub>n</sub>						-.034	.159	-.020	-.171	-.196	-.115	.324	.062	-.195	-.102	-.037
Ba <sub>n</sub>							.747	-.215	.375	.381	-.197	-.223	.340	.172	.333	.424
Sr <sub>n</sub>								-.128	.250	.300	-.307	-.215	.252	.237	.505	.447
Mean									-.140	-.186	-.006	.249	-.286	.159	-.062	.037
Dispn.										.404	.191	.064	.322	.038	.160	-.118
Mn <sub>b</sub>										.503	-.083	.234	.173	-.059	-.105	
Cu <sub>b</sub>											.742	.083	.793	-.052	.210	
Zn <sub>b</sub>												-.097	.948	-.281	.074	
Fe <sub>b</sub>														-.113	-.003	.083
Ag <sub>b</sub>															-.235	.468
Ni <sub>b</sub>																.095
Ti <sub>b</sub>																

Table F  
CORRELATION COEFFICIENTS

DVB SAMPLES

	<u>Mg Pct</u>	<u>Ba ppm</u>	<u>Fe ppm</u>	<u>Sr ppm</u>	<u>Zn ppm</u>	<u>Mn ppm</u>	<u>Cr ppm</u>
Ca Pct	.917	.205	.145	.312	.080	.195	.451
	.973	.279	.315	.119	.490	.476	.338
	.925	-.148	.096	.265	.089	.655	.171
Mg Pct		.422	.226	.439	.215	.349	.428
		.211	.392	.074	.559	.554	.338
		-.139	.126	.123	.132	.650	.171
Ba ppm			.239	.677	.154	.243	.082
			-.074	.682	.012	-.095	-.034
			.505	.485	.304	.146	.237
Fe ppm				.172	.362	.732	-.079
				.266	.688	.535	.532
				.404	.733	.547	.538
Sr ppm					-.076	.134	-.105
					.219	-.062	.460
					.334	.383	.128
Zn ppm						.814	.407
						.613	.773
						.279	.915
Mn ppm							.153
							.620
							.217

Table G  
 CLAY X-RAY ANALYSIS  
 (REPRODUCIBILITY OF PEAK HEIGHT RATIOS)

<u>Sample Station</u>	<u>Kaolin I</u>	<u>Chlorite I</u>	<u>K/C</u>	<u>Difference in Ratio</u>
GBA 35A	17.5	19.0	.922	.020
35B	18.0	20.0	.902	
90A	11.0	142.0	.786	.101
90B	11.0	16.0	.687	
102A	13.0	18.0	.722	.015
102B	14.0	19.0	.737	
189A	10.5	9.5	1.100	.001
189B	15.0	13.5	1.110	
368A	11.0	15.0	.733	.034
368B	11.0	16.0	.698	
DVB 194A	15.0	12.0	1.250	.005
194B	30.0	23.0	1.300	
337A	45.0	47.0	.957	.043
337B	15.0	15.0	1.000	

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
12	2.00	1.80	1.10	-.18	.77
24	2.00	1.65	.85	-.41	.76
25	.00	.00	.00	.00	.00
31	2.60	2.85	.85	.29	.65
36	2.50	2.55	.55	.09	.91
37	2.50	2.50	.50	.00	.90
38	2.00	1.95	.45	-.11	.78
39	1.80	1.70	.70	-.14	1.07
40	2.50	2.55	.85	.06	.70
41	2.80	2.80	.60	.00	.50
43	3.50	3.50	.50	.00	1.30
44	2.50	2.60	.80	.12	.81
50	2.30	2.50	.70	.28	.71
51	3.00	2.95	.75	-.07	.53
52	2.60	2.60	.60	.00	.58
53	2.10	2.15	.55	.09	.64
54	3.20	3.00	.60	-.33	.42
57	1.50	1.70	1.00	.20	.60
58	1.70	1.75	1.05	.05	.62
59	2.60	2.55	.95	-.05	1.26
61	2.20	2.20	.50	.00	.80
62	2.10	2.05	.55	-.09	.54
63	1.10	1.50	.90	.44	.94
64	1.40	1.00	.90	-.44	.56
66	2.10	2.05	.45	-.11	.67
67	1.70	1.80	1.20	.08	.58
68	2.30	2.15	.65	-.23	1.15
72	1.60	1.95	1.25	.28	.60
73	2.30	2.40	1.30	.08	.65
74	1.80	2.00	1.20	.17	.42

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
75	2.50	2.50	.80	.00	.81
76	1.40	1.35	1.45	-.03	.34
78	2.10	2.40	1.30	.23	.46
79	2.30	2.20	1.10	-.09	.45
80	2.90	2.60	1.10	.27	.68
81	1.80	1.25	1.25	-.44	.20
82	2.20	2.15	.45	-.11	.67
84	1.50	1.35	.65	-.23	.61
85	2.30	2.15	.65	-.23	.77
88	2.20	2.40	1.20	.17	.54
89	1.70	1.50	1.50	-.13	.40
92	2.00	1.95	.55	-.09	.82
93	3.20	3.00	.80	-.25	.62
94	1.70	1.80	1.10	.09	.91
95	2.70	2.55	1.15	-.13	.48
97	2.20	2.10	.40	-.25	.62
98	2.30	2.35	.55	.09	.82
99	1.80	1.85	.45	.11	.78
100	2.00	2.05	.45	.11	.67
101	2.60	2.60	1.00	.00	.75
102	2.20	2.10	.50	-.20	.60
103	2.00	2.05	.55	.09	1.00
107	1.90	1.95	1.35	.04	.55
108	1.70	1.30	1.30	-.31	.27
109	3.20	2.70	1.40	-.36	.43
115	1.90	1.95	1.05	.05	.76
116	2.30	2.30	.80	.00	.94
118	1.90	2.00	.50	.20	.60
119	2.10	1.90	.60	-.33	.75
120	1.80	1.90	.70	.14	.78

Table H

## -TEXTURAL DATA-

GRA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
121	2.70	2.60	1.40	-.07	.46
124	1.80	2.05	1.25	.20	.64
125	2.30	2.20	.70	-.14	1.21
126	2.30	2.50	1.40	.14	.50
130	2.50	2.55	.95	.05	.68
131	2.50	2.45	.45	-.11	1.11
132	3.40	3.10	1.50	-.20	.40
133	2.60	2.75	.95	.16	.68
134	1.40	1.35	.55	-.09	.82
135	2.30	2.40	.90	.11	1.44
136	2.80	2.80	.50	.00	.80
137	1.80	1.85	.45	.11	.89
138	2.10	2.00	.50	-.20	.60
139	1.80	1.85	.95	.05	.79
140	2.50	2.60	1.10	.09	.59
142	2.70	2.85	1.15	.13	.61
143	1.80	1.35	1.45	-.31	.55
144	2.30	2.25	.65	-.08	1.23
145	2.00	2.00	.90	.00	.83
146	3.30	3.05	1.05	-.24	.67
149	3.30	3.15	.85	-.18	.70
155	1.20	.60	1.60	-.37	.25
156	2.60	2.35	1.15	-.22	.48
157	2.20	1.80	1.00	-.40	.45
158	2.20	2.20	.50	.00	.50
159	1.70	1.60	.40	-.25	2.00
161	1.60	1.45	.95	-.16	1.21
162	1.70	1.45	.85	-.29	1.17
163	2.70	2.75	1.05	.05	.67
165	2.30	2.45	1.25	.12	.68

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
166	1.80	2.15	1.35	.26	.44
168	1.60	1.45	.45	-.33	1.00
171	2.60	2.65	.35	.14	1.57
172	2.00	2.00	.70	.00	.71
173	1.80	1.60	.80	-.25	1.43
174	1.70	1.70	.50	.00	1.10
175	1.90	1.90	.40	.00	.75
176	1.70	1.40	1.00	-.30	.55
177	2.20	2.05	1.25	-.12	.64
179	1.70	1.55	1.05	-.14	.57
180	1.80	1.85	.55	.09	.82
181	1.80	1.80	.50	.00	.90
182	2.10	1.85	.75	-.33	1.73
183	2.30	2.30	.70	.00	1.07
184	3.00	2.95	1.35	-.04	.52
187	2.30	2.25	1.05	-.05	.62
188	1.50	1.30	1.10	-.18	.95
189	1.70	1.75	1.35	.04	.96
191	2.20	2.40	1.60	.12	.44
192	.80	.45	1.65	-.21	.24
193	3.20	2.85	.85	-.41	.82
194	2.20	2.30	1.00	.10	.75
195	2.80	2.30	1.50	-.33	.40
196	1.90	2.00	.70	.14	1.00
203	.00	.00	.00	.00	.00
204	1.70	1.70	.90	.00	.88
205	2.00	2.30	1.30	.02	.42
206	3.10	2.75	.95	-.36	.63
207	.00	.00	.00	.00	.00
208	3.10	2.00	2.00	.55	.17



Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
209	.00	.00	.00	.00	.00
210	.00	.00	.00	.00	.00
211	.00	.00	.00	.00	.00
212	.00	.00	.00	.00	.00
213	.00	.00	.00	.00	.00
214	.00	.00	.00	.00	.00
215	.00	.00	.00	.00	.00
215	1.70	1.70	.00	.00	.00
216	.00	.00	.00	.00	.00
217	.00	.00	.00	.00	.00
218	.00	.00	.00	.00	.00
219	2.50	2.40	.90	-.11	.72
220	1.80	1.95	1.05	.14	.57
221	.00	.00	.00	.00	.00
222	2.00	1.50	1.30	-.38	.46
223	1.30	1.30	1.40	.00	.39
224	.00	.00	.00	.00	.00
225	.00	.00	.00	.00	.00
226	.00	.00	.00	.00	.00
227	.00	.00	.00	.00	.00
228	2.15	2.22	.82	-.28	1.30
229	2.25	1.40	1.40	-.60	.32
230	2.35	2.40	.60	.08	.62
231	2.45	2.35	.55	-.18	.63
232	.00	.00	.00	.00	.00
233	.00	.00	.00	.00	.00
234	.00	.00	.00	.00	.00
235	.00	.00	.00	.00	.00
236	-.05	1.00	1.25	.84	.30
237	2.10	2.52	.92	.45	1.35

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
238	1.75	2.10	1.15	.30	.45
239	.00	.00	.00	.00	.00
240	3.15	2.96	.83	-.23	.69
240	.00	.00	.00	.00	.00
241	1.75	1.35	1.40	-.28	.30
242	.00	.00	.00	.00	.00
243	.00	.00	.00	.00	.00
244	.00	.00	.00	.00	.00
245	-.10	1.07	1.32	.89	.29
246	3.30	3.19	.74	.15	.76
247	.00	.00	.00	.00	.00
248	.00	.00	.00	.00	.00
249	.00	.00	.00	.00	.00
250	.00	.00	.00	.00	.00
251	2.15	1.77	1.02	-.37	.69
252	.00	.00	.00	.00	.00
253	.00	.00	.00	.00	.00
254	.00	.00	.00	.00	.00
255	.00	.00	.00	.00	.00
256	.00	.00	.00	.00	.00
257	.00	.00	.00	.00	.00
258	3.08	2.56	1.33	-.39	.23
259	.00	.00	.00	.00	.00
260	.00	.00	.00	.00	.00
261	2.40	2.41	.90	.01	.90
262	.00	.00	.00	.00	.00
263	.00	.00	.00	.00	.00
264	1.51	1.28	1.00	-.23	.64
265	1.55	1.44	.74	-.15	1.04
266	2.73	2.80	.90	.08	.50

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
267	.00	.00	.00	.00	.00
268	.00	.00	.00	.00	.00
269	.00	.00	.00	.00	.00
270	.00	.00	.00	.00	.00
271	1.32	.88	1.02	-.43	1.48
272	.00	.00	.00	.00	.00
273	.00	.00	.00	.00	.00
274	.25	1.08	1.36	.61	.32
275	1.62	1.02	1.22	-.49	.22
275	2.17	2.12	.87	-.06	.84
275	2.04	1.95	1.05	-.08	.46
276	1.89	1.77	1.02	-.12	.56
277	.00	.00	.00	.00	.00
278	2.35	2.45	1.05	.09	.76
279	2.54	2.58	1.09	.09	.70
280	.00	.00	.00	.00	.00
282	2.30	2.40	.90	.11	.83
283	2.40	2.70	1.00	.30	.60
284	2.10	2.35	1.15	.22	.61
285	1.80	1.50	1.20	-.25	.58
286	.00	.00	.00	.00	.00
287	.00	.00	.00	.00	.00
288	.00	.00	.00	.00	.00
289	.00	.00	.00	.00	.00
290	1.80	1.70	1.00	-.10	.80
291	1.90	2.00	1.20	.08	.58
292	2.90	2.90	.50	.00	1.00
293	.00	.00	.00	.00	.00
294	1.80	1.70	1.10	-.09	.64
295	.00	.00	.00	.00	.00

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
296	1.80	1.50	1.20	-.25	.42
297	.00	.00	.00	.00	.00
298	1.90	1.95	.95	.02	.84
299	.00	.00	.00	.00	.00
300	.00	.00	.00	.00	.00
301	2.60	2.50	1.70	.06	.44
302	2.00	1.90	1.20	-.08	.58
303	.00	.00	.00	.00	.00
304	3.30	3.05	.95	-.26	.68
305	.00	.00	.00	.00	.00
306	2.30	2.25	.65	-.08	1.15
307	2.10	2.10	.50	.00	.70
308	2.00	1.95	.55	-.09	1.09
309	2.40	2.40	1.10	.00	.59
309	.00	.00	.00	.00	.00
310	1.80	2.05	.75	.33	.80
311	2.50	2.50	.90	.00	.78
312	3.30	2.70	1.50	-.40	1.67
313	2.30	2.25	.75	-.07	.87
314	2.00	1.90	.70	-.14	.86
315	.00	.00	.00	.00	.00
316	2.80	2.65	1.15	-.13	.61
317	2.70	2.70	.80	.00	.62
318	2.40	2.40	.60	.00	.92
319	3.00	3.10	1.00	.10	1.50
320	.00	.00	.00	.00	.00
321	2.50	2.55	.75	.07	.87
322	2.00	1.70	1.00	-.30	.55
323	3.10	3.00	.80	-.12	.81
324	2.10	2.05	.55	-.09	1.73

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
325	1.90	1.85	.65	-.08	1.00
326	2.30	2.10	.60	-.33	1.00
327	1.90	1.90	.40	.00	1.37
328	2.10	2.05	.45	-.11	.56
329	1.90	1.95	.45	.11	1.00
330	2.10	2.05	.45	-.11	.78
331	2.30	2.20	.40	-.25	.50
332	1.70	1.80	1.00	.10	.70
333	1.70	1.55	.95	-.16	.79
334	1.90	1.95	.45	.11	.89
335	1.80	1.95	.75	.20	1.40
336	3.10	2.80	.90	-.33	.55
337	2.20	2.35	.95	.16	.68
338	1.80	2.05	1.35	.18	.74
339	2.10	2.10	.60	.00	1.33
340	.00	.00	.00	.00	.00
341	1.50	.85	.95	-.68	.42
342	1.60	1.35	.95	-.26	.79
343	2.50	2.45	.75	-.07	.67
344	2.80	2.80	.60	.00	.67
345	.00	.00	.00	.00	.00
346	.00	.00	.00	.00	.00
347	.00	.00	.00	.00	.00
348	.30	.90	1.10	.54	.36
349	2.10	2.05	.55	-.09	.54
350	2.00	2.05	.37	.14	.86
351	2.10	2.10	.50	.00	.50
352	1.60	1.45	.55	-.27	.73
353	1.90	1.95	.55	.09	.73
354	1.60	1.45	.55	-.27	1.09

Table H

## -TEXTURAL DATA-

GBA Sample Number	Median	Mean	Dispersion	Skewness	Kurtosis
355	1.70	1.75	.45	.11	.89
355	2.05	2.15	.65	.15	.90
356	1.80	1.75	.45	-.11	1.00
357	2.42	2.27	.62	-.24	1.14
358	2.90	2.62	1.22	-.23	.88
358	.00	.00	.00	.00	.00
359	.00	.00	.00	.00	.00
360	3.10	2.85	.65	-.38	.69
361	2.90	2.60	1.10	-.27	.36
361	.00	.00	.00	.00	.00
362	.00	.00	.00	.00	.00
363	2.60	2.60	.60	.00	.75
364	1.60	1.40	.60	-.33	1.00
365	3.50	3.45	.65	-.08	.85
366	2.30	2.25	.85	-.06	1.35
367	1.00	1.50	.45	.33	1.22
368	1.80	1.55	.75	-.33	.87
369	1.80	1.40	1.20	-.33	.42
370	.00	.00	.00	.00	.00
371	3.10	2.85	1.15	-.22	.61
372	.00	.00	.00	.00	.00
373	1.60	1.30	1.00	-.30	.45
373	.00	.00	.00	.00	.00
374	.40	.55	.75	.20	.40
375	2.00	1.95	.65	-.08	.77
376	.00	.00	.00	.00	.00
378	-.10	1.35	1.65	-.88	.30
378	.00	.00	.00	.00	.00

-BULK SAMPLE ELEMENTAL DATA-

Table

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
2	.2160	-	-	3.9580	-	-	-	.0013
3	.1670	-	-	3.5300	-	.0320	-	.0035
4	.1520	-	-	5.6800	-	-	-	.0047
5	.0985	-	-	5.4200	-	-	-	.0072
6	.0820	-	-	2.7700	-	-	-	.0058
7	.0618	-	-	1.0260	-	-	-	.0006
8	.1265	-	-	5.5500	-	-	-	.0044
9	.1640	-	-	3.7180	-	-	-	.0009
10	.1990	-	-	8.4200	-	-	-	.0058
11	.1440	-	-	1.9900	-	-	-	.0018
12	.0335	-	-	1.2500	-	.0136	-	.0006
13	.1750	-	-	2.8700	-	-	-	.0013
14	.0886	-	-	2.0500	-	-	-	.0038
15	.0851	-	-	4.2800	-	-	-	.0052
16	.0780	-	-	1.4050	-	-	-	.0005
17	.1670	-	-	1.5800	-	-	-	.0021
18	.0457	-	-	1.5420	-	-	-	.0009
19	.0689	-	-	1.1700	-	-	-	.0001
20	.1360	-	-	2.5100	-	-	-	.0009
21	.0574	-	-	8.8100	-	-	-	.0053
22	.2620	-	-	5.4480	-	-	-	.0018
23	.1400	-	-	4.0400	-	-	-	.0053
24	.3050	-	-	2.5290	-	-	-	.0003
25	.2180	-	-	7.2400	-	-	-	.0052
26	.0153	-	-	9.0700	-	-	-	.0072
27	.1560	-	-	1.8200	-	-	-	.0018
28	.2860	-	-	11.9500	-	-	-	.0102
29	.2715	-	-	3.4700	-	-	-	.0032
30	.1175	-	-	2.8200	-	-	-	.0008
31	.0355	-	-	6.1010	-	-	-	.0020

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
32	.2320	-	-	3.6080	-	-	-	.0019
33	.1825	-	-	1.4140	-	-	-	-
34	.0555	-	-	.9027	-	-	-	.0005
35	.1340	-	-	6.8800	-	-	-	.0042
36	.0866	-	-	4.9700	-	-	-	.0051
37	.0540	-	-	.9969	-	-	-	.0006
38	.4580	-	-	1.1600	-	-	-	.0018
39	.0422	-	-	.6350	-	-	-	-
40	.0671	-	-	2.2100	-	-	-	.0029
41	.0187	-	-	.6408	-	-	-	.0003
42	.0970	-	-	1.3640	-	-	-	.0013
43	.0604	-	-	.9684	-	-	-	.0002
44	.0967	-	-	1.4750	-	-	-	.0020
45	.2550	-	-	3.8200	-	-	-	.0022
46	.1652	-	-	3.2500	-	-	-	.0015
48	.0845	-	-	1.5600	-	-	-	.0007
49	.0855	-	-	1.6900	-	-	-	.0018
50	.0620	-	-	.6140	-	-	-	-
51	.0427	-	-	1.1550	-	.01677	-	.0002
52	.0284	-	-	.9285	-	-	-	-
53	.0579	-	-	.6870	-	-	-	1.5000
54	.0497	-	-	.3200	-	-	-	1.0000
56	1.5480	-	-	4.3020	-	-	-	.0016
58A	5.6900	-	-	6.8200	-	-	-	6.5600
58B	4.4750	-	-	6.5000	-	.00006	-	5.1200
59	.5170	-	-	21.1550	-	-	-	.0071
60	.1355	-	-	3.4670	-	-	-	.0022
61	.0945	-	-	2.8870	-	.00500	-	.0011
62	.0570	-	-	.9562	-	-	-	.0004
63	.0378	-	-	18.7570	-	.01508	-	.0016



Table I

GIBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
64	.3530	-	-	3.5010	-	-	-	.0019
66	.0298	-	-	2.6270	-	-	-	.0005
67	6.7500	-	-	6.3570	-	-	-	.0010
68	1.8400	-	-	6.8540	-	.03210	-	.0048
69	.1915	-	-	10.2640	-	-	-	.0200
70	.0772	-	-	1.2670	-	-	-	.0002
71	.1625	-	-	3.7090	-	-	-	.0016
72	9.5000	-	-	3.9300	-	-	-	.0009
73	.0780	-	-	3.0430	-	-	-	.0042
74	9.6300	-	-	4.5220	-	-	-	.0069
76	4.4500	-	-	.8144	-	-	-	.0003
78	1.2920	-	-	3.8350	-	-	-	.0017
79	3.1900	-	-	7.5700	-	-	-	.0045
80	1.6030	-	-	2.3970	-	-	-	.0034
81	6.1500	-	-	11.8260	-	-	-	.0153
82	.0445	-	-	.8375	-	.02184	-	-
84	.0501	-	-	3.6560	-	-	-	-
85	1.3440	-	-	6.4330	-	-	-	.0021
86	.0700	-	-	3.4490	-	-	-	.0016
87	.1610	-	-	3.7870	-	-	-	.0053
88	5.3400	-	-	4.1960	-	-	-	.0056
89	5.3500	-	-	17.7140	-	-	-	.0201
90	.3950	-	-	5.2620	-	-	-	.0027
91	.0458	-	-	5.7070	-	-	-	.0022
92	.0462	-	-	5.5160	-	-	-	.0056
93	.5500	-	-	4.5260	-	.04070	-	.0020
94	1.7400	-	-	2.8650	-	.00410	-	.0016
95	2.1400	-	-	4.1210	-	-	-	.0016
96	.7250	-	-	4.4250	-	-	-	.0013
97	.1090	-	-	1.9600	-	-	-	.0005

Table 1

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
98	.0814	-	-	.8432	-	-	-	-
99	.0956	-	-	1.5520	-	-	-	-
100	.0634	-	-	50.7940	-	-	-	.0073
101	.1980	-	-	1.2860	-	-	-	.0002
102	.4140	-	-	4.9980	-	.06738	-	.0010
103	.4250	-	-	2.5820	-	-	-	-
104	.6580	-	-	4.6060	-	-	-	.0031
105	.1068	-	-	4.5480	-	-	-	.0026
106	.2200	-	-	3.0250	-	-	-	-
107	5.0500	-	-	5.6171	-	-	-	.0097
108	6.2700	-	-	17.5050	-	.08037	-	.0044
109	.0815	-	-	1.7230	-	-	-	-
111	.1530	-	-	2.3200	-	-	-	.0006
112	.0940	-	-	1.4110	-	-	-	.0009
113	.0547	-	-	1.6880	-	-	-	.0009
114	.1129	-	-	1.5640	-	-	-	.0009
115	.0505	-	-	3.0720	-	.01574	-	.0005
116	.1198	-	-	4.2710	-	-	-	.0045
118	.2095	-	-	.9577	-	.42100	-	-
119	1.9080	-	-	11.2720	-	.02590	-	.0050
120	3.5450	-	-	16.7100	-	.01485	-	.0421
121	2.5150	-	-	4.0980	-	-	-	.0008
122	.1127	-	-	2.5970	-	-	-	.0022
123	.1409	-	-	4.2680	-	-	-	.0162
124	8.1700	-	-	16.8380	-	-	-	.0103
125	.0665	-	-	1.9510	-	-	-	.0006
126	11.4700	-	-	8.6220	-	-	-	.0109
127	.5300	-	-	5.5360	-	-	-	.0015
128	.6330	-	-	9.7760	-	-	-	.0047
129	.6370	-	-	2.1430	-	-	-	.0002

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
130	.2478	-	-	1.5880	-	-	-	-
131	.1729	-	-	1.5230	-	-	-	.0003
132	.1040	-	-	1.6610	-	-	-	.0006
133	.1912	-	-	2.4830	-	-	-	-
134	.1100	-	-	2.8570	-	-	-	.0038
135	.5240	-	-	2.9821	-	.01642	-	.0009
136	.1022	-	-	.6035	-	-	-	-
137	.0336	-	-	1.5190	-	.00001	-	.0015
138	.0917	-	-	2.7410	-	-	-	.0003
139	3.1900	-	-	3.4330	-	.06550	-	.0012
140	3.3080	-	-	7.6090	-	.08050	-	.0078
141	.9700	-	-	4.9490	-	-	-	.0034
142	.5010	-	-	1.5740	-	-	-	-
143	4.6600	-	-	11.0640	-	-	-	.0042
144	.0716	-	-	1.1820	-	.00890	-	.0005
145	.2920	-	-	lost sample	-	-	-	-
146	.3205	-	-	2.3790	-	-	-	.0005
147	.3165	-	-	5.3800	-	-	-	.0024
148	.2480	-	-	6.8200	-	-	-	-
149	.1520	-	-	2.0690	-	-	-	-
150	.3870	-	-	5.4940	-	-	-	.0016
151	.3055	-	-	6.7480	-	-	-	.0023
152	.3000	-	-	4.7520	-	-	-	.0024
153	.3680	-	-	5.9670	-	-	-	.0028
155A	.2080	-	-	2.6300	-	.00102	-	.1000
155B	4.0600	-	-	-	-	±.00070	-	-
156	4.5900	-	-	7.7610	-	-	-	.0083
157	1.1100	-	-	9.8850	-	.00680	-	.0033
158	.0346	-	-	.9535	-	-	-	-
159	.4230	-	-	5.3150	-	.09520	-	.0021

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
160	.1430	-	-	2.4070	-	.07420	-	.0008
161	1.3730	-	-	25.0000	-	.01090	-	.0124
162	1.5820	-	-	7.3590	-	-	-	.0020
163	1.9200	-	-	3.3760	-	-	-	.0044
164	.1472	-	-	2.2900	-	.02320	-	.0012
165	.3495	-	-	3.2870	-	.05290	-	-
166	3.8300	-	-	7.7400	-	-	-	.0067
167	.7750	-	-	5.6760	-	-	-	.0018
168	.0645	-	-	2.3040	-	-	-	-
169	.6650	-	-	3.8520	-	-	-	.0028
170	.3660	-	-	5.5640	-	-	-	.0025
171	.1230	-	-	1.7180	-	.04280	-	-
172	.8220	-	-	6.4550	-	.07880	-	.0023
173	3.6300	-	-	17.8920	-	-	-	.0078
174	.1049	-	-	2.0910	-	-	-	-
175	.1045	-	-	4.8520	-	-	-	-
176	4.0400	-	-	18.0410	-	-	-	.0077
177	6.2200	-	-	18.4200	-	.03150	-	.0168
179	4.4700	-	-	37.7920	-	-	-	.0072
180	.1320	-	-	2.4240	-	.05770	-	.0006
181	.0531	-	-	2.0310	-	-	-	-
182	1.8330	-	-	13.5910	-	.15710	-	.0035
183	1.5040	-	-	3.4410	-	-	-	.0032
184	.6120	-	-	4.6120	-	.000007	-	.0006
185	.1398	-	-	3.3520	-	-	-	.0014
186	.1590	-	-	3.5590	-	-	-	.0013
187	4.0900	-	-	2.0330	-	-	-	-
188	7.1500	-	-	4.4900	-	.03920	-	.0071
189	.5140	-	-	1.4360	-	-	-	.0002
190	.2170	-	-	6.6010	-	-	-	.0030

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
191	1.0000-1.5000	-	-	7.4090	-	-	-	.0097
192	2.2200	-	-	11.3810	-	-	-	.0047
193	.0829	-	-	2.3620	-	-	-	.0019
194	3.0850	-	-	6.9890	-	.02520	-	.0085
195	1.9400	-	-	6.1810	-	.03030	-	.0037
196	.2260	-	-	1.4390	-	-	-	.0010
203	.8960	-	.0163	13.2780	.0010	-	-	-
204	.9990	-	.0763	.1000	.0001	.00600	-	-
205	1.8790	-	-	6.4880	-	-	-	-
206	1.3990	-	.0388	.5794	.0001	-	-	-
207	.6440	-	.0398	-	.0004	-	-	-
208	.4478	-	-	.6900	-	-	-	-
209	.3900	-	-	6.3220	-	-	-	-
210	.7670	-	-	-	-	-	-	-
211	.9950	-	.0296	13.3760	.0006	-	-	-
212	.4440	-	.0830	13.6200	.0002	-	-	-
213	.4276	.1490	-	8.3620	-	-	-	-
214	.3120	-	-	17.0230	-	-	-	-
215A	1.3400	-	.0150	8.9050	-	-	-	-
215B	18.5020	-	.0076	7.0010	-	-	-	-
216	.4760	-	.0960	13.5830	.0003	-	-	-
217	.3530	-	-	13.9120	.0002	-	-	-
218	.5180	-	-	13.2850	.0001	-	-	-
219	3.2780	-	-	1.2270	.0004	-	-	-
220	27.1800	-	-	.8510	.0005	.00900	-	-
221	.4370	-	.0298	1.6270	.0002	-	-	-
222	8.0558	.0350	-	.5660	-	-	-	-
223	7.3108	-	.0250	11.4250	.0001	-	-	-
224	37.2720	-	-	.1214	.0002	-	-	-
225	.2500	-	-	8.0300	-	-	-	-

Table 1

GRA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
226	.3446	.3550	.0242	7.7130	-	-	-	-
227	.0821	.0320	-	.1190	-	.0109	-	-
228	.1148	-	-	.8197	-	.0055	-	-
229	.0404	.0430	-	.0892	-	.0038	-	-
230	.0235	.0230	.0081	.1387	.0004	.0083	-	-
231	.0886	.1180	.0066	.3860	-	-	-	-
232	.0697	-	-	23.1500	-	.0393	.1870	-
233	.0961	-	.0288	.1245	-	-	.1740	-
234	.1221	-	-	12.6100	.0008	-	-	-
235	.9598	.4150	-	10.3720	-	-	-	-
236	3.2197	-	.0123	17.3630	.0001	-	-	-
237	.4695	-	.0167	1.5180	-	-	.0390	-
238	.0375	.0370	.0108	.9754	.0002	.0085	.0440	-
239	.8285	-	-	13.6800	-	-	-	-
240A	.0496	.0520	.0024	4.0070	-	-	.0470	-
240B	.0482	.0450	.0058	3.6900	-	-	.0940	-
241	3.8745	-	-	8.2490	.0002	-	-	-
242	.1309	-	.0067	7.1590	-	-	-	-
243	.7379	.2240	.0220	17.9720	-	-	-	-
244	.1962	-	-	10.0800	-	.0786	.2570	-
245	15.6560	-	.0080	6.8040	.0129	-	-	-
246	.0593	-	.1397	.0410	-	-	-	-
247	.0896	-	.0081	3.9730	-	-	.0220	-
248	-	-	-	18.0480	.0001	-	-	-
249	.1062	-	-	11.8990	-	-	.0150	-
250	.0786	-	.0328	.0270	.0003	-	.0850	-
251	.9905	.1490	.0169	8.7020	-	-	-	-
252	.4061	.5100	.0344	15.2330	-	-	-	-
253	.1136	-	-	.0030	-	-	.1550	-
254	.0802	-	.0047	12.0700	-	-	.1420	-

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
255	.1303	-	.0092	2.8510	-	-	-	-
256	.0691	.1140	-	.3939	-	.0390	.1290	-
257	.0743	-	.0047	10.8000	-	-	.1150	-
258	.2311	-	-	6.6080	.0002	-	-	-
259	.0591	.0890	.0070	.2263	-	-	-	-
260	.0851	-	-	.2026	-	.0049	.2210	-
261	.2037	-	-	22.2630	-	-	-	-
262	-	.2540	.0110	8.9380	.0001	-	-	-
263	.0910	.0480	-	10.7610	-	-	.0900	-
264	1.3320	-	-	6.9970	.0001	-	-	-
265	1.2050	-	-	9.7580	-	.0039	-	-
266	.1046	-	-	.4137	.0001	.0493	.0230	-
267	.2765	-	-	.1318	-	.0532	-	-
268	.4099	1.0490	-	.0540	-	-	-	-
269	.0844	-	-	.2013	-	.0670	.0840	-
270	.2694	-	.0100	3.2460	-	.0307	-	-
271	.9736	-	.0700	4.1030	.0001	-	-	-
272	.1978	-	-	.0664	-	-	-	-
273	.3015	.0380	-	3.0130	-	.0172	.0610	-
274	8.5731	1.1280	.0330	22.6500	-	-	-	-
275A	3.0920	.1050	.0044	4.8550	-	-	.0830	-
275B	2.7620	.5810	.0133	.1415	.0003	-	.1370	-
276	.0365	.5000	-	8.3330	.0002	-	-	-
277	.2108	-	-	7.5040	-	.0215	.2020	-
279	2.2510	.0940	-	.3066	.0004	.0090	-	-
280	.0988	-	-	9.5130	-	-	.1110	-
282	.7439	-	-	-	-	-	.0470	-
283	-	1.8100	.5110	.0039	5.0920	-	-	-
284	1.5150	-	-	.0740	-	-	-	-
285	1.7870	.0530	-	.0779	-	.0781	.0240	-

Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
286	.0819	.0580	-	21.2600	-	-	.6100	-
287	.0735	.0770	-	24.0400	.0013	-	.1620	-
288	.0860	-	-	7.8140	-	-	-	-
289	.7439	-	-	2.2260	-	.0319	.0470	-
290	10.5700	-	-	25.2290	-	-	-	-
291	2.0040	.0460	-	6.9210	.0123	-	-	-
292	.1109	-	-	15.1230	-	-	.0340	-
293	.0748	-	-	2.0670	-	.0185	-	-
294	1.2580	-	.0110	9.7840	.0003	-	-	-
295	.0300	-	.0039	5.1670	.0001	-	-	-
296	1.2960	-	-	16.0500	-	.0330	.0300	-
297	.1715	-	-	9.4320	-	-	.0810	-
298	9.4550	-	-	5.7970	-	-	-	-
299	.0687	-	-	-	-	-	-	-
300	.3960	-	-	10.4440	.0002	-	-	-
301	1.3650	-	.0127	7.5040	.0001	-	-	-
302	1.5030	-	.0250	.5915	-	.0132	-	-
303	.0971	-	-	.3022	-	.0532	.1370	-
304	1.7830	-	-	5.8000	-	-	-	-
305	.7221	-	.0079	7.7510	-	-	-	-
306	.0570	-	.0174	4.2210	-	-	.0300	-
307	.0320	-	-	2.7470	-	.0081	.0340	-
308	.2706	.0790	-	.0121	-	.0084	.0620	-
309A	.5490	.1590	-	.3638	.0006	.0203	-	-
309B	.1803	.1180	-	.6050	-	.1970	-	-
311	.0798	.1110	-	2.2800	.0003	.0219	.0430	-
312	.7461	.0250	-	3.7870	.0001	-	.0520	-
313	4.5380	.7640	-	6.2840	.0001	-	-	-
314	.6951	.0610	-	9.9930	-	-	.0210	-
315	.5660	-	-	11.8220	.0001	-	-	-



Table I

GBA Sample Number	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)
316	.8294	-	-	5.5430	-	-	.1580	-
317	1.8440	.9060	.0060	.4330	.0001	-	-	-
318	.2364	.0710	.1081	.0915	.0002	-	-	-
319	.0713	-	.0023	7.4750	.0001	-	-	-
320	.1252	.0190	-	.0845	-	-	-	-
321	14.1070	-	-	1.4920	.0002	-	-	-
323	.2889	.0850	-	.5329	.0003	.0061	.1230	-
324	1.0120	-	.0094	.1780	.0001	.0050	-	-
326	.1750	-	-	.1904	-	.0099	.0640	-
327	.4638	-	-	.0820	-	-	-	-
328	.2437	-	.0083	.0191	-	.0530	-	-
329	.0395	-	.0034	4.8110	-	-	.0520	-
330	.0594	-	-	.1132	-	.0212	.1560	-
331	.0371	-	-	1.8160	-	.0038	.1230	-
332	.0742	-	.0113	7.9230	-	-	.0512	-
333	1.2080	.0293	-	11.7100	-	.0035	.0356	-
334	.3610	.2910	.0167	.3090	.0001	-	-	-
335	.2290	-	-	6.5310	-	.0043	.0382	-
336	.0399	.0176	.0207	4.3840	-	-	.2041	-
337	.0443	-	-	3.0720	.0001	-	.0476	-
338	1.7260	-	-	8.3710	-	.0062	-	-
339	1.9460	-	.0124	.1400	.0002	.0160	-	-
340	.0923	-	-	.5120	-	.0017	-	-
341	.0891	.0130	-	1.5760	-	.0060	.0127	-
342	.1403	-	-	2.5200	-	-	.0273	-
343	.0208	-	.0078	2.9250	-	.0029	.1386	-
344	.0184	.0445	-	4.0750	.0001	.0066	-	-
345	.1048	.0452	-	10.4920	-	.0099	.0801	-
346	.2340	-	.0457	.5620	.0007	-	-	-
347	.2780	-	.0490	8.9430	.0002	-	-	-

GBA Sample Number	Table I									
	Mn (Bulk %)	Cu (Bulk %)	Zr (Bulk %)	Fe (Bulk %)	Ag (Bulk %)	Ni (Bulk %)	Ti (Bulk %)	Co (Bulk %)		
348	.1452	-	-	6.9600	-	-	.1505	-	-	-
349	.0590	-	.0100	.0810	.0001	-	-	-	-	-
350	.0072	-	-	2.1840	.0001	.0042	.0413	-	-	-
351	.0313	-	.0037	3.4780	-	-	.2015	-	-	-
352	.0372	-	.0013	4.9080	-	-	.1546	-	-	-
353	.0694	.0354	-	4.9190	-	.0076	.2216	-	-	-
354	.2048	-	.0070	.2570	-	.0069	-	-	-	-
355	.0750	-	.0224	.0068	.0002	-	-	-	-	-
356	.0323	-	-	3.4890	-	.0055	.0277	-	-	-
357	.2598	-	-	7.0870	.0001	.0066	-	-	-	-
358A	.1531	.0907	-	2.7540	-	.0033	.0971	-	-	-
358B	.1573	-	-	11.6630	-	-	.0605	-	-	-
359	.4310	-	.0082	11.6420	-	-	-	-	-	-
360	.0579	.0137	-	1.2460	-	.0037	-	-	-	-
361A	.8610	-	.0170	.2390	.0004	.0090	-	-	-	-
361B	.8820	-	.0320	15.8070	.0001	-	-	-	-	-
362	.0554	-	.0120	5.9130	.0002	-	.1066	-	-	-
363	.0190	.0097	-	3.2150	-	-	-	-	-	-
364	.0165	.0275	-	1.1330	-	-	-	-	-	-
365	.0684	.0375	-	4.0520	-	.0027	.0628	-	-	-
366	.1868	.0295	-	4.4840	-	.0031	-	-	-	-
367	.0251	.0136	-	1.7730	-	.0039	-	-	-	-
368	.0587	.0094	-	2.1080	-	.0023	-	-	-	-
369	6.0510	.5240	-	1.3930	.0002	-	-	-	-	-
370	.0418	-	-	6.5920	-	-	.3477	-	-	-
371	9.8530	-	-	1.1950	-	-	-	-	-	-
372	.1096	-	-	5.5420	-	.0017	.2867	-	-	-
373A	1.7840	.1273	-	11.7000	-	-	.1393	-	-	-
373B	6.9490	-	.0147	.0900	.0002	.0025	-	-	-	-
374	.0678	-	-	4.8670	-	.0081	-	-	-	-
375	.3367	.0869	.0126	4.0890	-	-	-	-	-	-
376	.0946	.0479	-	8.5440	-	-	.1414	-	-	-
378A	25.5550	-	-	41.9940	-	-	-	-	-	-
378B	24.5460	-	-	24.8600	.0005	-	-	-	-	-

Table J

-BULK SAMPLE ELEMENTAL DATA-

DVB Sample Number	PER CENT		PARTS PER MILLION						
	Ca	Mg	Al	Ba	Fe	Sr	Zn	Mn	Cr
106	6.750	3.060	16000.	285.	8350.	58.1	35.3	995.	50.0
107	5.220	2.470	>30000.	344.	19700.	52.6	67.5	498.	60.9
109	1.620	.855	19200.	318.	4770.	<10.0	<10.0	166.	<30.0
110	3.550	1.850	>30000.	479.	21300.	61.9	95.9	582.	81.1
111	2.710	1.150	>30000.	497.	13100.	50.3	55.6	360.	48.0
115	2.040	.907	>30000.	410.	20800.	34.9	222.0	391.	169.0
116	2.000	.928	>30000.	391.	16500.	36.6	162.0	312.	120.0
117	2.200	1.210	>30000.	448.	>25000.	66.6	183.0	387.	104.0
118	1.830	.876	>30000.	525.	16100.	60.4	100.0	254.	70.2
125	3.350	1.540	24700.	375.	12000.	36.0	39.5	393.	30.9
126	3.170	1.460	>30000.	445.	22900.	42.5	88.9	679.	54.1
132	2.230	.865	15100.	237.	6080.	27.2	<10.0	181.	<30.0
133	2.810	1.270	16500.	267.	7760.	23.6	24.8	222.	<30.0
135	1.020	.505	18100.	253.	6250.	<10.0	24.8	148.	<30.0
136	.807	.400	15900.	292.	6120.	<10.0	36.3	165.	32.6
137	.849	.307	19000.	331.	7380.	17.2	22.2	174.	<30.0
141	.678	.338	15600.	276.	5610.	<10.0	20.6	149.	<30.0
143	1.280	.621	24400.	456.	8140.	26.0	30.7	234.	<30.0
164	4.190	2.470	23700.	395.	9240.	75.9	<10.0	309.	<30.0
166	.565	.329	21400.	306.	7380.	23.6	42.9	222.	58.3
173	1.940	.918	26200.	487.	15000.	30.1	42.9	902.	35.3
175	.774	.360	22600.	431.	8140.	<10.0	49.5	358.	44.9
180	1.450	.761	>30000.	500.	>25000.	31.9	130.0	1360.	62.0
181	<.500	.157	15600.	365.	7160.	13.1	10.6	204.	<30.0
182	<.500	.145	19400.	384.	5860.	12.2	<10.0	144.	<30.0
183	1.350	.682	16600.	253.	12200.	24.7	76.2	478.	<30.0
184	5.250	1.640	21900.	391.	12700.	55.6	41.0	404.	31.9
185	.820	.485	18100.	378.	24600.	25.3	31.5	510.	39.4
186	.766	.351	16200.	318.	13900.	31.8	<10.0	287.	<30.0
187	3.480	.430	11900.	156.	5510.	52.5	<10.0	161.	<30.0
188	.553	.216	13000.	225.	6320.	<10.0	10.0	212.	<30.0
189	<.500	.174	15300.	314.	8800.	<10.0	14.8	239.	<30.0
191	2.240	.912	21900.	270.	>25000.	36.6	38.8	496.	43.1
194	2.090	.781	>30000.	547.	11900.	57.9	31.5	382.	36.0
195	<.500	.166	12900.	195.	5260.	25.9	14.2	193.	<30.0
196	1.100	.430	19400.	383.	5110.	24.7	<10.0	152.	<30.0
198	.703	.284	25300.	530.	12600.	46.6	20.4	309.	<30.0
203	.540	.211	25100.	613.	7010.	37.1	34.1	217.	<30.0
206	1.690	.744	>30000.	737.	8830.	82.0	36.3	289.	<30.0
209	1.540	.697	28900.	577.	8930.	54.1	48.4	319.	<30.0

Table J

## -BULK SAMPLE ELEMENTAL DATA-

DVB Sample Number	PER CENT		PARTS PER MILLION						
	Ca	Mg	Al	Ba	Fe	Sr	Zn	Mn	Cr
210	2.000	.886	>30000.	722.	10200.	75.8	42.4	354.	<30.0
211	2.440	1.180	29900.	616.	8820.	51.7	27.7	261.	<30.0
212	3.080	1.380	>30000.	709.	8030.	72.7	29.5	281.	<30.0
213	1.190	.515	>30000.	712.	8130.	43.0	34.1	302.	<30.0
214	.991	.415	>30000.	697.	7100.	45.4	25.8	239.	<30.0
215	2.060	1.050	>30000.	708.	11500.	74.3	47.3	431.	34.3
216	<.500	<.100	15400.	325.	4070.	16.1	<10.0	116.	<30.0
217	1.320	.450	15100.	286.	4340.	18.1	<10.0	124.	<30.0
218	<.500	.203	14200.	318.	4560.	10.2	<10.0	177.	<30.0
219	4.150	1.980	24700.	650.	9530.	31.2	49.0	381.	<30.0
220	7.550	3.950	23100.	643.	8330.	54.8	34.9	503.	<30.0
221	<.500	.203	18300.	384.	6700.	10.2	<10.0	199.	<30.0
225	1.060	.475	23100.	486.	6930.	<10.0	26.1	224.	33.9
229	1.100	.535	15600.	303.	7130.	<10.0	24.0	209.	31.9
231	.983	.545	21700.	506.	9150.	38.9	30.7	302.	50.4
234	4.820	2.120	>30000.	712.	13200.	68.8	45.1	508.	64.2
239	<.500	.207	19000.	375.	7040.	<10.0	13.6	233.	<30.0
244	.916	.515	22400.	461.	8220.	17.1	32.0	279.	<30.0
248	.811	.505	18400.	313.	16000.	14.1	35.8	460.	45.5
249	1.940	1.010	23100.	402.	11200.	25.9	45.4	350.	<30.0
250	.690	.386	17100.	239.	13100.	11.2	27.7	367.	<30.0
251	2.050	1.040	24000.	437.	9140.	18.1	39.3	352.	42.8
252	1.690	.875	17700.	302.	12800.	31.2	39.3	345.	31.2
253	1.770	.881	23200.	478.	7340.	23.6	37.1	342.	39.0
255	1.120	.525	19000.	431.	7130.	31.2	29.7	552.	<30.0
256	1.650	.818	29500.	628.	8910.	43.6	40.0	322.	50.4
258	2.140	1.040	27200.	566.	9880.	44.8	29.7	370.	<30.0
259	2.820	1.530	18600.	310.	14500.	36.0	50.1	684.	57.1
260	1.320	.600	27100.	605.	6710.	49.0	27.9	240.	34.9
261	1.700	.896	17300.	224.	11600.	17.1	28.7	408.	<30.0
262	2.150	1.140	15400.	234.	7060.	<10.0	40.0	390.	56.3
263	1.290	.625	29000.	606.	12400.	49.0	38.8	391.	44.9
264	.561	.207	14100.	246.	3710.	<10.0	<10.0	248.	<30.0
265	1.090	.480	26100.	586.	6800.	57.2	33.2	241.	39.7
266	1.920	.912	26800.	581.	10700.	64.9	27.9	364.	<30.0
267	2.290	1.060	21400.	443.	8300.	24.2	34.6	414.	32.5
269	1.310	.620	17200.	329.	10500.	<10.0	14.2	273.	<30.0
271	1.410	.615	18200.	339.	5720.	<10.0	26.4	158.	39.0
274	2.390	1.210	18200.	334.	9750.	21.8	35.8	377.	33.2
276	.899	.450	17000.	307.	7600.	16.1	29.7	298.	31.5

Table J

## -BULK SAMPLE ELEMENTAL DATA-

DVB Sample Number	PER CENT		PARTS PER MILLION						
	Ca	Mg	Al	Ba	Fe	Sr	Zn	Mn	Cr
278	4.090	2.020	28200.	625.	10500.	41.3	50.6	513.	53.4
279	.828	.386	16300.	300.	9710.	17.1	27.9	345.	< 30.0
280	3.780	1.470	22600.	462.	10300.	32.4	43.9	445.	52.6
282	1.940	1.060	15900.	244.	7050.	13.1	33.7	251.	41.1
283	11.700	7.210	12900.	190.	9330.	14.1	60.6	584.	79.8
285	9.790	5.800	21300.	329.	16000.	44.2	82.0	859.	70.9
290	2.230	1.270	14200.	253.	7140.	< 10.0	28.2	272.	44.5
291	2.930	1.650	15100.	283.	6640.	23.6	21.9	263.	< 30.0
292	6.580	3.330	15100.	337.	8360.	32.4	34.6	462.	37.0
294	2.220	1.220	14600.	225.	6320.	< 10.0	29.2	283.	37.0
295	10.000	5.110	13500.	372.	5520.	39.5	51.2	423.	86.2
296	3.590	1.980	16300.	316.	5610.	17.1	49.8	242.	55.2
299	7.010	4.080	11500.	308.	3160.	< 10.0	27.7	192.	46.6
300	8.980	5.210	18200.	405.	15400.	27.1	99.4	629.	73.9
309	2.710	.797	18800.	300.	5770.	49.0	23.2	170.	30.5
310	2.710	.959	15500.	246.	6440.	33.6	< 10.0	189.	< 30.0
316	1.430	.676	14800.	283.	7330.	28.3	27.1	256.	34.6
319	4.270	1.650	27900.	437.	18500.	51.0	40.5	487.	51.1
320	1.380	.671	18800.	313.	9710.	22.4	33.7	305.	< 30.0
322	1.560	.645	17500.	328.	7090.	15.1	20.9	211.	< 30.0
325	1.850	.964	15200.	261.	9030.	17.1	33.4	457.	36.7
333	< 500	.182	20000.	413.	6870.	< 10.0	15.4	200.	< 30.0
334	< 500	.216	20000.	394.	12900.	13.1	< 10.0	296.	< 30.0
335	1.450	.630	17500.	395.	8680.	< 10.0	20.9	240.	< 30.0
336	1.740	.635	15300.	288.	4960.	< 10.0	22.2	212.	< 30.0
337	.686	.275	21100.	413.	6280.	< 10.0	< 10.0	153.	< 30.0
338	4.520	1.540	23300.	394.	9880.	27.7	46.2	394.	47.9
339	5.210	1.630	28200.	569.	11000.	56.4	49.5	460.	53.0
340	1.190	.400	14500.	264.	3750.	< 10.0	< 10.0	132.	< 30.0
342	7.640	2.360	> 30000.	568.	15200.	54.8	51.5	493.	86.6
347	.674	.311	30000.	556.	12100.	30.6	47.0	331.	< 30.0
354	2.680	1.470	29800.	339.	235.00	41.3	71.7	565.	55.6
355	1.460	.692	> 30000.	424.	19100.	63.4	55.1	430.	62.7
357	15.700	4.330	12100.	236.	7470.	67.3	53.1	619.	68.7

Table K  
SIGNIFICANT CORRELATIONS (.95 CONFIDENCE COEFFICIENT)  
GBA SAMPLES

<u>Data Set</u>	<u>r</u>	<u>Min. rho.</u>	<u>Max. rho.</u>	<u>Number points</u>
Mg(n) <sup>1</sup> -Mn(n)	.867	.79	.91	105
Mg(n)-Sr(n)	.739	.61	.82	104
Zn(n)-Cr(n)	.004	-.19	.19	101
Mn(n)-Ba(n)	.780	.68	.84	105
Mn(n)-Sr(n) <sub>4</sub>	.735	.60	.80	105
Mn(n)-Mean	-.002	-.19	.19	104
Fe(n)-Fe(b)	.112	-.075	.30	97
Cr(n)-Ba(n)	-.034	-.05	.12	100
Cr(n)-Mean	-.020	-.21	.17	100
Ba(n)-Sr(n)	.747	.56	.82	109
Mean(mm)-Dia(n)	.552	.47	.75	97

<sup>1</sup><sub>n</sub> = ferromanganese nodules

<sup>2</sup><sub>b</sub> = bulk sediment sample

<sup>3</sup>Dia(n) = nodule diameter (mm)

<sup>4</sup>Mean = mean sediment particle size (phi units)

Table L  
SIGNIFICANT CORRELATION (.95 CONFIDENCE COEFFICIENT)  
DVB SAMPLES

<u>Data Set</u>	<u>r</u>	<u>Min. rho.</u>	<u>Max. rho.</u>	<u>Number Points</u>
Ca-Mg (N) <sup>1</sup>	.917	.81	.94	34
Ca-Mg (E) <sup>2</sup>	.973	.92	.99	27
Ca-Mg (S) <sup>3</sup>	.925	.85	.95	43
Sr-Ba (N)	.677	.41	.81	35
Sr-Ba (E)	.682	.43	.87	23
Zn-Al (S)	.006	-.36	.36	31
Zn-Fe (S)	.733	.50	.83	39
Cr-Zn (S)	.915	.80	.95	30

<sup>1</sup>Northern Sample Station (See Map 11 )

<sup>2</sup>Eastern Sample Station (See Map 11 )

<sup>3</sup>Southern Sample Station (See Map 11)

Table M

-ELEMENTAL DATA-

GBA Sample Number	Diameter (mm)	Mg (%)	Fe (ppt)	Cu (ppt)	Zn (ppt)	Mn (ppt)	Cr (ppt)	Al (ppm)	Ba (ppm)	Sr (ppm)
301	1.0	1.70	285.	.182	.730	68.000	.116	10300.	8500.	229.
302	1.0	2.00	310.	.112	.520	89.000	.159	7600.	14500.	273.
304	.5	3.20	85.	.198	.940	135.000	.099	25100.	9100.	286.
306	-	.99	320.	.112	.420	26.800	.104	4200.	2990.	166.
308	1.4	1.20	330.	.112	.340	39.500	.122	5100.	5600.	166.
311	1.2	1.20	340.	.143	.450	17.000	.193	8100.	1940.	213.
312	1.5	1.50	272.	.112	.920	65.000	.122	4200.	8300.	229.
313	.7	2.00	232.	.102	.850	108.000	.136	8700.	17100.	229.
314	1.2	1.50	290.	.112	.470	55.500	.185	3800.	9400.	242.
316	.7	2.20	222.	.198	.780	90.000	.198	19300.	7800.	286.
317	.6	.91	220.	.176	.490	35.500	.104	24000.	3950.	166.
322	1.4	2.70	250.	.112	.420	138.000	-	2200.	26700.	319.
324	1.3	1.90	320.	.112	.570	94.000	.148	4700.	15500.	242.
325	1.2	1.30	325.	.176	1.120	64.500	.145	2500.	10300.	233.
326	1.0	1.20	350.	.242	1.510	20.600	.148	3000.	1380.	178.
332	1.1	1.70	305.	.198	3.750	65.000	.187	4200.	8000.	242.
333	2.3	2.00	290.	.154	.360	115.000	.136	2500.	22900.	301.
334	1.1	1.70	340.	.264	.510	72,400	.170	5900.	10500.	229.
335	1.4	.99	382.	.154	.390	15.000	.116	6000.	1380.	166.
338	1.6	1.50	320.	.165	.550	56.400	.136	6100.	11400.	229.
339	1.4	1.30	380.	.242	.510	21.700	.181	4900.	2290.	188.
342	-	1.30	320.	.154	.390	19.600	.148	19900.	1820.	213.
357	1.3	.91	295.	.422	2.030	10.050	.164	3900.	690.	178.
358	4.0	1.40	270.	.154	.340	48.400	-	5600.	6900.	213.
361A	-	-	-	-	-	-	-	-	-	-
361B	-	-	-	4.300	.009	-	-	-	-	-
366	-	-	-	-	-	-	-	6700.	3490.	200.
369	1.4	2.00	255.	.288	.440	112.000	.116	7200.	18100.	286.
371	.5	3.--	112.	.288	1.340	140.000	.110	21800.	8700.	286.
373	-	-	-	-	-	-	-	-	-	-
375	-	-	-	-	-	-	-	-	-	-
376	-	-	-	-	-	-	-	-	-	-
378	3.7	2.50	210.	.154	.550	128.000	.122	3800.	20200.	301.



Table M  
-ELEMENTAL DATA-

GBA Sample Number	Diameter (mm)	Mg (%)	Fe (ppt)	Cu (ppt)	Zn (ppt)	Mn (ppt)	Cr (ppt)	Al (ppm)	Ba (ppm)	Sr (ppm)
161	1.6	2.70	255.	.165	.630	130.000	.187	-	-	-
162	1.3	1.90	255.	.154	.260	70.800	.187	12500.	9400.	316.
163	.8	2.20	191.	.200	.490	88.000	.198	18100.	13200.	301.
166	.8	2.00	235.	.154	.750	112.000	.170	18100.	13900.	270.
172	.8	2.00	300.	.154	.390	105.000	.164	4200.	21600.	316.
173	1.7	2.70	250.	.178	.550	124.000	.198	4200.	17800.	365.
176	1.1	2.90	215.	.200	.830	145.000	.175	4200.	24600.	386.
177	1.3	2.80	192.	.265	.810	122.000	.198	14300.	16900.	365.
179	1.1	1.50	355.	.189	.550	57.200	.198	2500.	8900.	210.
180	.6	1.30	370.	.200	.520	12.500	.216	5100.	680.	208.
182	.9	2.00	340.	.200	.920	94.000	.187	2500.	15500.	316.
184	.6	2.00	255.	.165	.940	88.000	.175	15500.	13600.	284.
187	.8	2.30	69.	.122	.720	135.000	.273	22400.	9400.	256.
188	.8	3.20	99.	.233	.890	152.000	.152	30100.	11200.	284.
191	.3	2.80	69.	.200	.490	134.000	.146	33400.	18100.	292.
194	.9	3.00	147.	.189	.890	134.000	.164	22400.	19700.	402.
195	1.2	2.30	240.	.154	1.710	112.000	.148	12000.	11200.	256.
196	.9	.99	350.	.112	.440	14.500	.148	4700.	520.	139.
204	1.6	1.30	255.	.112	.380	32.000	.159	27900.	2290.	200.
222	2.4	2.50	235.	.112	.380	120.000	-	6600.	29700.	286.
223	.9	1.70	232.	.112	.240	63.000	.110	25100.	15500.	178.
236	4.0	2.00	320.	.154	.310	27.800	.159	19900.	2180.	188.
241	2.8	1.50	171.	.064	.170	25.700	.099	54000.	5200.	166.
254	-	3.20	188.	.112	.450	140.000	.099	2500.	25600.	358.
255	-	-	19.	-	-	4.690	-	610.	427.	117.
265	.7	2.70	265.	.143	.630	115.000	.187	6100.	20400.	319.
266	.7	2.50	155.	.154	.700	108.000	.164	25800.	9400.	301.
271	2.5	1.90	92.	.073	.100	22.200	.142	75000.	1380.	319.
274	2.0	1.70	250.	.102	.170	49.800	.148	38000.	6300.	205.
275A	2.1	1.70	230.	.092	.250	56.000	.122	39000.	5200.	213.
275B	.6	3.30	85.	.187	.630	160.000	.089	24300.	11900.	242.
276	-	3.30	102.	.143	.780	155.000	.094	27900.	11900.	273.
279	.5	3.00	147.	.143	.810	130.000	.136	33400.	7200.	242.
282	-	1.50	250.	.143	.530	21.700	.164	25800.	4570.	213.
284	.7	2.50	149.	.112	.550	108.000	-	39000.	12800.	213.
285	1.9	3.00	225.	.154	.660	145.000	.122	6600.	24400.	334.
290	1.2	2.40	215.	.154	.570	122.000	.142	12000.	13400.	273.
291	.7	3.10	122.	.112	.860	138.000	.110	21800.	15200.	301.
296	1.2	1.70	340.	.112	.660	49.800	.148	9800.	5800.	213.
298	.7	3.40	120.	.176	.144	150.000	.142	22400.	8900.	270.

Table M  
-ELEMENTAL DATA-

GBA Sample Number	Diameter (mm)	Mg (%)	Fe (ppt)	Cu (ppt)	Zn (ppt)	Mn (ppt)	Cr (ppt)	Al (ppm)	Ba (ppm)	Sr (ppm)
24	3.6	2.50	300.	.167	.360	107.000	.187	28700.	14500.	346.
57	.9	2.70	205.	.280	.808	155.000	.164	16100.	18500.	437.
58	1.1	2.10	215.	.432	.800	120.000	.152	12500.	14500.	346.
59	.3	1.20	77.	.259	.440	58.800	.305	46000.	7800.	281.
64	1.6	1.40	480.	.202	.320	21.375	.314	4300.	3450.	221.
66	1.1	.93	345.	.134	.388	20.300	.175	12500.	430.	221.
67	1.2	3.20	187.	.225	1.588	155.000	.198	12500.	24100.	455.
68	.8	1.60	300.	.167	.468	20.800	.198	4200.	11900.	245.
72	.6	3.20	69.	.191	.780	120.000	.127	25100.	9600.	402.
74	.5	3.90	64.	.225	5.748	155.000	.152	19900.	13600.	331.
78	.0	2.10	280.	.167	.568	25.200	.239	20000.	11900.	237.
79	.0	2.50	200.	.180	.688	118.000	.216	26400.	16200.	417.
80	.5	1.50	152.	.134	.340	32.500	.187	35000.	5500.	281.
81	1.2	3.50	210.	.193	1.088	135.000	.187	4200.	23500.	473.
84	.8	1.20	380.	.156	.308	4.360	.216	5200.	220.	170.
88	.6	2.10	90.	.145	.428	118.000	.102	30700.	11400.	281.
89	1.7	3.20	225.	.134	.600	155.000	.170	7600.	47400.	455.
92	1.0	2.10	133.	.134	.320	22.700	.121	52000.	3690.	208.
93	.4	1.80	235.	.202	.420	81.000	.193	19300.	9800.	281.
94	.9	2.40	144.	.180	.570	108.000	.198	25100.	10300.	313.
97	.7	1.80	380.	.202	.660	15.500	.239	2500.	5600.	281.
101	1.0	1.30	310.	.180	.920	29.400	.305	8100.	4150.	251.
102	.9	2.80	325.	.235	.600	115.000	.221	2200.	22100.	352.
103	.7	.93	200.	.104	.260	46.900	.152	14800.	6900.	237.
108	.8	3.20	220.	.156	.520	150.000	.198	3800.	34900.	437.
119	.7	2.80	250.	.198	.550	140.000	.175	7000.	23100.	417.
120	.6	2.20	123.	.202	.850	110.000	.175	25100.	13200.	331.
124	.5	2.20	230.	.235	.530	108.000	.198	19300.	19200.	289.
126	.7	3.00	71.	.378	.480	138.000	.127	29300.	23600.	256.
133	.5	1.30	300.	.200	.310	15.500	.198	8100.	1821.	198.
134	-	1.70	64.	.092	.160	1.700	.152	8100.	1820.	198.
135	.9	1.50	255.	.154	.670	52.700	.102	22400.	7400.	256.
139	.9	2.30	230.	.233	.660	115.000	.150	12000.	16400.	301.
140	.8	2.90	123.	.165	.830	142.000	.127	22400.	17400.	316.
143	1.4	2.50	275.	.292	.890	131.000	.175	6200.	29300.	301.
145	.7	3.80	115.	.165	.240	53.600	.175	78000.	8000.	349.
155	1.1	2.90	230.	.278	.810	132.000	.193	10300.	16600.	316.
156	.8	2.70	191.	.154	.750	131.000	.140	12500.	20200.	365.
157	.8	1.50	300.	.154	.480	74.800	.164	4200.	13400.	240.
159	.8	1.30	380.	.154	.440	24.700	.193	8100.	3770.	210.

Table N  
 AVERAGE FERROMANGANESE NODULE COMPOSITIONS  
 FRESH WATER AND SALT WATER

<u>Location</u>	<u>Reference</u>	( <u>Fe</u> %)	( <u>Mn</u> %)	( <u>Co</u> ppm)	( <u>Ni</u> ppm)	( <u>Cu</u> ppm)	( <u>Zn</u> ppm)
Grand Lake	Harriss (70)	16.6	33.0	196	296	14	1665
Ship Harbor Lake	Harriss (70)	16.7	26.6	221	112	7	475
Mosque Lake	Harriss (70)	40.2	15.7	135	95	10	250
English Lake District	Gorham (65)	15.2	11.1	40	20	10	250
Nova Scotia	Kindle (35)	13.6	22.5	-	-	-	-
New Hampshire	Kindle (35)	26.5	14.5	-	-	-	-
Swedish Ores	Ljunggren (55)	32.5	17.0	230	40	-	50
Karaluu-Finnish Lake	Manheim (65)	22.5	14.0	130	40	-	-
Swedish Ores	Manheim (65)	35.6	4.7	80	40	40	-
Green Bay	This Study	23.1	8.6	-	-	17.5	69.1
Pacific Ocean	Mero (62)	14.0	24.2	0.35	.99	.53	.47
Atlantic Ocean	Mero (62)	17.5	16.3	0.31	.42	.20	-
General Oceanic	Cronan & Tooms (69)	12.2	16.8	.356	.62	.34	-

Table 0  
 ELEMENTAL AVERAGES  
 MARINE VS. FRESH WATER NODULES

<u>Element</u>	(weight %)				
	<u>Nodules<sup>1</sup> Green Bay 120 Samples</u>	<u>Nodules<sup>2</sup> F.W.</u>	<u>Nodules<sup>3</sup> Oceanic 95 Samples</u>	<u>Assoc. Sed.<sup>1</sup> Green Bay 249 Samples</u>	<u>Assoc. Sed.<sup>3</sup> Oceanic 34 Samples</u>
Mn	8.64	17.6	16.84	0.31	0.51
Fe	23.1	24.3	12.2	0.956	4.43
Cu		0.0016	0.342	0.008	0.023
Zn	0.0691	0.2688	-	-	-
Cr	0.0164	-	0.011	-	-
Ni	-	0.0091	0.62	0.00078	0.028
Ti	-	-	-	0.0042	0.307
Co	-	0.0147	0.356	-	0.0109

<sup>1</sup>This Study

<sup>2</sup>From Harriss (70)

<sup>3</sup>From Cronan and Tooms (69)

Table P  
PHOSPHORUS IN NODULES & BULK SEDIMENTS

Sample Number	Nodule Phosphorus Value (in ppt)	Bulk Phosphorus Value (in ppt)
74	1.83	
76	6.68	
79	5.18	
80	12.9	
85	4.26	
88	4.03	
89	6.34	
103	5.77	
108	5.79	
124	3.91	
126	5.29	1.05
140	3.55	.35
148		1.77
152		2.03
153		2.01
155		1.46
156	1.63	
161	6.56	.620
172	5.55	
173	5.45	1.5
186		1.74
188	2.02	
191	3.13	
194	.97/1.164/.26/2.58/0.60	.68/.41/1.5
204	3.52	
231		.27
235		2.95
238		.277
243		2.84
261		.46
275	1.89	
276	10.86	
279	2.7	.984
284	6.07	
290	3.12	.419
291	3.79	.968
298	2.47	.46
302	3.84	
304	3.36	
314	2.99	.424
332	3.73	
373	7.15	
378	6.69	



## FIGURES





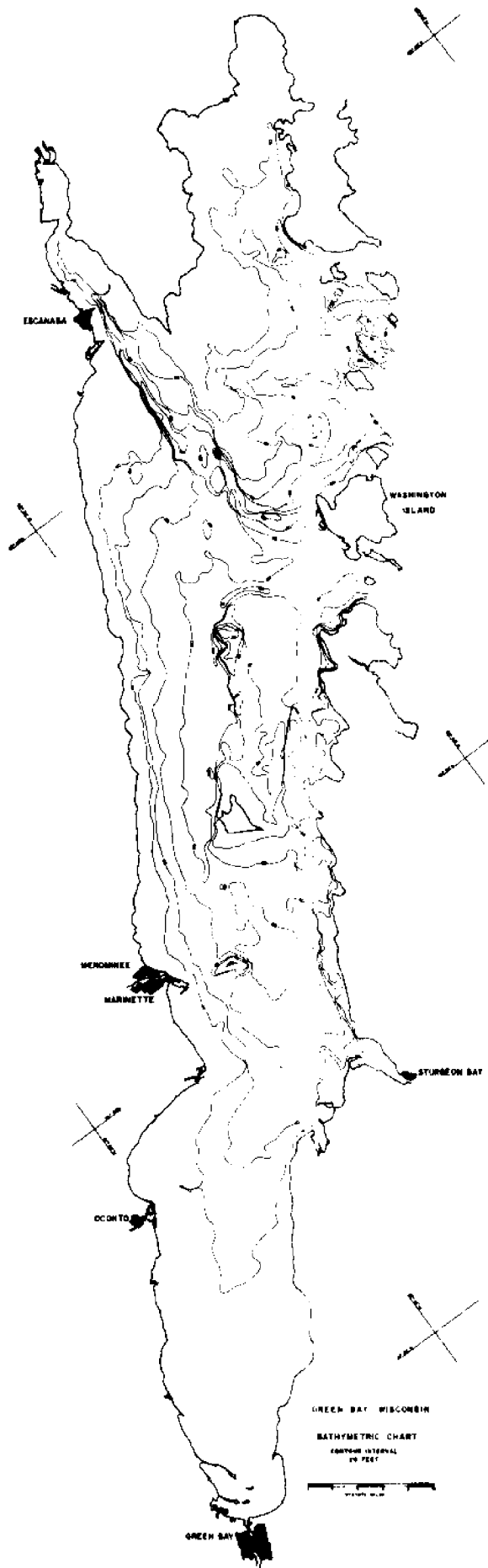


Figure 1

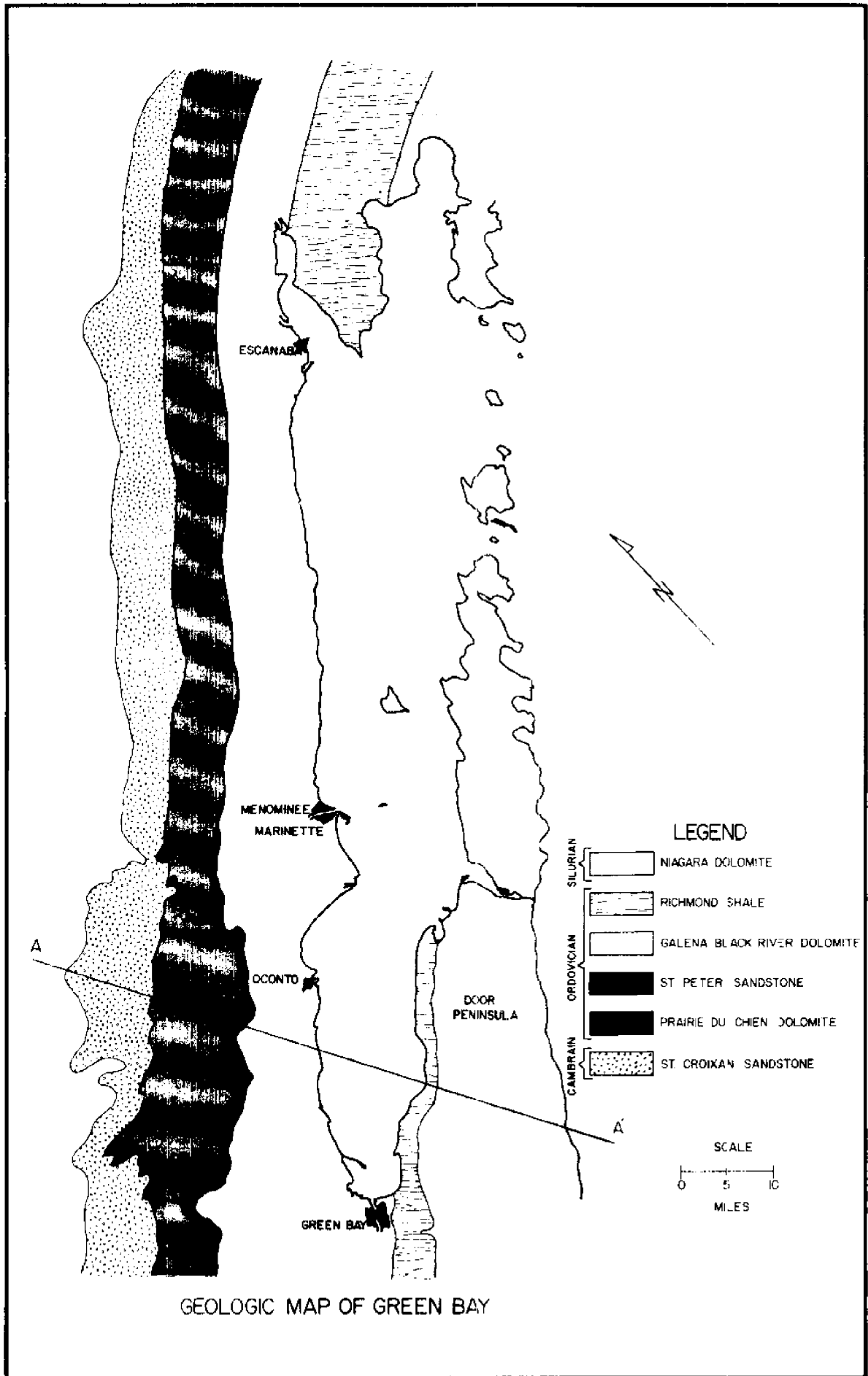


Figure 2

STRUCTURE SECTION  
 THROUGH GREEN BAY, WISCONSIN, ALONG LINE TRENDED S37E

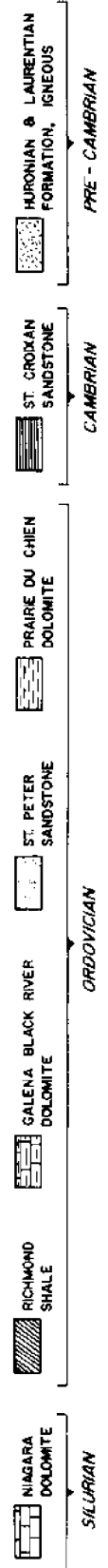
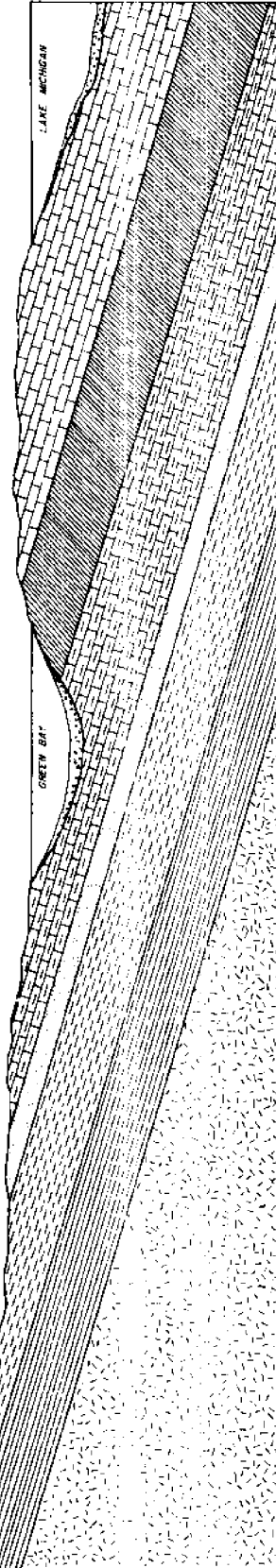
A

TRUE ANGLE OF DIP LESS THAN 1°

A

FEET

8000  
 7000  
 6000  
 5000  
 4000  
 3000  
 2000  
 1000  
 0  
 SEA  
 LEVEL



PLATE

Figure 3

GREEN BAY  
HIGH RESOLUTION PROFILES

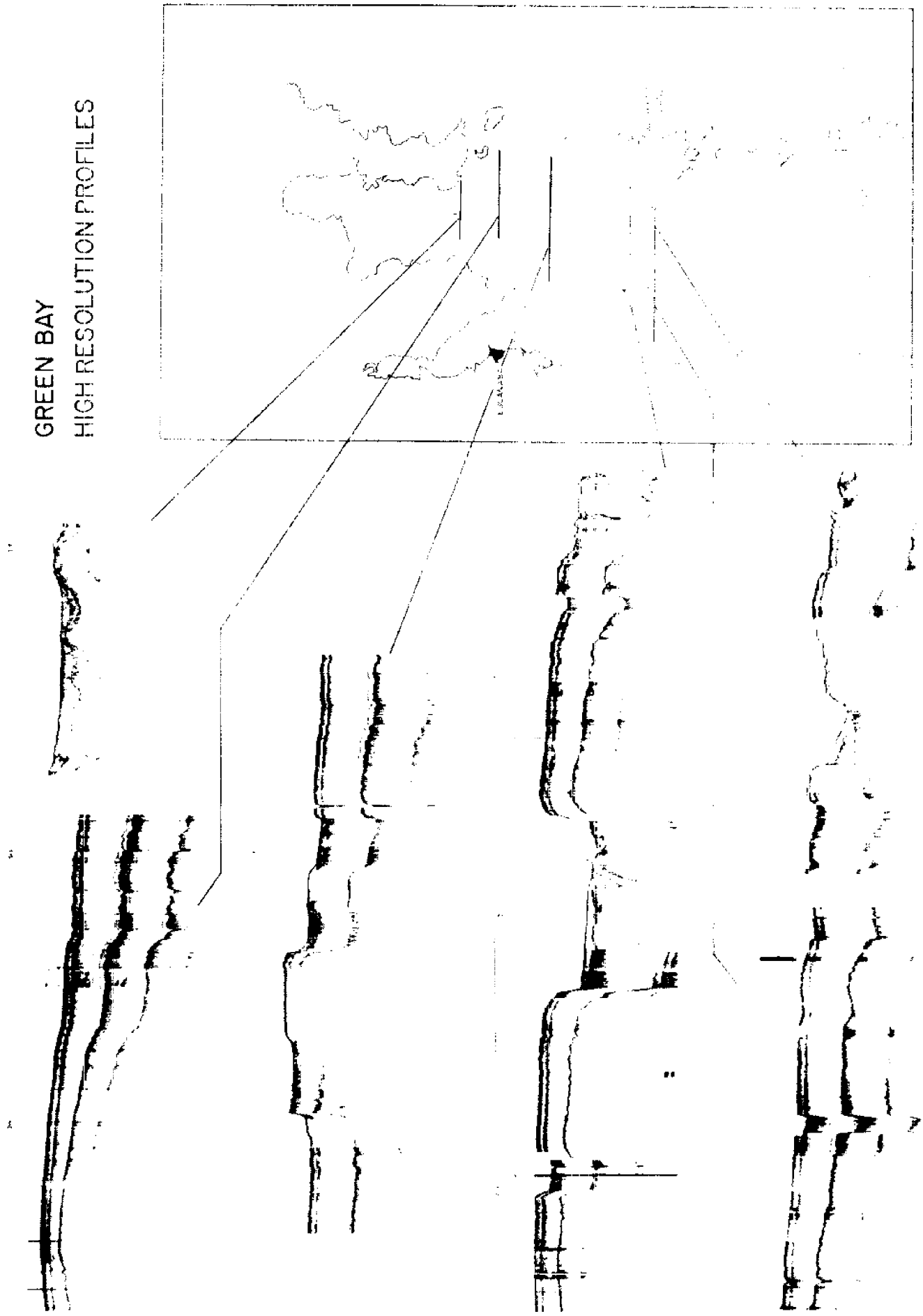


Figure 40

**GREEN BAY  
HIGH RESOLUTION PROFILES**

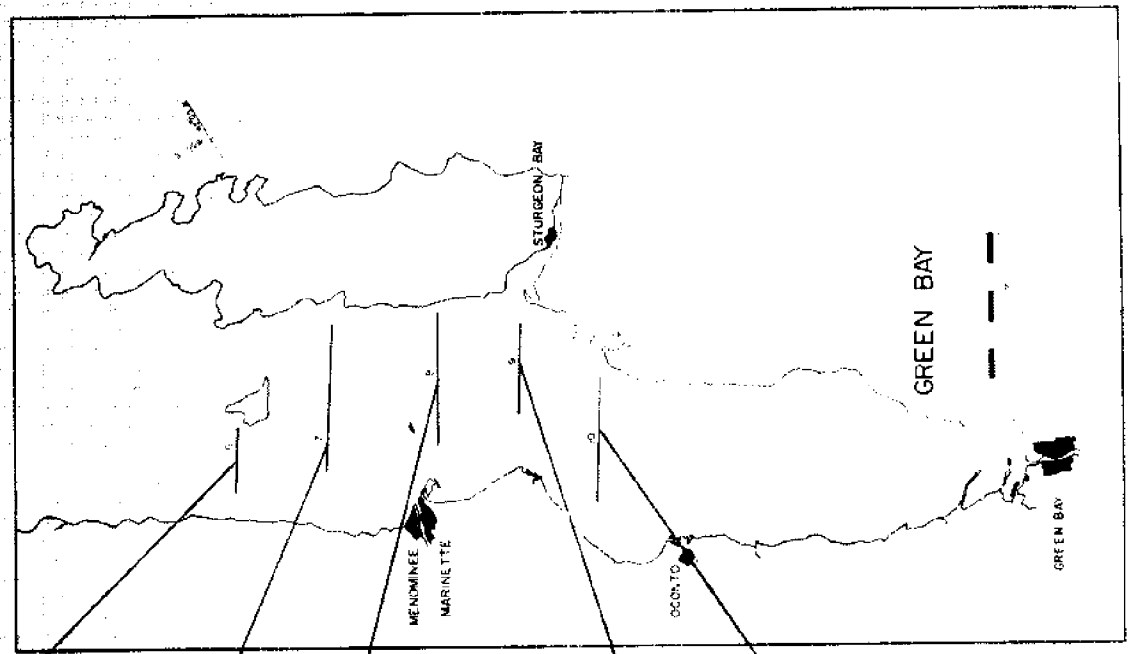
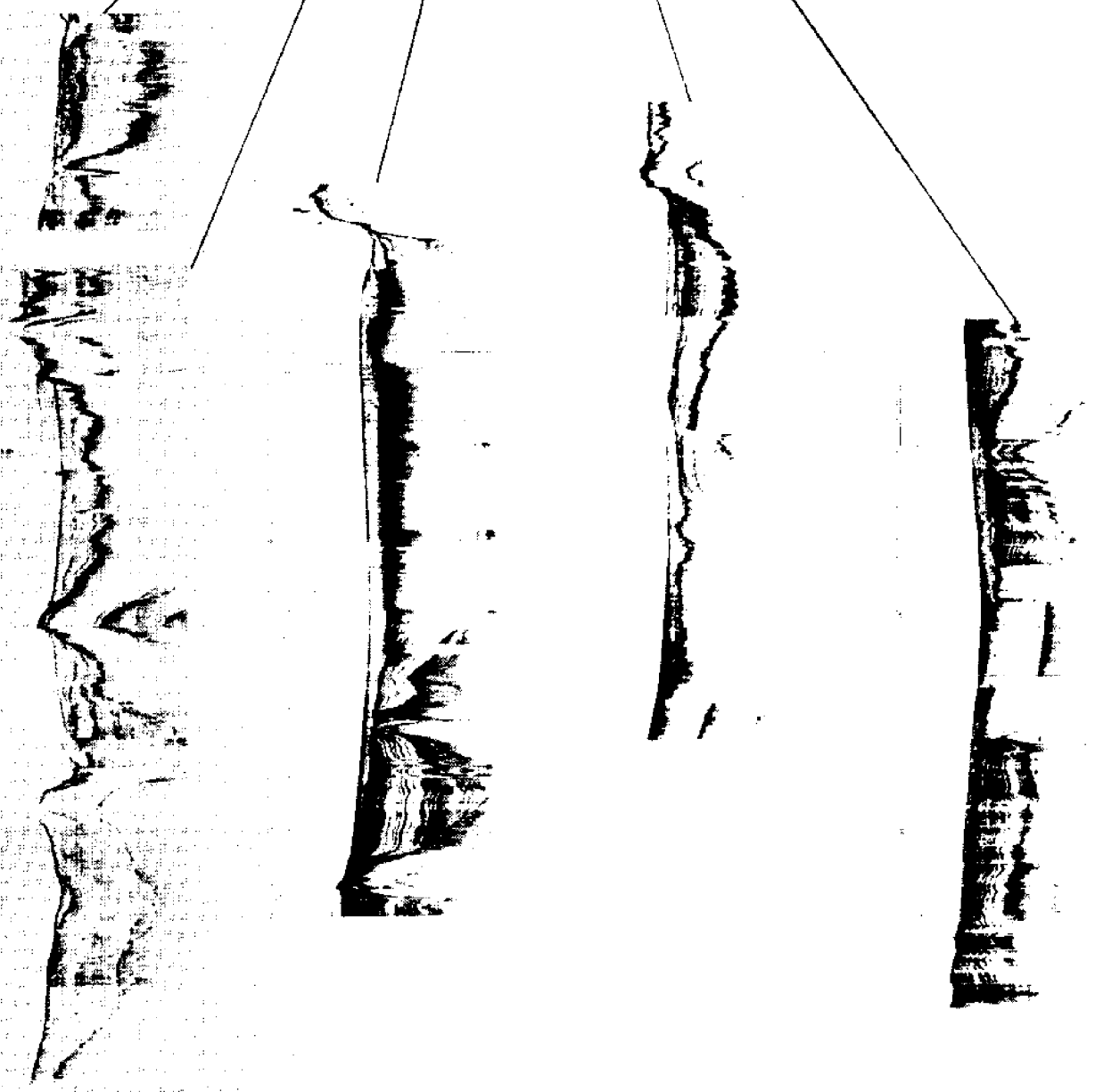


Figure 4b



FUNCTIONAL BLOCK DIAGRAM

SHIP'S BRIDGE

PORTABLE LABORATORY

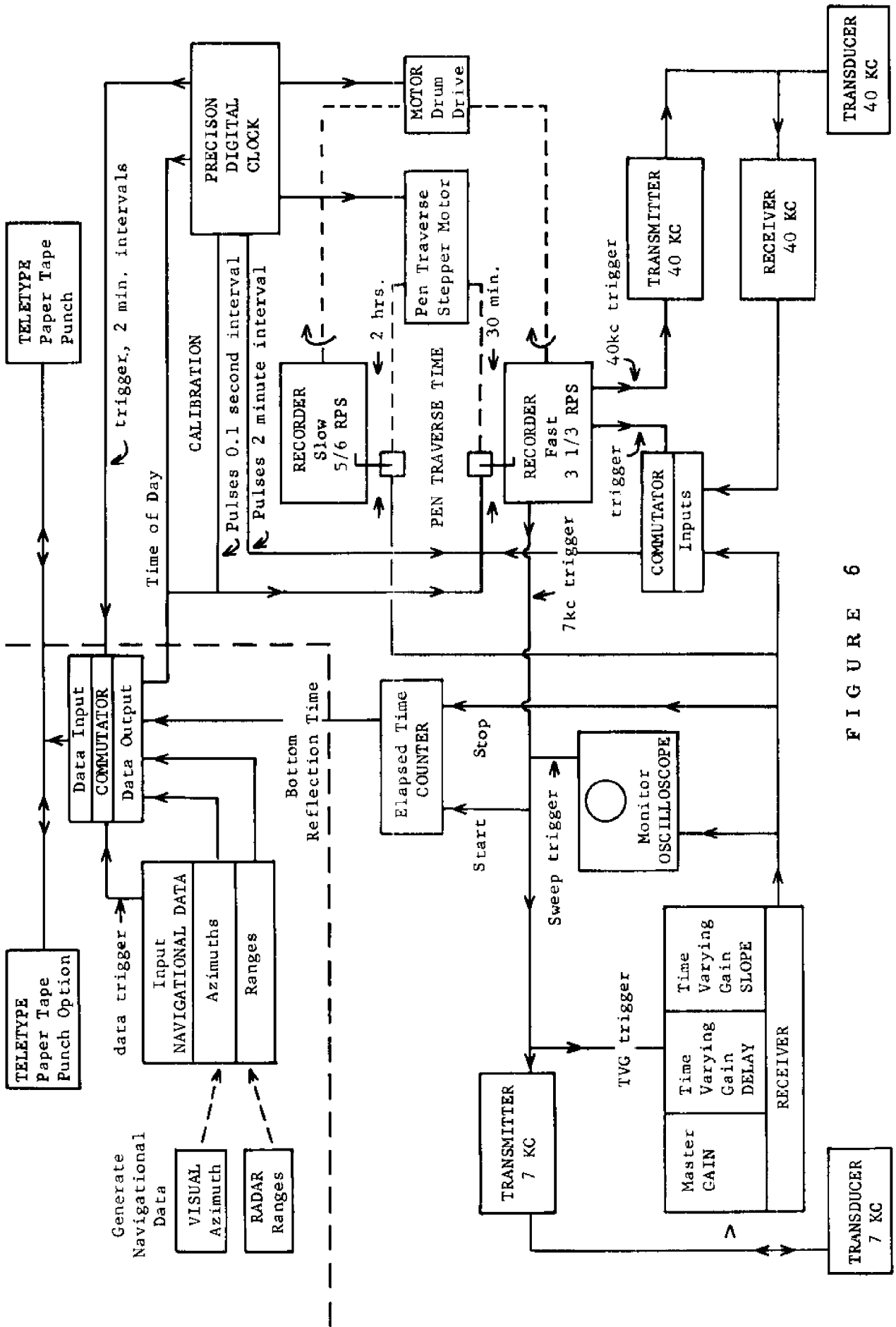


FIGURE 6

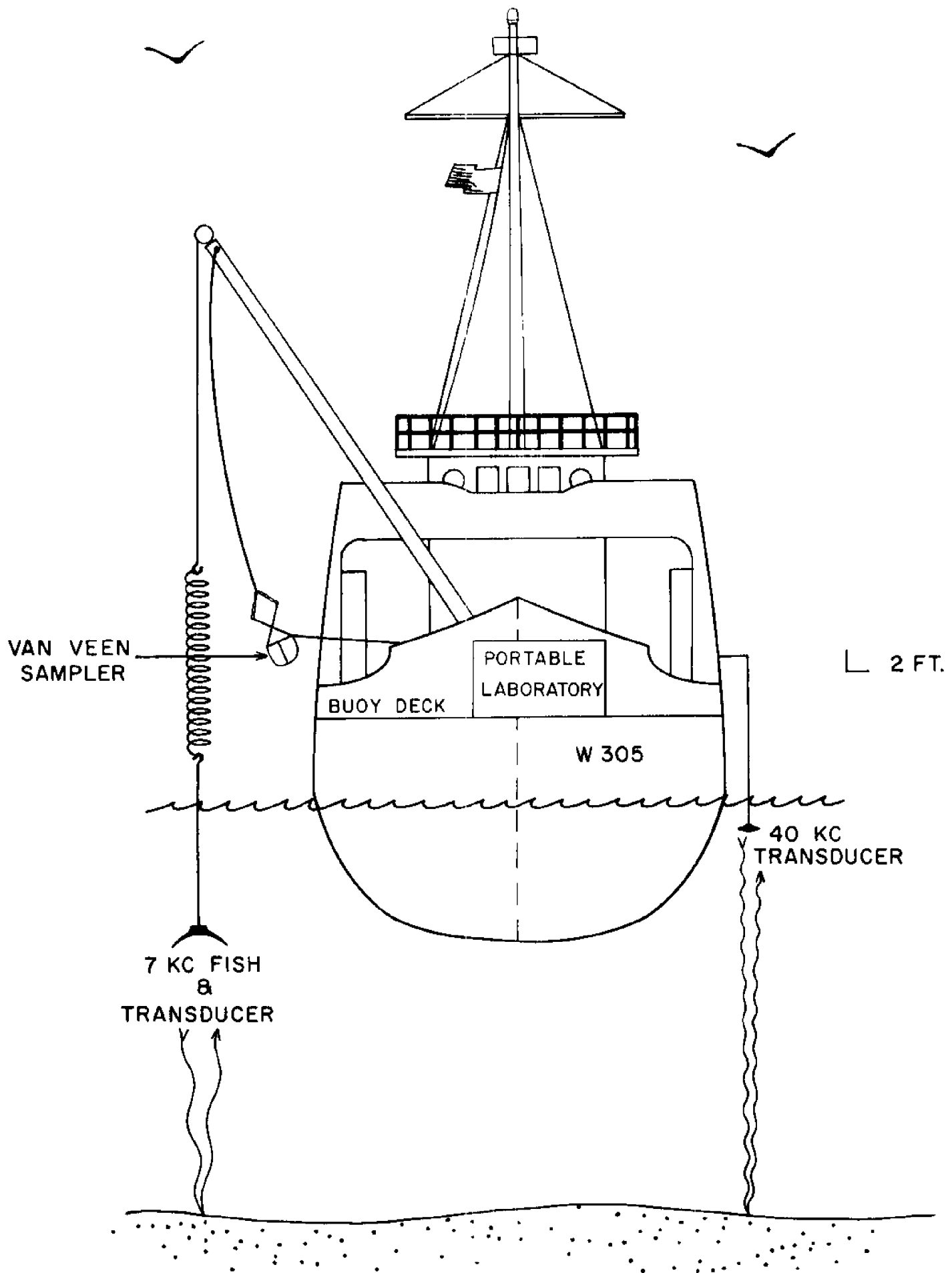


FIGURE 7



PRELIMINARY  
BATHYMETRIC MAP  
GREEN BAY, LAKE MICHIGAN

1968 DATA UNIVERSITY OF WISCONSIN

FROM  
HIGH RESOLUTION PROFILE DATA  
CONTOUR INTERVAL 0.025 SEC · 6 FT  
DATUM = 576.8 FT

FROM  
LAKE SURVEY CHART #703  
DATA OF 1950 & 1943  
CONTOUR INTERVAL 6 FT  
DATUM = 576.8 FT



FIGURE 8

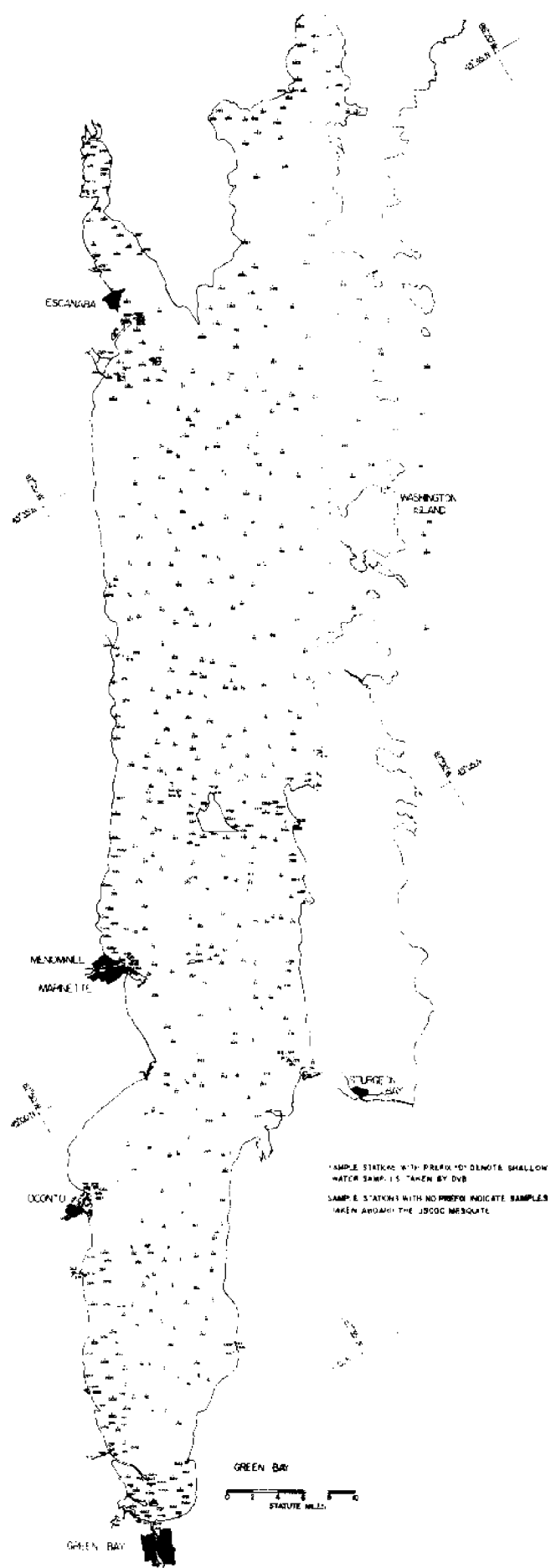


Figure 9

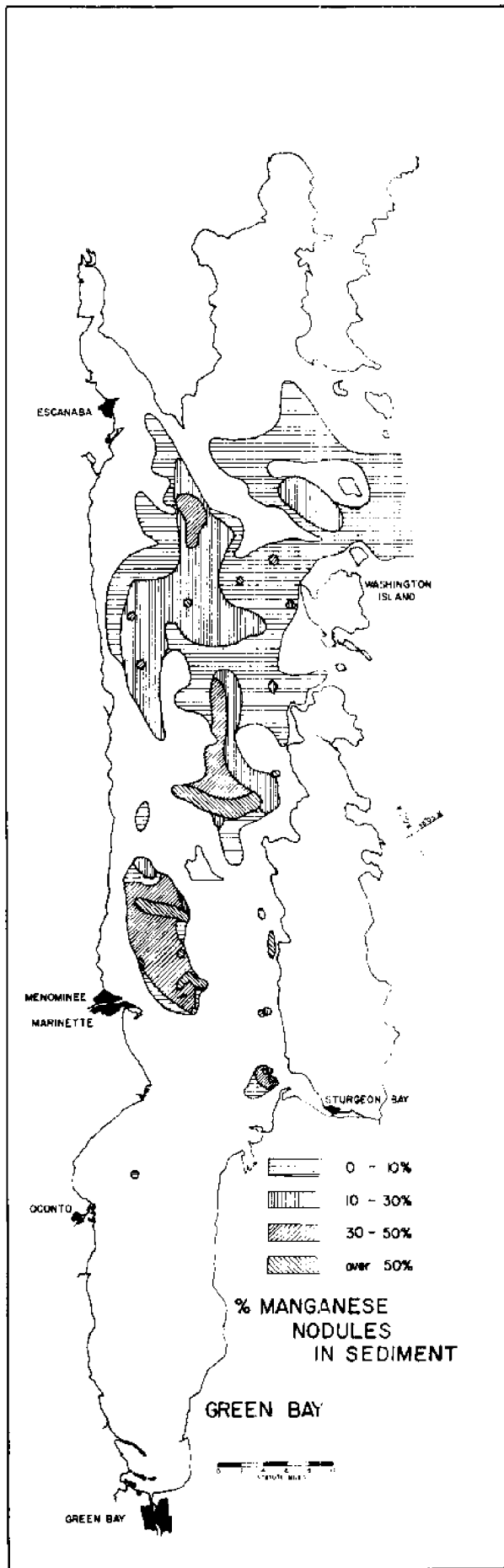


Figure 10

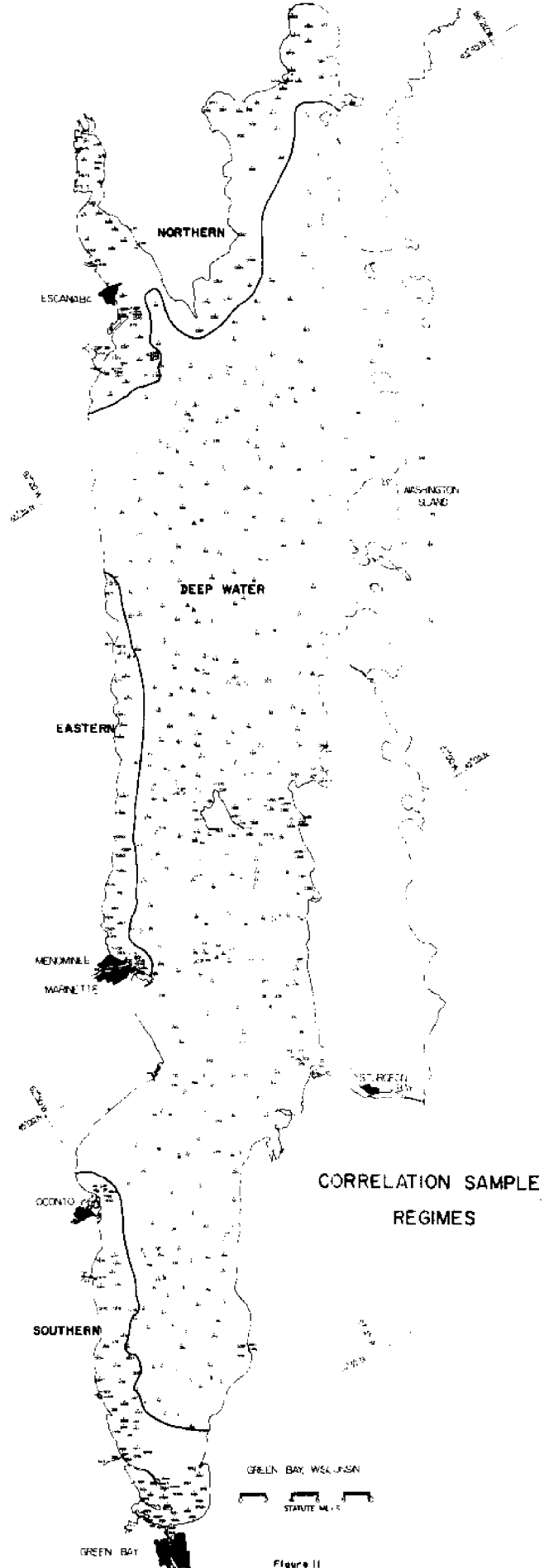


Figure II

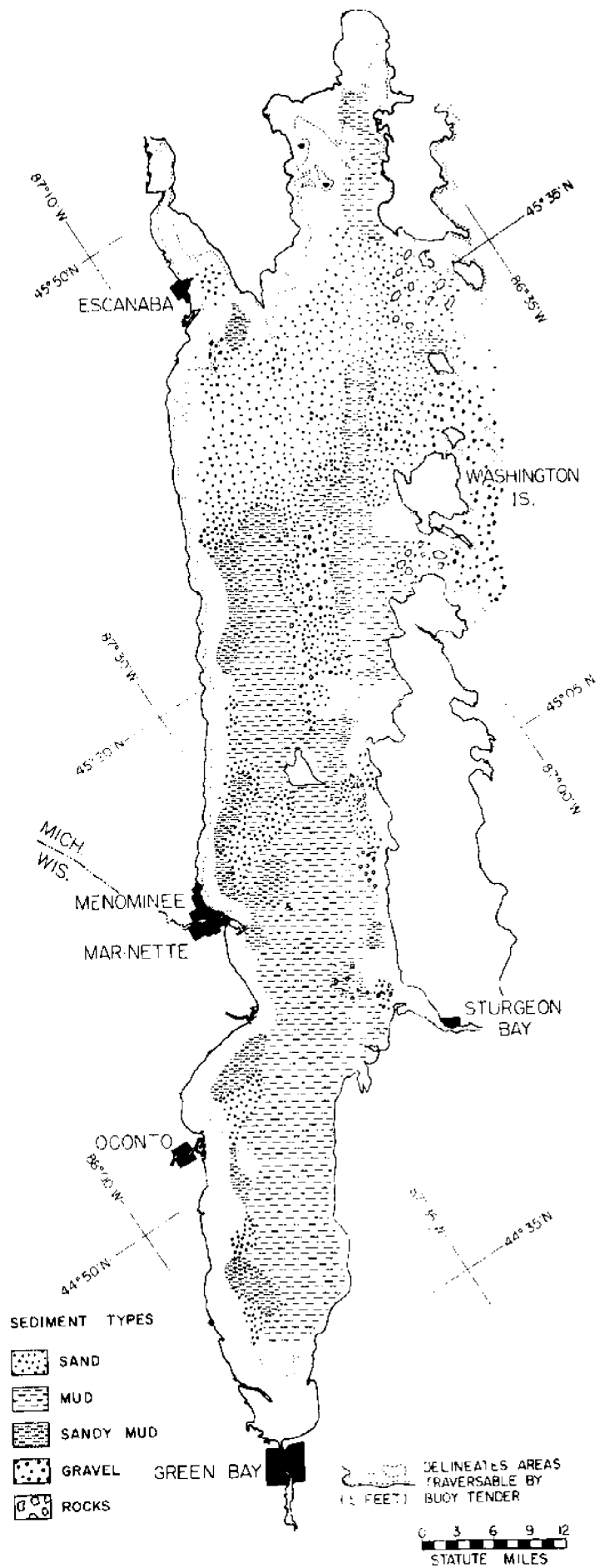


FIGURE 12



SEDIMENT FACIES MAP

WFO 006 3

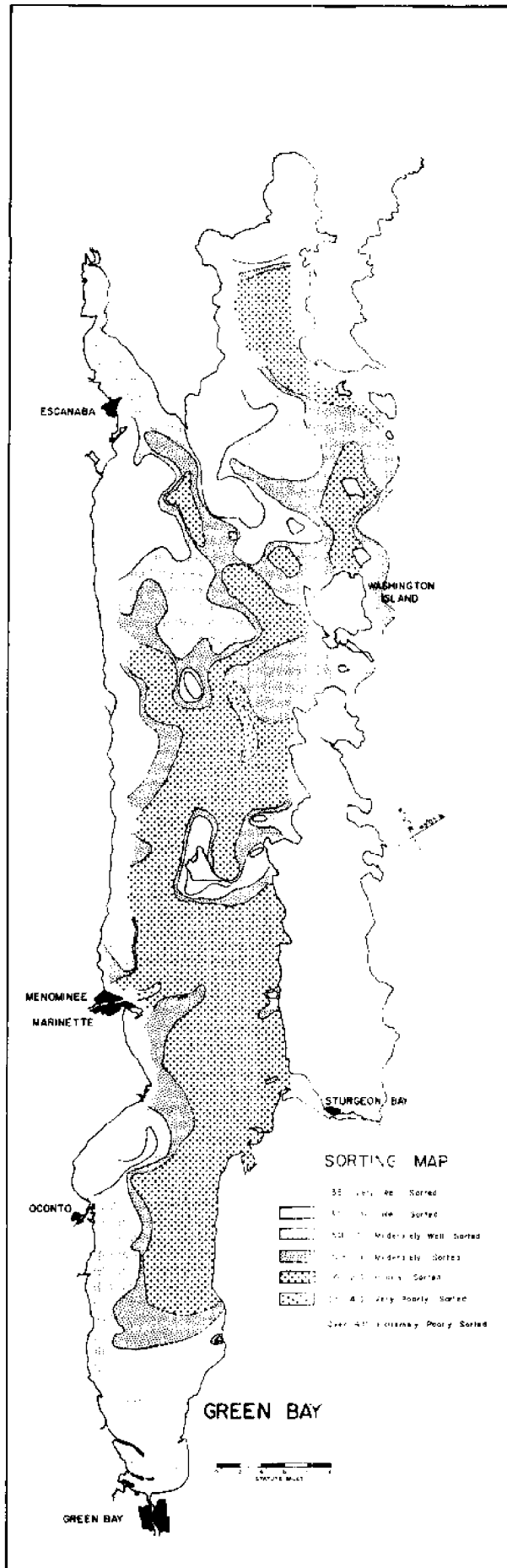


Figure 14

# PROPOSED RELICT BEACH

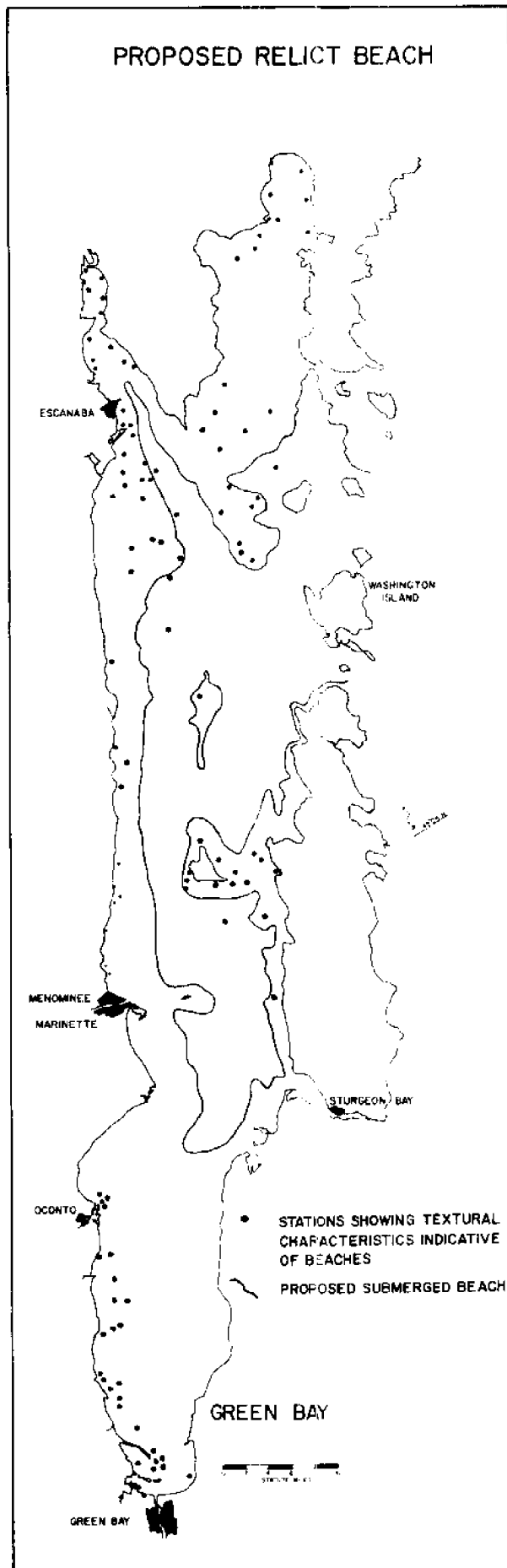


Figure 15



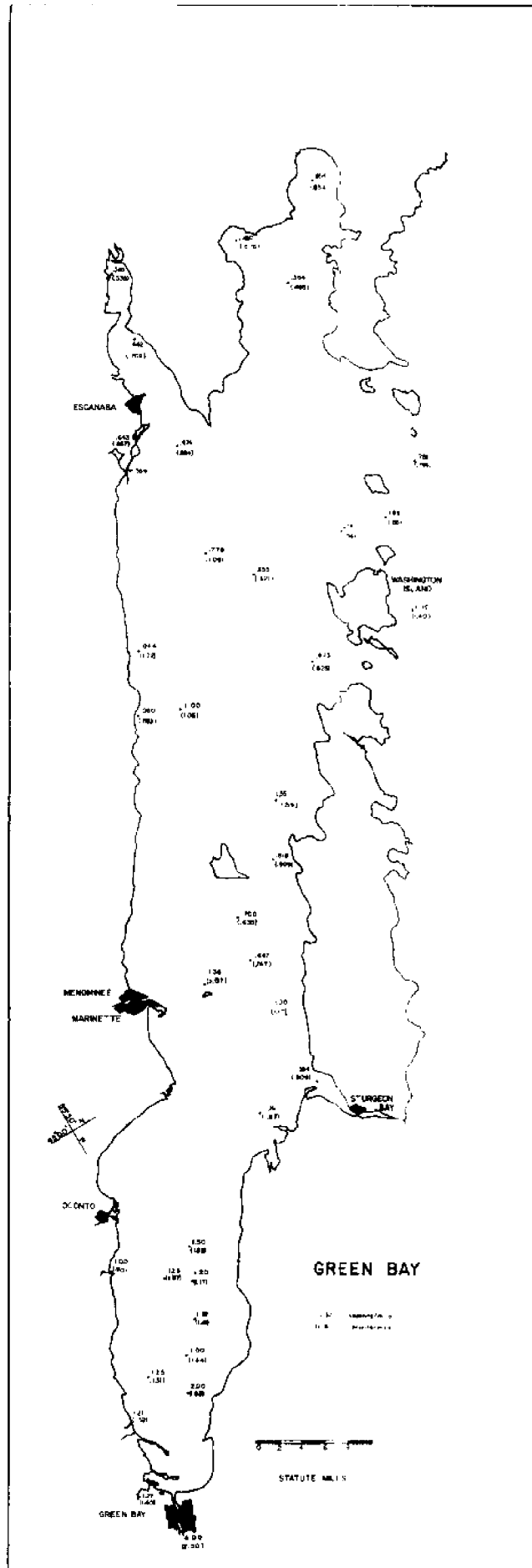


Figure 16

GREEN BAY  
FERROMANGANESE NODULES



Photomicrograph; 10X  
Showing concentric  
banding

Photomicrograph; 10X  
Subangular quartz nucleus



FIGURE 17

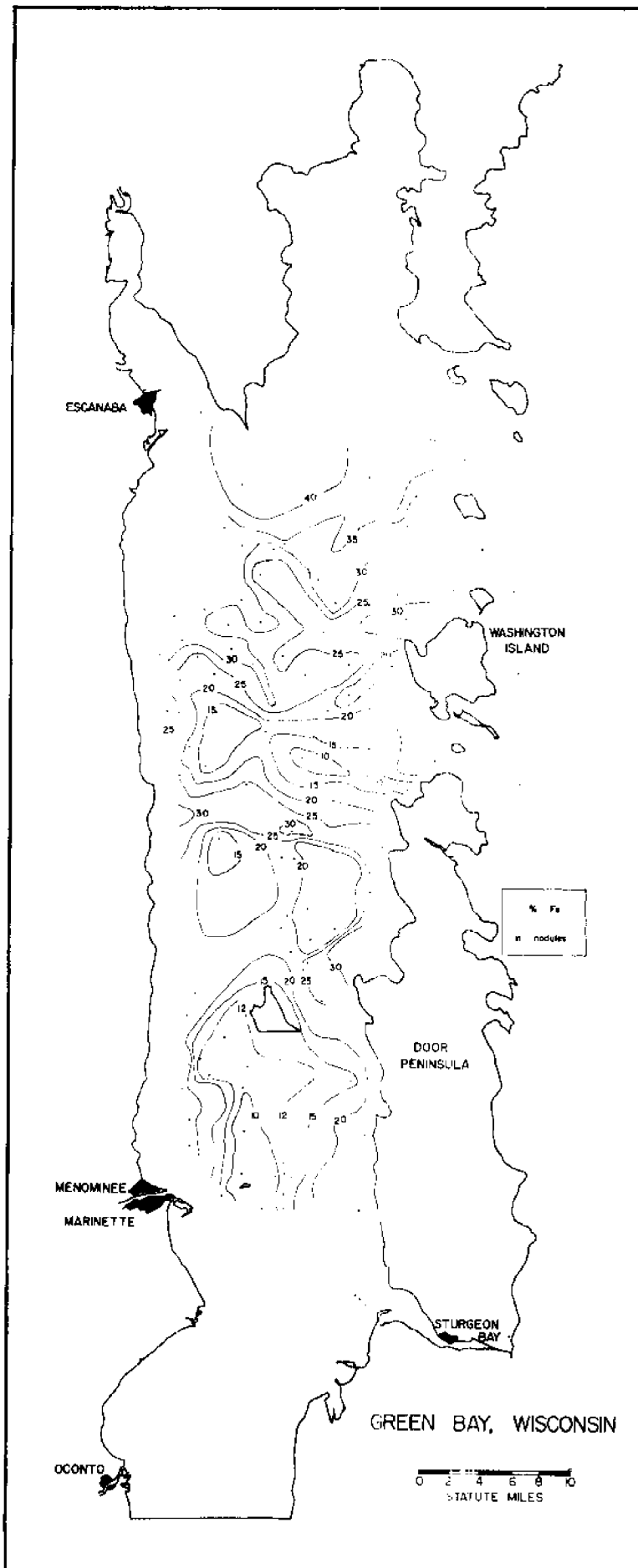


Figure 18

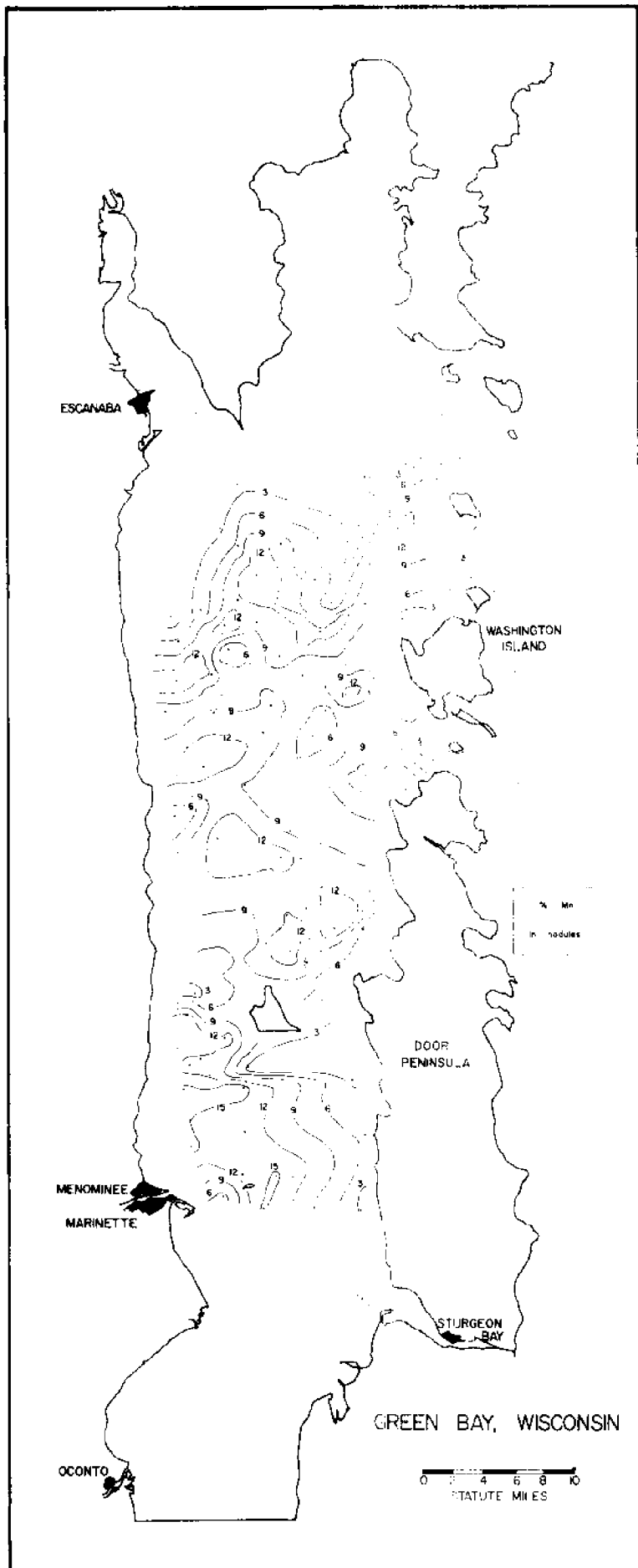


Figure 19

