

TRACE ELEMENTS IN THE SEDIMENTS  
OF LAKE SUPERIOR

By

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## TABLE OF CONTENTS

	Page
TABLE OF CONTENTS -----	11
LIST OF FIGURES -----	vii
LIST OF TABLES -----	ix
INTRODUCTION -----	1
Nature and Purpose of the Study -----	1
Previous Studies -----	3
Acknowledgments -----	4
THE SEDIMENTARY FRAMEWORK OF LAKE SUPERIOR -----	5
Topography and Origin of the Lake Superior Basin -----	5
Pleistocene and Recent History -----	7
Stratigraphy of the Sediments of Lake Superior -----	8
General	
Till	
Brown sand	
Red clay with silt layers	
Varves	
Gray clay	
Brown sediments	
Non-deposition or erosion	
The Rate of Sedimentation in Lake Superior -----	12
Varves	
The rate of post-varve sedimentation	
The rate of post-gray clay sedimentation	
Summary	
THE BIOLOGIC FRAMEWORK OF LAKE SUPERIOR -----	16
THE HYDROGRAPHIC FRAMEWORK OF LAKE SUPERIOR -----	19
The Water Balance and its Hydrochemical Implications -----	19
Currents -----	23
Thermal Structure -----	24
The Chemical Characteristics of Lake Superior -----	25
General	
Lake Superior is not merely a "collecting basin"	
Variation of ionic concentrations within	
Lake Superior	
Calcium	
Potassium	
Trace elements	

	Page
DISTRIBUTION OF MAJOR ELEMENTS -----	33
Surface Sediments -----	33
General relationships	
Near-surface phenomena	
Silicon	
Calcium	
Iron	
Sediments at Depth -----	40
MINERALOGY OF LAKE SUPERIOR SEDIMENTS -----	42
OTHER ASPECTS OF GENERAL GEOCHEMISTRY -----	47
Eh-pH Relationships in Lake Superior	
Water and Sediments -----	47
Water measurements	
Surface sediments	
Gray clay	
Red clay and till	
Carbonates in Lake Superior Sediments -----	53
Colloidal Properties of Lake Superior Sediments -----	56
Supposed Oxidation-Reduction Phenomena in	
Lake Superior Sediments -----	58
Red and gray sediments	
Redox phenomena at the gray clay-brown sediment	
contact	
TRACE ELEMENTS IN LAKE SUPERIOR SEDIMENTS -----	65
Zirconium -----	65
Titanium -----	68
Manganese -----	72
General	
Sorption	
Detrital manganese silicates	
Precipitated manganese species	
Manganese crusts	
Summary	
Nickel -----	87
Zinc -----	91
Sorption	
Precipitation	
Regional aspects of zinc distribution	
Conclusion	

	Page
Copper -----	100
General	
Sorption	
Precipitation	
Firmly bound components of detrital minerals	
Regional aspects	
Lead -----	110
Vanadium -----	113
Gallium -----	117
Bromine -----	120
General	
Evidence from the literature	
Cause of the near-surface enrichment often observed in Jenkins cores	
Explanation of the behavior of bromine at depth	
Lithium -----	125
Boron -----	127
Rubidium -----	131
Strontium -----	134
THE ROLE OF ORGANISMS AND ORGANIC MATTER IN THE DISTRIBUTION OF TRACE ELEMENTS IN LAKE SUPERIOR -----	139
Theoretical -----	139
General	
Scavenging effect	
Organisms as environmental controls	
Organic matter as a chemical "host"	
Evidence from Lake Superior Sediments -----	145
Zinc	
Copper	
Strontium	
Manganese	
Lead	
Lithium	
Zirconium and titanium	
Other elements	
Summary	
THE NATURE AND CAUSE OF SURFACE ENRICHMENTS -----	152
Introduction -----	152
A Decrease in the Rate of Detrital Inorganic Sedimentation -----	153

	Page
Sampling -----	214
Jenkins surface mud sampler	
Hydroplastic corer	
Orange peel sampler	
Zumberge-Cast-Global Marine coring	
Shipboard Analyses -----	218
pH	
Eh	
Carbonate saturometer	
Sample handling and storage	
Laboratory Analyses -----	221
Sample preparation	
Trace elements: X-ray spectrographic analyses	
Trace elements: emission spectrochemical analyses	
Trace elements: exchangeable trace elements	
Major element analyses	
Size fraction separations	
Mineralogical analyses	
APPENDIX 8. APPLICATION OF STANDARD ADDITION TECHNIQUE TO X-RAY SPECTROCHEMICAL ANALYSIS -----	231
APPENDIX 9. DIFFUSION IN LAKE SUPERIOR SEDIMENTS -----	238

LIST OF FIGURES

	Page
1. Index Map of Lake Superior -----	6
2. Generalized Stratigraphic Column for Lake Superior, Showing Average Rates of Sedimentation -----	9
3. Major Element Provinces in Lake Superior -----	24
4. Variation of Quartz content with the Plagioclase/Potassic Feldspar Ratio in Lake Superior Sediments -----	44
5. Variation of Quartz Content with the 9.4 Ångstrom Mixed-layer Clay/Illite-Muscovite Ratio in Lake Superior Sediments -----	46
6. Eh-pH Measurements in Lake Superior -----	48
7. Eh-pH diagram for the System Fe-O-OH-S-CO <sub>2</sub> at 1 Atm. and 25° C -----	51
8. Trace Elements in Size Fractions of GS-2-62-OP -----	66
9. Variation of Zirconium Content with Titanium Content in Lake Superior Sediments at Depth -----	70
10. Variation of Zirconium Content with Titanium Content in Lake Superior Surface Sediments -----	71
11. Trace Elements in a Jenkins Surface Mud Profile, GS-18-62 -----	73, 74
12. Trace Elements in a Jenkins Surface Mud Profile, GS-10-62 -----	75
13. Eh-pH Diagram for the System Mn-O-OH-S-CO <sub>2</sub> at 1 Atm. and 25° C -----	78
14. Variation of Zinc Content with Alumina Content in Lake Superior Sediments at Depth -----	93
15. Eh-pH Diagram for the System Cu-Fe-S-O-OH-CO <sub>2</sub> at 1 Atm. and 25° C -----	102, 103
16. Anomalously High and Low Copper/Zinc Ratios in Lake Superior Surface Sediments -----	109

	Page
17. Variation of Bromine Content with Bromine/Organic Carbon Ratio in Lake Superior Sediments -----	122
18. Variation of Strontium Content with Calcium Content in Lake Superior Sediments -----	136
19. Diagrammatic Summary of the Copper Cycle in Lakes -----	141
20. Zinc and Organic Carbon in Jenkins Surface Mud Cores -----	146
21. Variation of Zinc Content with the Zinc/Bromine Ratio in Jenkins Cores -----	148
22. Jenkins Surface Mud Corer and Hydroplastic Corer -----	215

## LIST OF TABLES

	Page
1. Average Rates of Sedimentation for Post-varve Time -----	13
2. Biota of Lake Superior Water -----	17
3. Hydrographic Data for Lake Superior -----	20
4. Chemical Analyses of Lake Superior, 1906-7 and 1954 -----	22
5. Average Chemical Characteristics of Selected Waters -----	26
6. Trace Elements in Lake Superior Water -----	30
7. Analyses of Manganiferous Crusts and Adjacent Sediments -----	84
8. Nickel Content of Various Earth Materials -----	90
9. Zinc Sorption -----	95
10. Lead Content of Various Earth Materials -----	111
11. Vanadium Content of Various Earth Materials -----	116
12. Gallium Content of Various Earth Materials -----	119
13. Lithium Content of Various Earth Materials -----	126
14. Average Boron Content of Great Lakes Sediments and Waters -----	129
15. Rubidium Content of Various Earth Materials -----	132
16. Cation Exchange Capacity of Clay Minerals and Organic Matter -----	144
17. Reproducibility of X-ray Spectrographic Analyses of Trace Elements -----	223
18. Accuracy of X-ray Spectrographic Analyses of Trace Elements -----	224
19. X-ray Diffractometric Analysis of Lake Superior Sediments -----	230
20. Equation for Standard Addition Analysis by X-ray Spectroscopy -----	237

## INTRODUCTION

### Nature and Purpose of the Study

This is a study of the distribution of trace elements in the sediments of Lake Superior. The broad aim of the investigation is to determine the distribution of the elements, and, where possible, to determine what features of the Lake Superior environment control their distribution. Is the distribution largely a matter of the glacial and hydraulic dispersal of the detrital fraction of weathering processes, or is chemical sedimentation a factor? What roles do the inorganic and organic constituents of the lake water play in determining trace element concentrations in the sediments? Does the unique nature of the Great Lakes, large inland bodies of water intermediate in many respects between small lakes and the oceans, produce a unique suite of trace elements that may characterize similar lakes, present and past? Can the trace element distribution contribute to our knowledge of the past history of the lake or enable us to predict future changes? These and similar questions will be considered.

Because the trace elements cannot be considered in vacuo, several aspects of the general geochemistry of Lake Superior water and sediments have been studied also, and are included in this report.

Lake Superior was chosen for this study for several reasons. The University of Michigan - University of Minnesota deep coring operations of 1961 and 1962 afforded an opportunity to obtain deep samples and relate them to surface samples, thereby determining changes in lake conditions. The coring operations and seismic profile traverses preliminary to them were excellent opportunities for the collection of surface samples.

Moreover, Lake Superior would seem to be the best choice for initial Great Lakes studies for purely scientific reasons. It is the Great Lake least contaminated by the hand of man. Unlike Lakes Huron, Erie, and Ontario, it does not inherit the water chemistry of a large lake further up the Great Lakes chain. The bedrock geology offers maximum contrast with that of the basin of Lake Michigan, logically the next lake to study in detail.

In this report an introductory outline of the physical, chemical, and biological framework of Lake Superior precedes an outline of the geochemistry of the major elements and geochemical aspects of sedimentation. Next, data and conclusions about individual trace elements are followed by a general discussion of the processes governing trace element distribution in Lake Superior. The basic data and the methods of sampling and analysis are tabulated and discussed in appendices.

### Previous Studies

Potter et al. (1963) determined the trace elements in three sediment samples from Lake Michigan, Kleerekoper (1961) studied strontium in Lake Huron and Lake Erie sediments, and Swain and Prokopovich (1957) made analyses of manganese and titanium in sediments of the Silver Bay area of Lake Superior. No other studies of trace elements in the sediments of the Great Lakes are known to the writer. Significant published studies of Lake Superior sediments are the works of Swain and Prokopovich (1957) and Reid (1961). Liberal use has been made of unpublished internal reports of Farrand (1963) who is studying the general geology of the 1961-1962 deep cores from Lake Superior. Additional personal communications of Farrand are referred to in this report as Farrand (1965).

Source books for data on the chemistry of Lake Superior waters are the annual reports of the United States Public Health Service Water Quality Network and the compilations of the United States Fish and Wildlife Service (Beeton et al, 1959). Other general papers which contribute significantly to an understanding of the chemistry of the Great Lakes are the works of Ayers (1962) on the physical and chemical characteristics of Great Lakes waters, Bruce and Rodgers (1962) on the water balance of the Great Lakes, Kramer (1961) on the chemistry of Lake Erie waters and sediments, and Potter et al. (1963) on the trace element content of fresh water and marine sediments.

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## THE SEDIMENTARY FRAMEWORK OF LAKE SUPERIOR

### Topography and Origin of the Lake Superior Basin

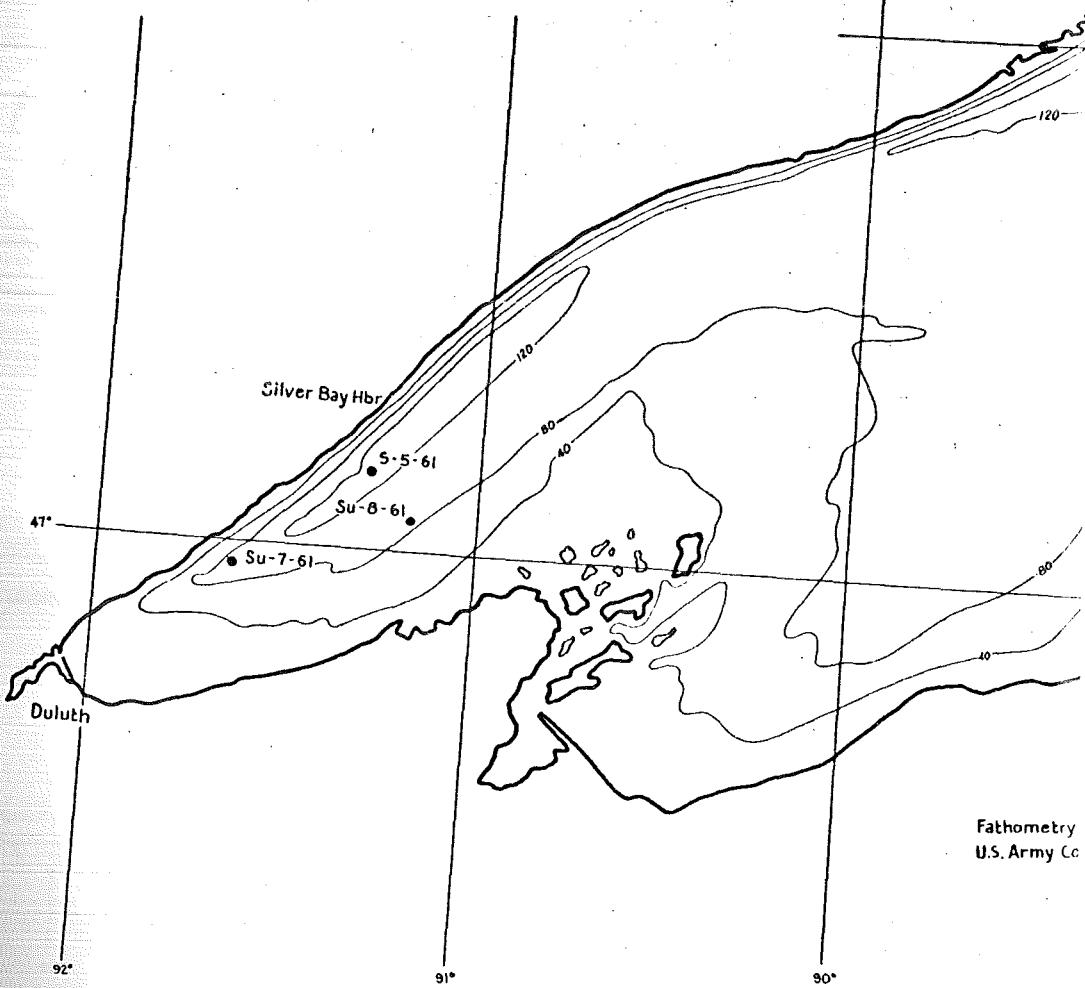
The bottom topography of Lake Superior is shown on the index map (Figure 1). Unlike the other Great Lakes the bottom configuration is exceedingly complex. A broad regular western basin contrasts strongly with the eastern half of the lake, where deep, north-south trending valleys are common. The valleys closely resemble the valleys of the Finger Lakes of western New York State in size and configuration, and possibly in origin also. They are apparently fluvial in origin (Zumberge, 1962), yet there is no outlet from the Lake Superior basin lower than the St. Mary's river, which is now 1300 feet above the deepest point in the valley system. Farrand (1965) has summarized evidence for faulting around the margins of the lake. He postulates that the valleys are the remnants of a former topography that was preserved in the lake by downfaulting and flooding and destroyed in surrounding areas by fluvial and glacial erosion. No matter what the exact history of the development of Lake Superior and its subaqueous topography may be, all contemporary investigators agree that glacial erosion has strongly modified an already-existing basin and valley system (Hough, 1958, Farrand, 1960, Farrand, 1965).

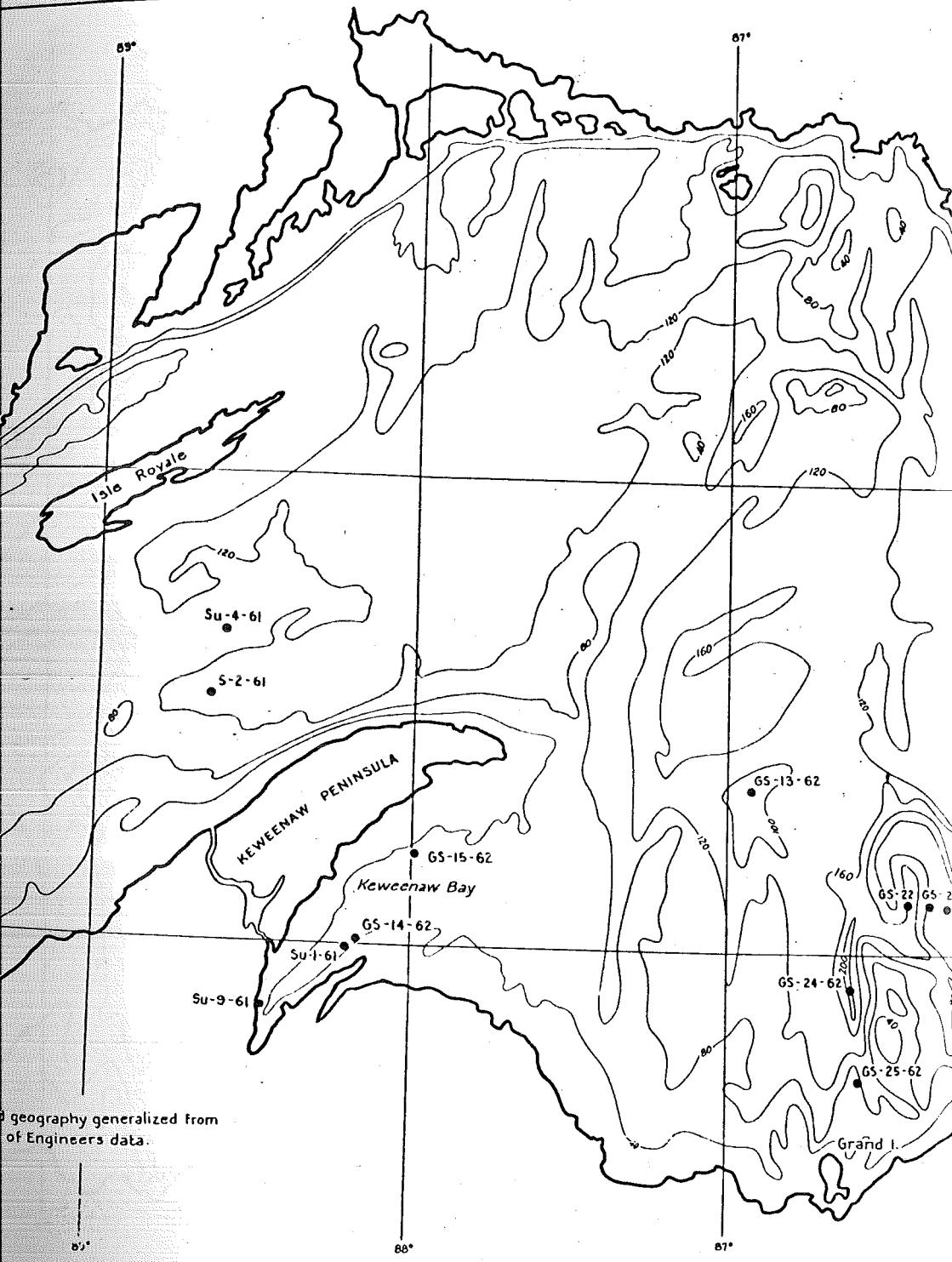
FIGURE 1

INDEX MAP OF LAKE SUPERIOR  
SHOWING SAMPLE LOCALITIES and FATHOMETRY

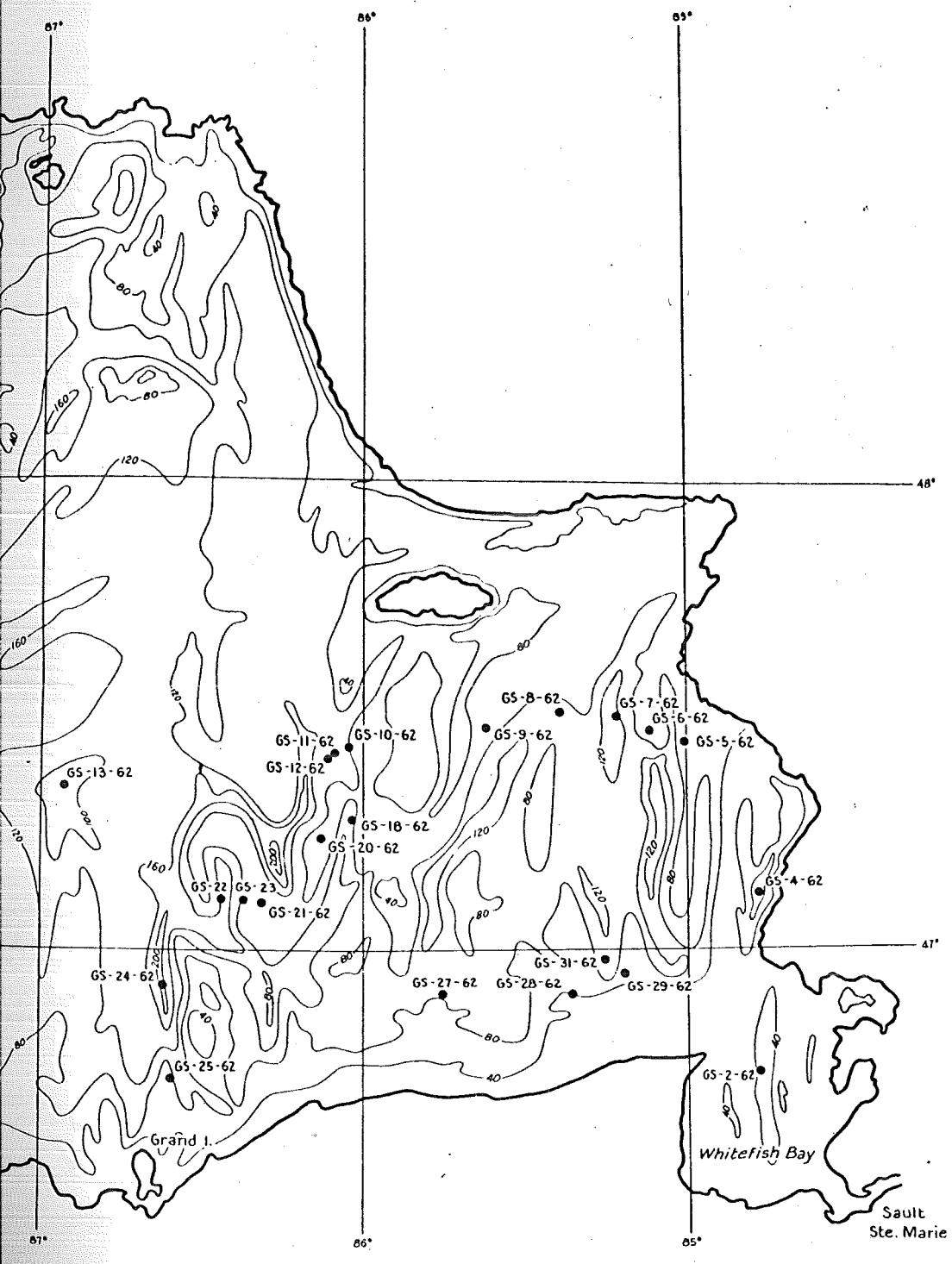
Depth in fathoms

10 5 0 10 20 30 40 50  
Miles





geography generalized from  
of Engineers data.



### Pleistocene and Recent History

The Pleistocene history of the Lake Superior region has been summarized by Hough (1958) and studied in detail by Farrand (1960). The following brief summary relies principally on the chronology of the latter investigator.

The last major ice advance of the Wisconsin glacial age was the Valders advance (maximum approximately 11,500 years B. P., Broecker and Farrand, 1963). A pre-Valders lake in the Superior basin, inferred from the conclusion that the red, clayey Valders till is largely reworked lake sediment, has been named Glacial Lake Keweenaw (Murray, 1953). The Valders ice sheet first retreated from the extreme southwest corner of the basin, ponding various small lakes (Nemadji, Brule, Ashland), which on further retreat united to form Glacial Lake Duluth. Drainage of Lake Duluth was to the southwest, until ice retreat opened an ice-margin channel southwest of the Huron Mountains and across the central part of the northern peninsula of Michigan. Farrand has named the lake drained by this new outlet Glacial Lake Washburn. Rapid retreat of the ice margin soon exposed all of the present lake. Lake Minong, occupying the basin at this time, was connected to Lake Sheguiandah (Lake Huron and Lake Michigan) by two straits. Gradual lowering of lake levels ended in a low water stage of Lake Superior, 360 feet above sea level (roughly 10,000 years B. P., Farrand, 1965). Gradual uplift culminated in the Nipissing Lake Superior (4,100 B. P.). Subsequently, erosion of the Port Huron outlet reduced levels of the three upper Great Lakes following which more uplift of the St. Mary's River outlet raised the Lake Superior level above that of Lakes Michigan and Huron.

## Stratigraphy of the Sediments of Lake Superior

General: The post-Valders history outlined above is replete with named lakes and lake stages that have been inferred largely from shoreline features. The sediments of Lake Superior are less well known. Moreover, this study is largely concerned with the sediments of the deep water portions of the lake, where sedimentation has been uninterrupted since the retreat of Valders ice.

No overall study of the sediments of Lake Superior has been published. The following summary draws on the work of Farrand (1963, 1965), Reid (1961), and Swain and Prokopovich (1957) in addition to the information obtained by the writer during the present study. The stratigraphic section will be described chronologically, starting with till. Where sample numbers are used they refer to sample locations for the 1961 and 1962 expeditions, as explained in Appendix 1 and located on Figure 1.

Till: Wherever the entire thickness of lake sediment has been penetrated it is underlain by till. Two types of till are present, a clay-rich red till, and a silt-rich red till (Farrand, 1963). The red coloration is due to finely divided ferric oxides and hydrated oxides, derived from local ferruginous bedrock common in the Lake Superior basin (Murray, 1953; Farrand, 1965).

Brown sand: In the southeastern portion of the lake a deposit of "well sorted light brown sand" was found. This deposit "occurs between two different till sheets or is interbedded in a single till sheet complex" (Farrand, 1963).

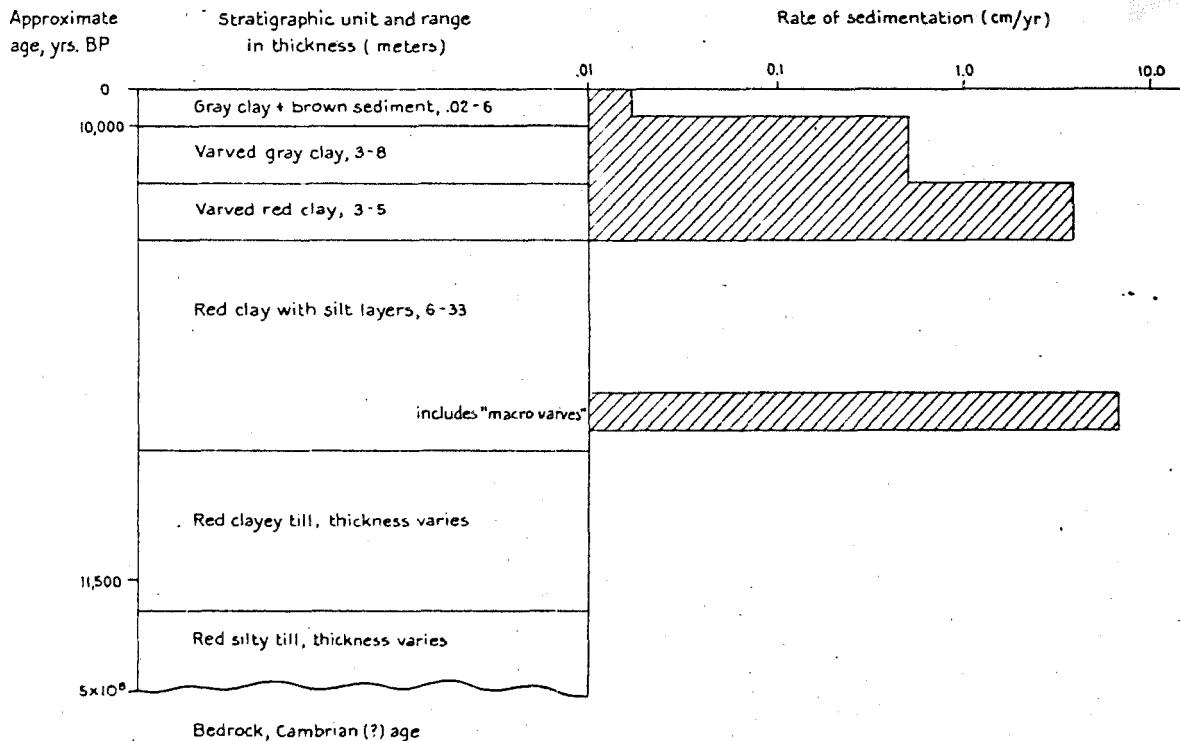


Figure 2. Generalized stratigraphic column for Lake Superior. (Basic data after Farrand, 1963)

Red clay with silt layers: Stratified red clay with silt layers occurs above the till. Both the clays and the silts of this unit are well sorted, and thickest sections of the unit are found in the central part of the lake (S-2, S-8). Bedding in the unit is distinct but irregular (Farrand, 1963).

Varves: Varved sediments overlie the red clay with silt layers in almost all cores. In each varve a light, carbonate-rich, silty layer with a sharp lower contact grades upward into a darker, clay-rich layer. The stratigraphically lower, thicker varves are red, but the stratigraphically higher, thinner varves are gray. The transition from red to gray varves is gradational in all of the five cores in which it is present. Gray coloration appears first in the light "summer" layer, while red coloration lasts longer in the dark "winter" layer. Gray varves are thinner and finer grained than red varves, and there may also be a difference in the heavy mineral suite (Farrand, 1963). Preliminary varve counts show 480 to 1300 varve years, of which the great majority are gray.

Gray clay: Overlying the gray varves is a gray, sticky clay, identical in appearance with the immediately underlying gray varved clay except for the absence of varving.

Brown sediments: Whereas the units described above are widespread, the more recent sediments of Lake Superior reflect strong local variations in provenance and dispersal. The color of these sediments varies considerably, but all are some shade of brown, red brown, or olive brown. They are "distinctly coarser than the underlying gray clay and gray varves,

averaging 35 to 70 percent finer than two microns in different cores" (Farrand, 1963).

The brown sediment deposits that are thickest and of the coarsest grain size are found in areas with abundant local sediment supply, as is the case in Keweenaw Bay (S-1) and in the trench in Whitefish Bay (GS-2), where the brown sediment is at least 3 meters thick. The bottoms of the deep trenches of the eastern half of the lake have thicker deposits of brown sediment than the slopes of the trenches and the adjacent topographic highs, presumably because finer materials is being swept past and off the topographic highs and into the deep trenches. The "red clay" overlying gray clay described by Swain and Prokopovich (1957) in the Silver Bay area of Lake Superior is probably the brown sediment of this investigation. They document the thinning of the brown sediment away from shore, and concluded that the unit is absent in the deepest parts of the area studied. However, if they had sampled with a surface mud sampler they probably would have found a minimum of two centimeters of brown sediment in all localities.

Non-deposition or erosion: Many localities of intermediate water depth (200-600 feet) have evidence of non-deposition or erosion of sediment, particularly in the eastern half of the lake, where gray clay (GS-15), varved gray or red clay, and red clay (GS-19) are found close to the sediment-water interface, younger strata presumably having been eroded away, or in some cases never deposited. Typically, such sediments are capped by a thin (less than 5 cm) layer of poorly sorted silt.

### The Rate of Sedimentation in Lake Superior

No radiogenic age dating has been carried out on Lake Superior sediments, therefore estimates of rates of sedimentation must be based on other considerations.

Varves: If one assumes that the varves of Lake Superior are yearly alternations (and there is no reason to doubt this periodicity) the rate of sedimentation during "varved" times is easily determined. Farrand has measured varve thicknesses in the deep cores (1963). "Macro-varves" in the lowest part of the red clay and silt unit of core S-7 average 7 cm per varve year. Red varves below the normal red varve-gray varve transition average 3.5 cm per varve year in S-8 and 4 cm per varve year in S-9. Gray varves are considerably thinner, averaging only 0.5 cm per varve year. Therefore the general trend shown in the varve sequences is an upward decrease in the rate of sedimentation.

The rate of post-varve sedimentation: The Lake Superior drainage basin may have been free of glacial ice at approximately 10,000 B.P. (Farrand, 1965). If we assume that varve deposition ceased at that time we can calculate average rates of sedimentation for post-varve time, as has been done in Table 1. A determination of the exact time at which varving ceased involves stratigraphic and chronologic considerations that are beyond the scope of this paper. Farrand (1965) suggests and the writer uses 10,000 B. P. solely as a reasonable approximation. Also implicit in the calculation of sedimentation rates in Table 1 is the assumption that varving ceased everywhere at the same time. Although this is certainly

TABLE 1: AVERAGE RATES OF SEDIMENTATION  
FOR POST-VARVE TIME

Based on the assumption that all varving stopped in 10,000 B. P.

Core	Source of Data	Thickness of Sediment Above Varves, cm	Rate of Sedimentation, cm per year
S-8	1	107	.011
S-9(1)	1	336	.034
S-10(1)	1	274	.027
S-11	1	253	.025
Core 7	2	79	.008
Core 9	2	160	.016
GS-8	3	24	.002
GS-31	3	76	.009
Average		171	.017

Sources:

- 1 Farrand, 1963
- 2 Reid, 1961
- 3 This investigation

not true in detail it is probably a reasonable assumption for the type of calculations made in this paper.

The wide range of sedimentation rates tabulated in Table 1 is the result of the localized nature of thick deposits of brown sediment. If data on total thickness of post-varve sediments at S-1, GS-2, and GS-7 were available the maximum rate of sedimentation would be still higher, but the maximum of Table 1, 0.034 cm per year is still less than a tenth of the average gray varve sedimentation rate of 0.5 cm per year. Therefore, it is evident that the trend toward a decrease in the rate of sedimentation shown by a comparison of red and gray varves continued into post-varve time.

It might be logical to assume that the rate of sedimentation was higher at the beginning of post-varve time than it is now, but there is no information available to prove this differential or establish its magnitude.

The mean of the average sedimentation rates for the eight cores of Table 1 is .017 cm per year. This figure may be biased because of the usual tendency to take cores in areas where a greater sediment thickness is anticipated. Because of this and the other assumptions that enter the calculations this average probably should not be applied to the entire lake at this time. If varving in Lake Michigan ceased about 10,500 B. P., average rates of sedimentation in Lake Michigan during post-varve time are .021 to .085 cm per year (Data of Hough, as quoted in Reid (1961) and adjusted by the present writer to account for revised estimates of the time that varving ceased). Therefore the rate of sedimentation at the Lake Superior localities is less than but of the same order of magnitude as that in the Lake Michigan localities.

The rate of post-gray clay sedimentation: Another possible horizon for use in determination or comparison of rates of sedimentation is the contact of gray clay and brown sediment, but the age of this contact may be dependent on the local source of sediment. Therefore, it is likely that a hypothesis of contemporaneity of the gray clay-brown sediment contact will be less reliable than the hypothesis of contemporaneity of the varved gray clay-massive gray clay contact. Moreover, there is no way of determining the absolute age of the gray clay-brown sediment contact short of radiogenic measurement.

If we assume, however, that this boundary is synchronous for limited regions of the lake basin an extreme variation in rates of sedimentation during post-gray clay time is shown by the variation in thickness of the brown sediment, from about two centimeters to over three meters, as described above.

Summary: The rate of sedimentation in Lake Superior has decreased, although not continuously, from glacial times to the present. Sedimentation rates for post-varve time are .002 to .034 cm per year, with a mean of .017 cm per year. Based on thickness variation of the brown sediment, rates of sedimentation of brown sediment vary widely. They probably average less than .017 cm per year.

## THE BIOLOGIC FRAMEWORK OF LAKE SUPERIOR

Lake Superior is an oligotrophic lake, that is, it has a low level of organic productivity. The most satisfactory quantitative demonstration of this low productivity is the data of the U. S. Public Health Service National Water Quality Network data compilations. Table 2 lists the 1960-1961 data for Lake Superior and also for one Lake Michigan station as a basis for comparison. In addition to revealing its relative oligotrophy the data shows the relatively low degree of human contamination of Lake Superior.

Of particular interest are the benthic organisms that might be responsible for sediment mixing. The only organism of this type frequently observed in this study was the genus *Pontoporeia*, a small amphipod crustacean that is often trapped in Jenkins corer samples. The presence of *Pontoporeiid* species is sufficient to explain the absence of micro-stratification in the recent lake sediments, even though their sediment-mixing activity is confined to the uppermost 2 or 3 cm of sediment.  
(J. C. Ayers, 1964, personal communication).

TABLE 2: BIOTA OF LAKE SUPERIOR WATER

With data from Lake Michigan for  
comparative purposes

Source: U.S. Public Health Service National  
Water Quality Network data  
compilation, 1960-1961

(In each column the average is given, followed  
by the range in parenthesis. Data are number  
per milliliter, except macroplankton).

Datum	Lake Superior Duluth	Lake Superior St. Mary's River	Lake Michigan Milwaukee
Total Algae	121(0-400)	158(0-500)	1000(300-4400)
blue-green algae			
coccoid	0	1.6(0-20)	5(0-50)
filamentous	1.6(0-20)	1.6(0-20)	4(0-40)
green algae			
coccoid	23(0-150)	9(0-80)	26(0-150)
filamentous	0	0	0
Flagellates (pigmented)			
green	4(0-40)	6(0-20)	10(0-70)
other	9(0-210)	16(0-80)	16(0-60)
Diatoms			
centric	29(0-130)	33(0-170)	691(20-4050)
pennate	45(0-180)	93(0-330)	340(40-850)
Inert diatom shells			
centric	18(0-80)	19(0-70)	222(0-500)
pennate	43(0-270)	125(0-430)	150(0-500)

TABLE 2, continued

Datum	Lake Superior Duluth	Lake Superior St. Mary's River	Lake Michigan Milwaukee
Other microplankton, fungi, and sheathed bacteria (number per ml)	26(0-200) <sup>1</sup>	18(0-200)	13(0-90) <sup>2</sup>
Macroinvertebrates			
protozoa (number per ml)	2(0-20)	0.4(0-10)	3(0-20)
rotifers (number per liter)	1.5(0-18)	7(0-78)	15(0-125)
crustacea (number per liter)	.2(0-19)	1.3(0-14)	7(0-31)
nematodes (number per liter)	0	.04(0-1)	.2(0-3)
other (number per liter)	0	.04(0-1)	.1(0-3)
Total extractible Organic Matter, $\mu\text{g/l}$	105	117	153
chloroform extractible Organic Matter, $\mu\text{g/l}$	21	22	32
alcohol extractible Organic Matter, $\mu\text{g/l}$	84	95	121
5 day B.O.D. mg/l	0.4	N.D.	1.1
Coliforms per 100 ml	13(1-100)	7(1-49)	82(1-1300)

1) Excluding one bloom of 3540

2) Excluding one bloom of 2860

## THE HYDROGRAPHIC FRAMEWORK OF LAKE SUPERIOR

### The Water Balance and its Hydrochemical Implications

Data defining the water cycle in Lake Superior are listed in Table 3. The three estimates (part B) overdefine the system, and offer an opportunity to check the reliability of the estimates and the basic data. The agreement is poor. For example, an indirect calculation of runoff from land using the other tabulated data yields a value of  $44.5 \times 10^9 \text{ m}^3/\text{year}$ , radically different from the tabulated estimate, which is based on limited United States Geological Survey measurements of stream discharge. One or more of the estimates of part B must be wrong, and therefore an internally consistent hydrographic balance cannot be constructed at this time. The "derived" balance of part C of Table 3 is a forced compromise, in which it is assumed that all of the estimates of part B are somewhat in error, each being in error by a similar percentage.

Several conclusions may be drawn from Table 3 that are qualitatively independent of the uncertainties in the derived data. The evaporation to precipitation ratio of Lake Superior is probably between 0.55 and 0.65, considerably lower than the ratio of 0.88 derived by Hunt (1958) for Lake Ontario. The annual runoff from the surrounding land is probably only 55 to 65 percent of the annual discharge. Therefore, if for a first assumption net sediment-water transfer of dissolved species is neglected, equilibrium will be attained when the dissolved solids content of the runoff waters is about 1.6 to 1.8 times the dissolved solids content of the lake. This relationship cannot be tested until considerably more hydrographic and hydrochemical data are assembled.

TABLE 3: HYDROGRAPHIC DATA FOR LAKE SUPERIOR

A. Primary data

Lake Surface Area (1)	$21,820 \text{ mi}^2$	$= 82.414 \times 10^9 \text{ m}^2$
Land Area of Basin	$48,180 \text{ mi}^2$	$= 124.79 \times 10^9 \text{ m}^2$
Total Basin Area (1)	$80,000 \text{ mi}^2$	$= 207.2 \times 10^9 \text{ m}^2$
Avg. Annual Rainfall over Land (1)	29 inches/yr	$= .738 \text{ m/yr}$
Avg. Lake Depth (1)	475 feet	$= 144.9 \text{ m}$
Avg. Annual Discharge (1)	73,700 cfs	$= 65.82 \times 10^9 \text{ m}^3/\text{yr}$

B. Estimated data

Avg. Ratio of rainfall on water to rainfall on land (2)	$= 0.90$
Avg. Runoff from land (3)	$42,700 \text{ cfs} = 38.1 \times 10^9 \text{ m}^3/\text{yr}$
Avg. Evaporation from water surface (4)	$15.96 \text{ in} = .4054 \text{ m/yr}$

C. Derived data

(The system is overdetermined. Figures of this section, except for discharge and lake volume, are derived from the above data by a forced compromise, giving equal weight to each of the estimated data).

Rainfall on Water	$55 \times 10^9 \text{ m}^3/\text{yr}$	Discharge	$66 \times 10^9 \text{ m}^3/\text{yr}$
Runoff from land	$41 \times 10^9 \text{ m}^3/\text{yr}$	Evaporation from Lake Surface	$\underline{30 \times 10^9 \text{ m}^3/\text{yr}}$
	$\underline{96 \times 10^9 \text{ m}^3/\text{yr}}$	$=$	$96 \times 10^9 \text{ m}^3/\text{yr}$
Lake Volume - 2,864 $\text{mi}^3$	$= 11,938 \times 10^9 \text{ m}^3$		

Sources:

- (1) The Great Lakes Pilot
- (2) Hunt (1958) suggests 0.8, and Bruce and Rodgers (1962) suggest 1.0
- (3) Calculated for  $8,835 \text{ mi}^2$  (18% of land area) from U. S. Geological Survey data, and extrapolated for the entire basin.
- (4) Calculated by Horton (1927).

Both discharge and runoff are very small fractions of total lake volume (0.55 percent and about 0.3 percent, respectively). Therefore changes in the supply of an element will not cause changes in lake composition over short periods of time unless a), the change in supply is very great, or b), the change in supply is limited to a small portion of the lake, and complete mixing does not occur. Ayers (1962) has shown that the major element composition of Lake Superior has remained relatively constant over the past 50 years (Table 4 of this report). From the comments above it is evident that this observed uniformity could be evidence for equilibrium, but that it also might only show that the changes in supply are not large.

It is clear that quantitative calculation of the contribution of the lake bottom sediments to regulation of the chemical composition of the lake water is impossible at this time.

TABLE 4: CHEMICAL ANALYSES OF LAKE SUPERIOR,  
 1906-7 and 1954  
 (Ayers, 1962)

Element	1906-7 ppm	1954 ppm
Si	7.4	4.7
Fe	0.06	0.062
Ca	13	12.4
Mg	3.1	3.3
HCO <sub>3</sub>	56	59.4
SO <sub>4</sub>	2.1	1.2
NO <sub>3</sub>	0.5	0.15
Cl	1.1	2.6
Total Solids	60	59.0

### Currents

Harrington (1895) made studies of the surface currents of Lake Superior using drift bottles. A general counterclockwise motion, modified by outlet discharge, was found. More recent studies have tended to confirm this surface motion, but little more has been added to the detail. The currents at depth are unknown, and may be considerably complicated in the eastern half of the lake because of the bottom topography.

### Thermal Structure

Lake Superior is cold, because of its latitude and great average depth (475 feet). At the summer maximum the volume average temperature ( $41.7^{\circ}$  F, or  $5.4^{\circ}$  C) is within three degrees Fahrenheit of the concurrent minimum lake temperature, despite concurrent surface maximum temperatures of 56 to 65 degrees Fahrenheit (Anderson & Rodgers, 1963). The only synoptic survey executed to date (*ibid*) showed a well developed thermal stratification close to the surface. Thus Lake Superior is like the oceans in that for many purposes the epilimnion may be neglected in quantitative calculations. Chemical and thermodynamic calculations should be made at  $5^{\circ}$  C rather than the customary standard of  $25^{\circ}$  C wherever possible.

### The Chemical Characteristics of Lake Superior

General: The chemical characteristics of Lake Superior are shown in Table 5. Data on the other Great Lakes, rainwater of the Lake Superior region, the oceans, and waters draining various rock types are included for comparative purposes. The Lake Superior data are taken directly from the compilation of Beeton and Chandler (1963), but several items may be in error. When anion and cation milliequivalents are summed for Lake Superior, and Si is assumed to be present as  $H_4SiO_4$  or other noncharged species, the anion milliequivalents exceed the cation milliequivalents by 0.160, or 16 percent. One possible source of part of this discrepancy is the bicarbonate ion. Measurements of bicarbonate made during this study, listed in Appendix 6, average 51.6 ppm, or 0.845 meq, 0.1 meq less than the value of Table 5. Swain and Prokopovich (1957) also report lower bicarbonate than the data of Table 5.

Lake Superior is not a "collecting basin": It has been suggested that Lake Superior may be nothing but a large "rain barrel," collecting rain water and runoff before there is opportunity for equilibration with most basin rocks and sediments. Table 5 shows that such a generalization is false. Although the sulfate content of Lake Superior is little higher than that of rainwater, the contents of chloride and calcium are over ten times as high, hence rock solution, or sediment to water transfer of ions has clearly taken place somewhere in the Lake Superior basin.

Kramer has considered this problem from a different approach in his (1964) study of chemical models for lake waters with particular reference to the Great Lakes. He finds that most of the ionic concentrations of

TABLE 5: AVERAGE CHEMICAL CHARACTERISTICS OF SELECTED WATERS

Data are expressed first in ppm, then in meq/l

Lake	Source	Ca	Mg	K	Na	$\text{HCO}_3$	Cl	$\text{SO}_4$	Si	P
Superior	1	12.4 .62	2.8 .33	0.6 .015	1.1 .035	56 .94	1.9 .054	3.2 .064	2.1 .075	.005 .00016
Huron	1	22.6 1.1	6.3 .52	1.0 .025	2.3 .10	100 2.26	7.0 .20	9.7 .20	2.3 .082	.010 .00032
Michigan	1	31.5 1.6	10.4 .86	0.9 .023	3.4 .15	138 2.3	6.2 .18	15.5 .32	3.1 .110	.013 .00042
Erie	1	36.7 1.8	8.9 .73	1.4 .036	8.7 .38	116 1.9	21.0 .59	21.1 .44	1.5 .053	.061 .002
Ontario	1	39.3 1.95	9.1 .75	1.2 .031	10.8 .47	115 1.9	23.5 .66	32.4 .68	0.3 .010	-- --
Rain Water L. Superior Region	2	0.3 .015	?0.3 .015	0.2 .005	0.4 .017 $\text{H}_2\text{CO}_3$	1.2 .003	0.12 .005	2.3 --	-- --	-- --
Oceans	3	410 20.5	1300 107	390 10.0	10800 470	143 2.3	19500 548	2700 56	.0007- .0014meq	.00003- .003meq
Water Draining Granite	4	3.6 .17	.6 .054	.6 .015	2.1 .087	15.5 .26	.2 .006	3.3 .069	9.2 .33	-- --
Water Draining Quartzite	4	1.9 .095	.06 .0054	.3 .008	.5 .022	5.7 .095	.06 .017	1.8 .038	3.6 .13	-- --

TABLE 5: CONTINUED

Lake	pH	Spec. Cond. 18°C	Total Diss. Solids	Ionic Strength	Ca/K	Ca/Na	K/Na	Cl/HCO <sub>3</sub>
Superior	7.4	78.7	80.1	.0013	20.6	11.3	0.43	.058
Huron	8.1	168.3	151.2	.0029	22.6	9.8	0.25	.088
Michigan	8.0	225.8	209	.0040	35.0	9.3	0.15	.078
Erie	8.3	241.3	215.3	.0045	26.2	4.2	0.095	.31
Ontario	8.5	272.3	222.6	.0049	32.6	3.6	0.066	.35
Rain Water, L. Superior Region	4-5?	-	4.8	.00008	1.5	0.75	0.5	.16
Oceans	8.1		34200	1.4	1.05	0.038	0.036	239
Water Draining Granite	7.1	34 (25°C)	42.2	.00044	6.0	1.7	0.17	.013
Water Draining Quartzite	6.6	15 (25°C)	13.9	.00021	6.3	3.8	0.36	.010

## SOURCES:

- 1) Beeton and Chandler, 1963
- 2) Gorham, 1961, p. 804, Junge, 1958, Hutchinson, 1957, p. 549-51.
- 3) Sverdrup et al, 1942
- 4) Miller, 1961

Lake Superior water correspond rather closely to a mixture of two component waters:

- a) Runoff, assumed to be total land precipitation, in equilibrium with a mineralogic system that includes calcite, illite, K and Na-feldspars, kaolinite, quartz, hydroxyapatite, fluorapatite, and with arbitrarily assumed  $\text{Cl}^-$  and  $\text{SO}_4^{=}$  contents.
- b) Rainfall over the lake, assumed to be "distilled water."

Calcium in Lake Superior is higher than that predicted by the model, while sodium is considerably lower. Details of the calculations and results can be found in Kramer's original publication.

Variation of ionic concentrations within Lake Superior: Although many analyses of lake water have been made recently by the U. S. Fish and Wildlife Survey, no regional variation in the ionic concentration of major elements in Lake Superior waters has been recognized. The problem of recognition of variation is compounded by the fact that many of the ionic concentrations in the lake are at the lower limit of sensitivity of standard techniques of water analysis. For example, Beeton et al (1959) report 334 sodium analyses from all parts of the lake. Data are recorded to the nearest .05 ppm. The average and standard deviation for the analyses are 1.04 and  $\pm$  .07, which means that two thirds of the analyses are 1.00, 1.05, and 1.10 ppm! This is certainly no proof that regional variation does not exist, but does suggest that detailed synoptic chemical studies will require the application of more refined analytical techniques if significant results are to be obtained.

Calcium: One would expect that Lake Michigan, situated in a region rich in carbonate rocks, might have higher Ca/K and Ca/Na ratios than Lake

Superior, situated in a basin whose bedrock is lower in calcium. This is the case in fact, as shown in Table 5, but the table also reveals that the Lake Superior ratios of 20.6 and 11.3 are still considerably higher than ratios for waters draining granitic and metamorphic terrains. The data of Miller (1961) is included in Table 5 as an example. Conway (1942) gives average Ca/K and Ca/Na ratios of 7.0 and 1.6 respectively, based on a greater number of measurements of granitic terrains.

Note that the calcium concentration of Lake Superior is eighteen times the concentration of rain water. Because the bedrock of the Lake Superior basin is notably lacking in readily soluble Ca, whereas tills and glacial lake sediments have abundant calcite and dolomite, it is likely that dissolution of the carbonate of glacial debris is still a controlling factor in the Mg-Ca-carbonate-bicarbonate balance of the lake. Moreover, it is probable that solution of glacial debris is taking place in Lake Superior itself, because the Ca content of the lake is high relative to Kramer's runoff equilibrium calculations (Kramer, 1964).

Potassium: The progressive decline in the ratio of potassium to sodium in the "downstream" direction in the chain of the Great Lakes is caused by the fixation of K in clay minerals. Confirmation of this exchange in Lake Erie is found in the studies of Kramer (1961, 1964). The process is important in all natural waters (Hutchinson, 1957, p. 556-7).

Trace elements: Table 6 is a compilation of all the trace element analyses of Lake Superior waters that have been published, and estimates of the concentrations of ions that were looked for but not detected or have not been looked for in the water but are studied in the sediment in this

TABLE 6: TRACE ELEMENTS IN LAKE SUPERIOR WATER

<u>Element</u>	<u>Source of L. Superior analyses</u>	<u>Average concentration, pp billion</u>	<u>Source for L. S. Estimate</u>	<u>Estimate, pp billion</u>
Sb	1A	< 6		
Ba	1	7		
Be	1B	.001	6	
Bi	1A	< 3		
B	1	38		
Br			4	12
Cd	1A	< 2		
Cr	1	0.9		
Co	1A	< 1	4	0.5
Cu	1	3.8		
F	1	97		
I	7	> 0.1		
Fe	1	11.5		
Pb	1B	4	3	1
Li			4	0.7
Mn	1A,2	< 3; 148 (see note 8)		
Mo	1	1		
Ni	1	1.3		
Rb			4	1
Se	1A	< 10		
Sr			5	min 32
Sn	1A	< 1		
Tl			3	1.6
V	1A	< 1	3	0.6
Zn	1A	< 300	4	10
Zr			3	2.6

SOURCES OF DATA ARE LISTED ON NEXT PAGE

TABLE 6: Continued: Sources of Data

1. U. S. Dept. H. E. & W., National Water Quality Network, Data Compilations, 1959-60, 1960-61, Average of 8 determinations, of milliporefiltered water. Each water sample is a composite of 12 bi-monthly samples.
- 1A. Looked for but not detected by source 1: the number tabulated is the limit of sensitivity for the method.
- 1B. Looked for in all but detected in less than half of the analyses of source 1, therefore less reliable.
2. Swain & Prokopovich, 1957, for Silver Bay area.
3. Turekian & Kleinkopf, 1956, and Kleinkopf, 1960, lakes of Maine.
4. Livingstone, 1963, Worldwide composition of rivers and lakes. Estimates adjusted on basis of total dissolved solids.
5. Skougstad & Horr, 1963, give data for streams tributary to Lake Superior: Data adjusted on basis of dissolved solids and Ca/Sr ratios.
6. The data of Merrill, 1960, suggest that this average is of the correct order of magnitude, despite the fact that Be was above the limits of detection on only one out of eight analyses.
7. Hutchinson, 1957, pp. 562-3.
8. The samples of Source 2 may not have been filtered. In any case, Mn is subject to precipitation and sorption in storage, and neither figure quoted here can be considered a reliable estimate of Mn in solution at time of sampling. Reference 4 suggests that the world average is somewhat higher than 12 ppb.

report. Although the data of the Water Quality Network (reference 1) are reliable, it should be born in mind that their reference stations are in fact municipal water intakes, one at Duluth and the other in the upper St. Mary's river. The extent of contamination of these intakes by urban or industrial wastes is not known.

## DISTRIBUTION OF MAJOR ELEMENTS

### Surface Sediments

This section describes the distribution of major elements in brown sediments that are within 25 centimeters of the sediment-water interface. This is approximately the maximum interval recovered by the Jenkins surface mud sampler (Appendix 1).

General relationships: Comparison of the major element composition of the surface sediments from different localities shows that the content of Si is inversely related to the content of K, Al, and Fe. The mineralogic studies outlined below show that this is due to the inverse relationship of quartz to clay minerals and feldspars. The former consists only of  $\text{SiO}_2$ , while the latter two groups contain K, Al, Ca, and Fe as well as Si and O.

Two major sediment provinces are defined by major, and, as we shall see later, by trace-element distribution in the surface sediments of Lake Superior. The two provinces are shown diagrammatically in Figure 3. Basinal argillaceous sediments of eastern Lake Superior are relatively high in  $\text{SiO}_2$  (60-70%), and low in  $\text{CaO}$  (1.7-2.0%) and  $\text{Fe}_2\text{O}_3$  (7-9.5%), while basinal argillaceous sediments of western Lake Superior, including Keweenaw Bay, are relatively low in  $\text{SiO}_2$  (54-62%) and high in  $\text{CaO}$  (2.7-3.3%) and  $\text{Fe}_2\text{O}_3$  (9-12.5%). The western province, deriving much of its detritus from the predominantly basic Precambrian rocks of the Keweenaw peninsula and the northwest shore, contains sediments high in Ca and Fe and low in Si because of the abundance of plagioclase, amphiboles, and pyroxenes in

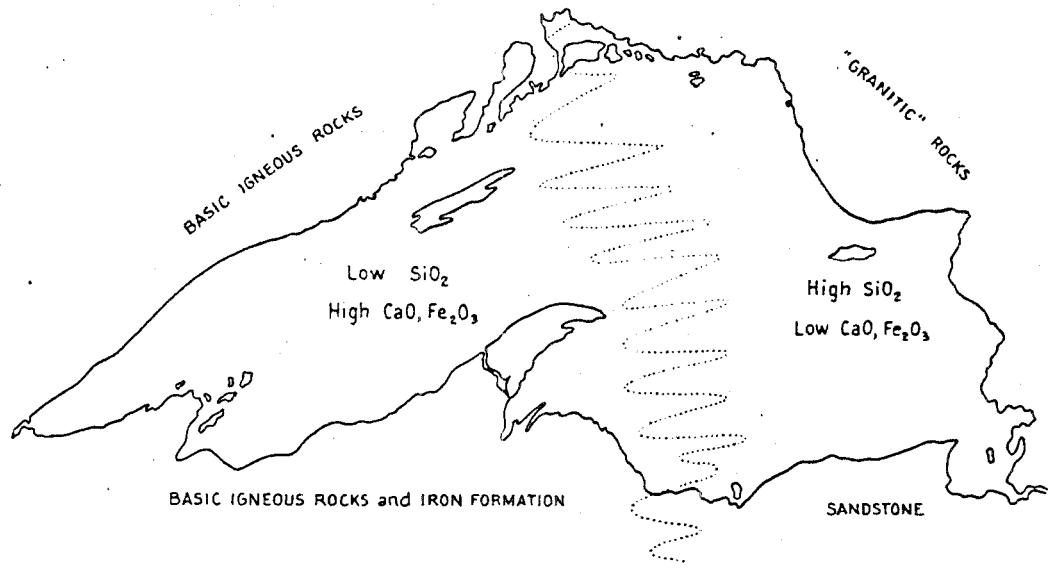


Figure 3. Major element provinces in Lake Superior sediments.

the source rocks. The eastern province, deriving much of its detritus from the predominantly acidic rocks of the eastern part of the Lake Superior basin, contains sediments low in Ca and Fe and high in Si because of the relative abundance of quartz and silica-rich feldspars in the source rocks.

Near-surface phenomena: Examination of the major element concentrations in the Jenkins surface mud profiles shows that at any given locality the Fe content of the sediment rises toward the surface, the increase being about 10 to 30 percent of the amount present. Over the same interval K, and to a lesser extent, Al, decrease toward the surface (15 and 10 percent of the respective amounts present). The Ca content remains constant or occasionally even increases slightly upward. Silicon decreases toward the surface in several cores, but occasionally remains constant, or even increases slightly upward, particularly in those Jenkins sequences that show the greatest decreases in K and Al.

The major cause for decreases in the percentage of K, Al, and sometimes Si, is an increase in the percentage of organic matter. Borchardt has analysed representative Lake Superior sediments for organic carbon, and his results are shown in Appendix 3. If we consider Jenkins profile GS-23 as an example, and multiply the percentage of organic carbon by 2.5 to approximate total organic matter (Borchardt, 1964, personal communication), the total organic matter in GS-23 increases from 5.7 percent at a depth of 25 cm to 13.5 percent at the surface. The percentage of the inorganic fraction in the total sample has decreased by 7.8 percent. Thus the systematic trends in K, Al, and Si are readily explicable as a dilution of the inorganic fraction of the sediment by organic matter.

The reasons for the upward increases in Si, Ca, and Fe are discussed in greater detail below.

Silicon: The fact that the silicon content increases upward in the Jenkins sequences in which the upward decrease in K and Al is strongest suggests that the upward silica increase is due to an upward increase in the percentage of quartz rather than an increase in the percentage of any other silicate. In sampling it was observed that the uppermost slices of Jenkins cores often contained a "grit" of fine and medium sized sand grains, even in Jenkins cores in which lower slices had no sand sized particles.

Calcium: Because the percentage of calcium usually remains constant in a given Jenkins core, and sometimes even increases slightly toward the surface, whereas the percentage of inorganic matter decreases upward in the same sequence, it is probable that a sizeable but as yet undetermined fraction of the Ca present is in the organic fraction of the sediment, possibly in the carbonate and phosphate tests of organisms. If such an increase in the percentage of organogenic Ca were permanently incorporated in the sediment column, the present position of the increase would be evidence that the relative importance of organic sedimentation is increasing. On the other hand, it may be that some of the carbonate now in surface layers will be dissolved before significant burial has occurred, because Lake Superior is undersaturated with respect to calcite. In that case the surface increase in organogenic carbonate would be a dynamic phenomenon, always found just below the sediment-water interface, but normally not preserved in the stratigraphic record. Its presence would

not indicate that the importance of organic sedimentation is increasing. Solution must be taking place, but the writer does not know whether the solution hypothesis will explain all of the increase in organogenic carbonate.

Iron: Although surface sediments from western Lake Superior contain more iron than those of eastern Lake Superior, upward increases of iron just beneath the sediment-water interface occur in both provinces. Jenkins core sequences in which the ratio of the concentration of iron in the uppermost Jenkins sample to the concentration of iron in the lowermost Jenkins sample is high are found in both provinces. This is not to say that the intensity of enrichment is independent of all geographic relationships, because two of the three Jenkins profiles that have the highest ratios as defined above are cores from troughs within bays (Su-1, Keweenaw Bay, and GS-2, Whitefish Bay). Also, the three cores with the highest ratios all lie close to major shipping lanes that are used to transport iron ore to ports on the lower Great Lakes (Su-1, GS-2, Su-7). This may be pure coincidence, but the possibility of human contribution to the surface enrichment should be considered.

Iron is present in the surface sediments in clay minerals, in other detrital silicates, in ferric oxides and hydrous oxides, and in complexes with organic matter. Mineralogic study shows that the surface enrichment is not caused by an increase in either of the first two categories listed, but it is not possible at this time to determine which of the last two categories is most important. It should be born in mind that the state in which the iron is presently found is not necessarily the state in which it was initially incorporated in the sediment.

Because of the high redox potential of the waters of Lake Superior and its tributary streams (Figures 6, 7), iron released by weathering processes should be precipitated quantitatively as colloidal and particulate oxides and hydrous oxides. The sedimentation of these inorganic products is thereafter an essentially detrital process. The upward increase toward the sediment-water interface could be caused by any combination of any of the following likely factors:

- a) An increase in the rate of supply of iron-rich detritus from the iron ore deposits of the Lake Superior basin, brought about by either natural or artificial means. Ore shipping on Lake Superior could be a factor in the distribution of this detritus.
- b) An increase in the supply of iron-rich oxide and hydrous oxide detritus from the B horizon of the podzolic soils of the region, brought about by the increased development of these zones from weathering of overlying soil zones as soil formation approaches a steady state in balance with removal.
- c) An increase in the supply of iron-rich detritus from the ash of forest fires (other, more soluble elements being carried away in true solution). Forest fire damage in the Lake Superior basin during the past century has been tremendous, and it is possible that there was less damage in prehistoric times.
- d) A decrease in the rate of sedimentation of all inorganic constituents other than iron-rich detritus. This possible factor will be discussed in greater detail in the chapters on the trace elements.

The surface increase of iron agrees with the increase of organic matter, but the former is smaller both in absolute and in relative

percentage. Combination of iron and organic matter in limnologic environments has been observed by several investigators (Hutchinson, 1957, pp. 711-714), but the exact nature of the association is not well defined. It is hard to conceive of a mechanism whereby organisms could significantly increase the supply of iron in a basically aerobic system such as Lake Superior, but given an increase in supply, organisms and organic matter could be a major factor in the sedimentation of the increased supply. Concrete evaluation of the role of organisms and organic matter in the sedimentation of iron in Lake Superior must await further study.

### Sediments at Depth

This section considers the distribution of major elements in brown sediments more than 25 centimeters below the sediment-water interface and in the gray clay, glacial lake sediments, and till. Because of the lesser amount of control, valid geographic conclusions about the distribution of the major elements in the sediments at depth cannot be made at this time. The following paragraphs outline some general observations about these sediments.

Where thick accumulations of brown sediment occur there is little variation in major element composition with depth below the uppermost 25 centimeters. GS-2-62-HPC and GS-7-62-HPC are examples in which the variation in both major and trace element compositions below 25 cm is hardly more than the analytical uncertainty.

Gray clay has a lower silica (52-56%) and a higher  $K_2O$  (3.4-4.1%) and  $Al_2O_3$  (13-16%) content than the overlying surface sediments, which normally contain 54-70%  $SiO_2$ , 2.3-3.6%  $K_2O$ , and 9-14%  $Al_2O_3$ . This is true because quartz, much of it of silt size, is more abundant in the average brown sediment than in the average gray clay. As the supply of detritus from the glacier itself ceases, and as the increase of vegetative cover retards erosion of the irregular layer of till mantling the lake basin, chemical weathering becomes more important, and quartz is concentrated relative to more easily altered minerals.

Varved gray, varved red, and red clays contain considerably more  $CaO$  (4% or more) and  $MgO$  (not determined quantitatively) than any of the sediments above, which contain 1.7 to 3.3%  $CaO$ . X-ray analyses show that this excess Ca and Mg is present as calcite and dolomite. The significance of

carbonates in Lake Superior sediments is discussed in a separate section below. There is a concomitant decrease in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{K}_2\text{O}$  that is nothing more than a dilution of the non-carbonate sediment by the carbonate.

Within a given alternation of light and dark varve layers the light layers are richer in  $\text{CaO}$  and  $\text{MgO}$  and the dark layers are richer in  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . This shows that the light layer is slightly richer in carbonate, while the dark layer is slightly richer in non-carbonate rock flour and clay minerals. Su-1-61, 899' 9" is a good example.

## MINERALOGY OF LAKE SUPERIOR SEDIMENTS

"The clay-size fraction of all units except the tills and brown sand was investigated by R. S. Liebling by means of X-ray diffractometer" (Liebling, in Farrand, 1963).

Liebling (*ibid*) finds "no definitive difference in clay minerals from the postglacial brown sediment down to and including the red clay and silt. Separate light and dark layers of both red and gray varves likewise show no difference in the clay mineral suite. Chlorite, illite, and vermiculite are universally present. Mixed layer clays also occur and perhaps show a slightly greater abundance in the uppermost two units."

The X-ray studies of this investigation, using the entire sediment rather than the clay-sized fraction, qualitatively confirm these results. The intensities of peaks at 9.4, 11.0, and 12.1 Å are independent of each other and of all other clay mineral peaks, and thus they are presumably the peaks of three distinct, although poorly crystalline, mixed layer clays.

Liebling (*ibid*) also found that "the only significant difference in the clay-size fraction is in the relative abundance of clay minerals to non-clay minerals. In the gray varves, gray clay, and brown sediment, the clays predominate. In the red clay units non-clay minerals, particularly quartz and calcite, exceed the clay mineral fraction in most samples, or, in other samples, the two fractions are nearly equal in abundance."

X-ray analyses of the entire sediment made in this investigation show that the transition from predominantly rock flour to predominantly clay mineral is <sup>more</sup> gradual than implied above, because the gray varved clay as well as the red varved clay contains considerable rock flour. Also, feldspars, as well as quartz, calcite, and dolomite are important constituents of the rock flour. The ratio of quartz to feldspars increases upward.

This investigation confirms Liebling's finding (*ibid*) that calcite and dolomite cannot be detected by X-ray means in any sediments above the gray varved clay.

Surface sediments were examined in greater detail to determine if X-ray diffractometry could aid in the delineation of depositional provinces or mineralogic associations. The results are to a great extent negative. Twenty eight mineral pairs or triplets from the minerals listed in Table 19 were examined, but of these only three showed geographic or mineralogic correlation worth noting:

- 1) Potassic feldspars form a greater percentage of the total feldspar content in coarser grained, quartz-rich sediments than they do in finer grained, quartz-poor sediments. This is shown by Figure 4. Although a moderate amount of scatter is present it is clear that the ratio of plagioclase to potassic feldspar decreases as the quartz content increases. Potassic feldspars are more resistant to weathering than are plagioclase feldspars (Goldich, 1938), therefore the observed trend would be consistent with the data on resistivity to weathering. But, an even more important factor might be the fact that quartz-rich igneous rocks often have very low ratios of plagioclase to potassic feldspars. Therefore the relationship shown by Figure 4 may be caused largely by the existence of a similar relationship in the source rocks.
- 2) Along the eastern shore (GS-3, 4, 5, 7, 8) the 11 Ångstrom mixed layer clay is less abundant than the 9.4 Ångstrom mixed layer clay mineral, whereas the reverse is true in the remaining parts of the lake.
- 3) Figure 5 shows that in quartz-rich sediments mica or illite is more abundant near the south shore than elsewhere in the lake. The micas and illite have the same basal reflection. However, because this trend is found in the coarser, quartz-rich sediments,

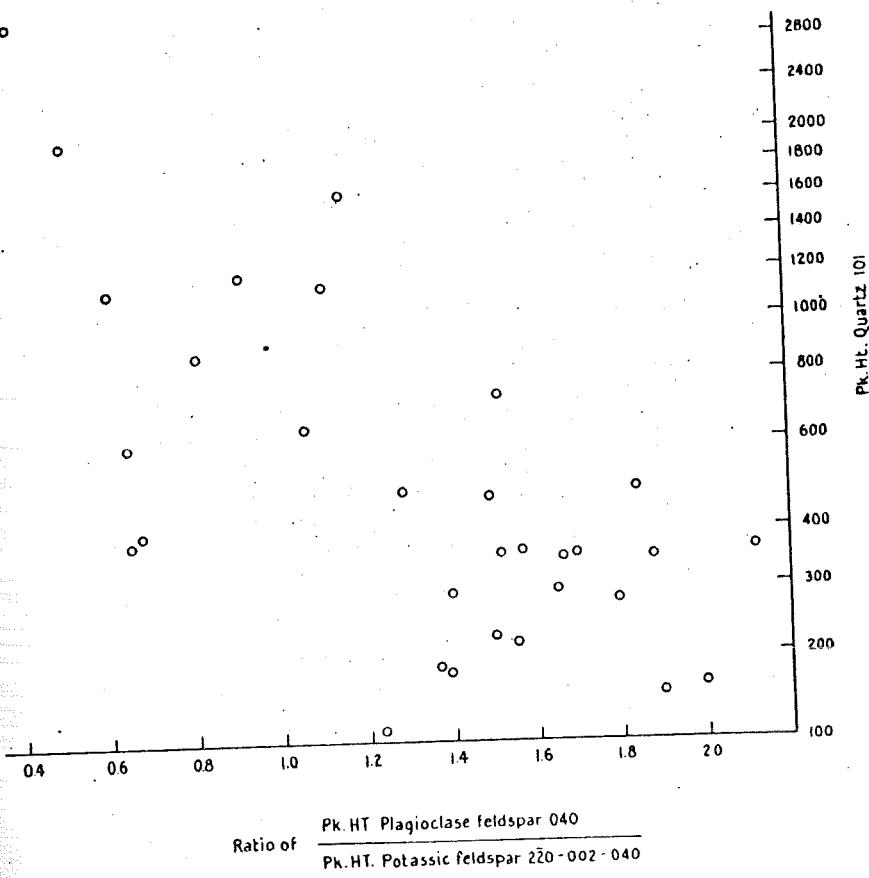


Figure 4. Variation of quartz with plagioclase/potassic feldspar ratio in Lake Superior sediments. Data from X-ray diffraction peak-height measurements.

it probably shows a trend in mica rather than illite, as the latter is usually fine grained. The 9.4 Angstrom mixed layer clay mineral is used here as a base because it is a rather constant constituent of Lake Superior sediments.

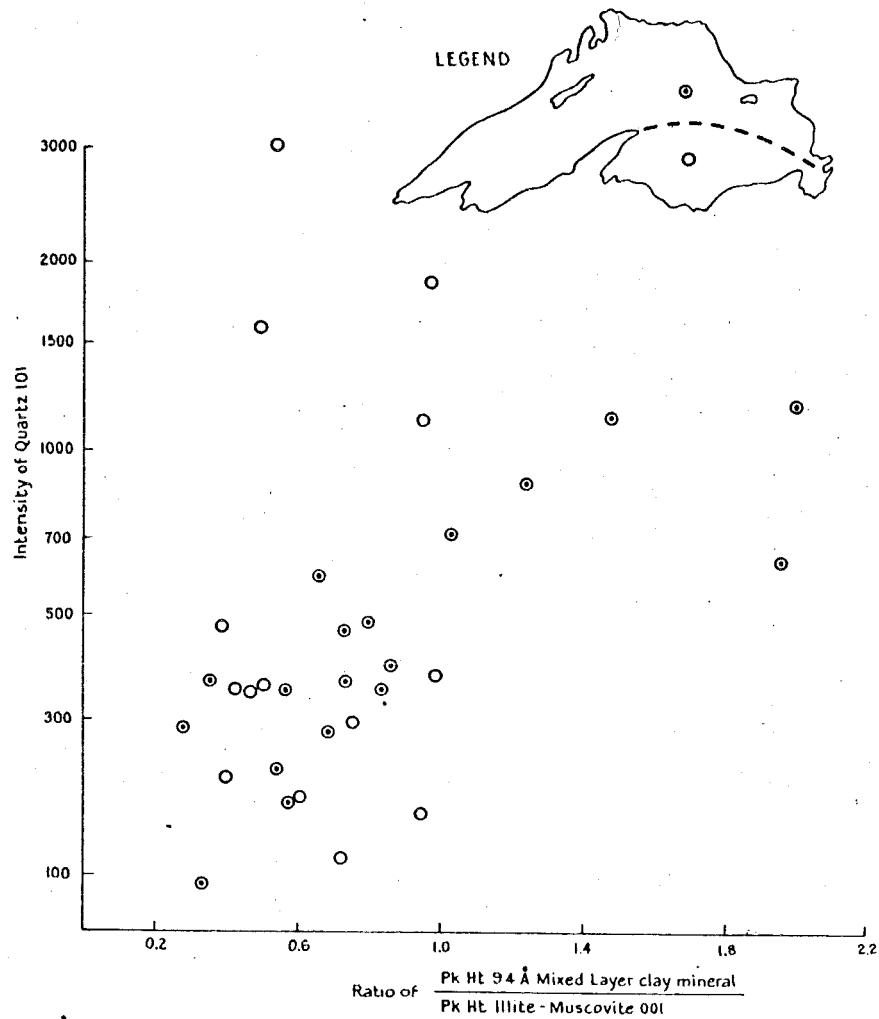


Figure 5. Variation of quartz with 94 Å mixed layer clay/illite-muscovite ratio in Lake Superior sediments.

## OTHER ASPECTS OF GENERAL GEOCHEMISTRY

### Eh-pH Relationships in Lake Superior

#### Water and Sediments

Eh and pH measurements of Lake Superior sediments and water are shown in Figure 6. No Donnan potential corrections have been made on this diagram, therefore the measurements of gray clays and red clays are 0.2 pH unit and 12 mv low, but the measurements for most of the brown sediments are correct as shown. As explained in the section on analysis, Eh measurements are not equilibrium measurements, and those indicating low values of Eh might represent actual potentials even lower.

Water measurements: All the measurements plotted are for hypolimnetic water, and lie close to the average values of +410 mv Eh and 7.71 pH. From alkalinity measurements made at the same time, the average bicarbonate content is 51.6 ppm. Calculated  $p\text{CO}_2$  for this average pH and bicarbonate content, using the equilibrium constants for 5° C, is  $8.1 \times 10^{-4}$ , higher than atmospheric  $p\text{CO}_2$ , which is between  $3.0 \times 10^{-4}$  and  $4.4 \times 10^{-4}$  (Hutchinson, 1957, p. 654-655). The excess  $\text{CO}_2$ , normal for hypolimnetic waters, is indicative of  $\text{CO}_2$  production by organisms.

The average pH of 7.7 observed differs from the average pH of 7.4 that is reported in the compilation of Beeton and Chandler (Table 5), but is close to the pH of the waters of western Lake Superior as reported by Swain and Prokopovich (1957).

The average Eh of +410 mv is normal for well oxygenated lakes. The U. S. Fish and Wildlife Service has never found significant oxygen

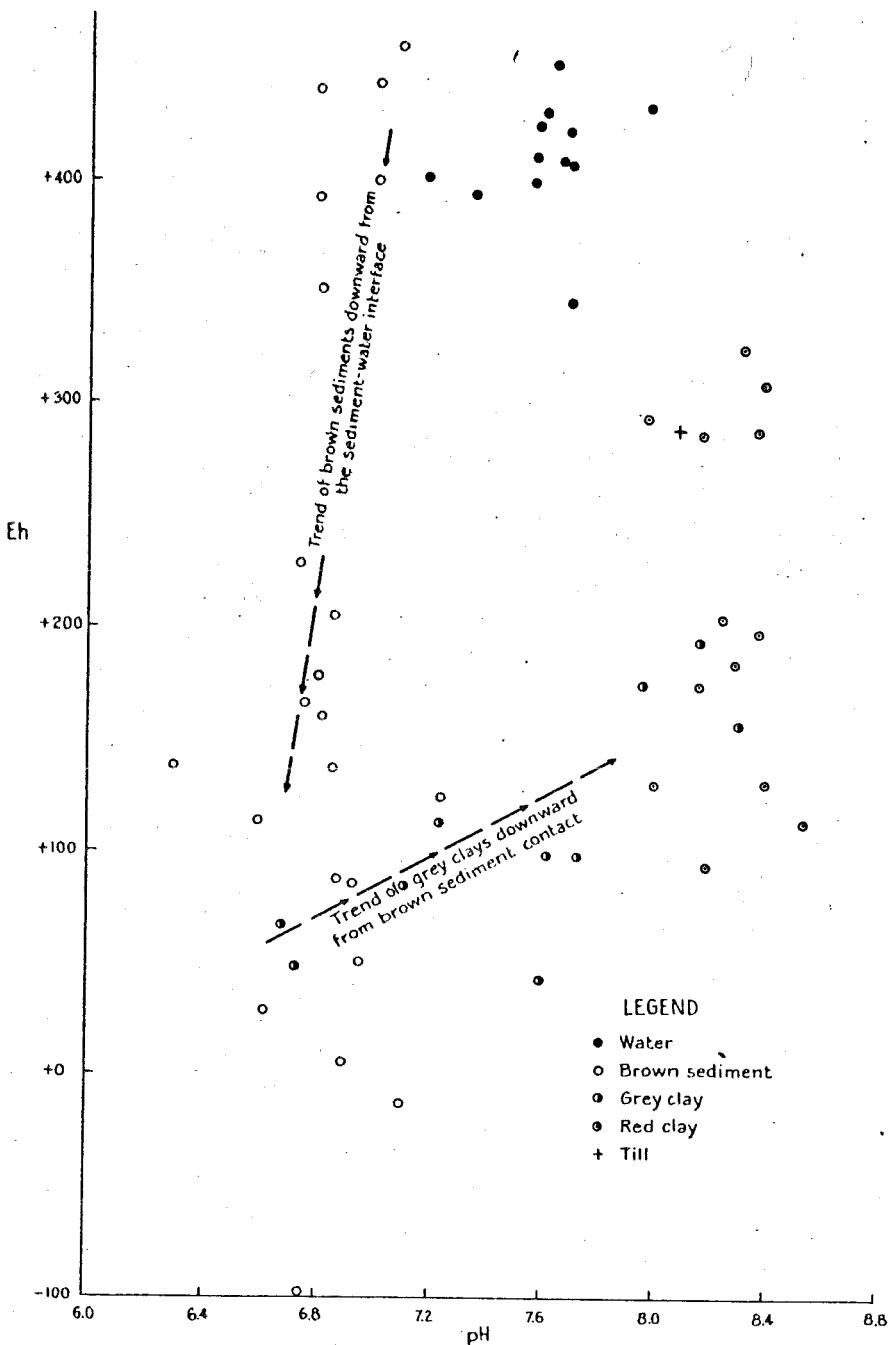


Figure 6. Eh-pH measurements in Lake Superior.

depletion in the lake (A. H. Beeton, personal communication, 1964).

Surface sediments: The brown sediments of Lake Superior all have a pH lower than that of the overlying water, typically 6.6 to 7.0, probably because of bacterial production of  $\text{CO}_2$ . The pH of the water above decreases slightly with depth (Appendix 6), suggesting that upward diffusion and convection of the excess  $\text{CO}_2$  from the sediment might be partially responsible for the high  $\text{pCO}_2$  observed in hypolimnetic waters.

The most regular feature of the Eh relationships in the fine-grained surficial sediments is a decrease in Eh downward. At the sediment-water interface the sediment Eh is identical to or just slightly lower than the Eh of the overlying water, but below the interface readings decrease for 7 to 10 cm, at which level they are within the range of potentials that prevail to the base of the gray clays (0 to +200 mv), and the downward trend may be reversed. For example, a reversal occurs in GS-2, whereas no reversal occurs in the 20 cm of Su-1 or the 27 cm of GS-23.

The depth in the sediment to which Eh readings within 30 mv of open-water values occur is variable. In silts and sands, where interstitial water movement should be fairly rapid, and organic activity comparatively low, most of the sample retained by an orange peel sampler will have the Eh of overlying waters (e.g., Su-6, GS-2-OP), which suggests that the depth of high readings is possibly as great as 5 cm. On the other hand, in fine muds the thickness of sediment in which high Eh readings occur is less than 2 cm, and may be that thick only because of mixing, caused by sampling, of the topmost sediment and overlying water (e.g., GS-7, GS-23). Su-1, which has a larger silt-sized fraction, is intermediate in this respect, as the top 4 cm have Eh readings close to that of the overlying

water.

The possibility that the water immediately overlying the sediment might be depleted of oxygen was tested early in this study by comparing the oxygen content of the water in the Jenkins sampler with the oxygen content of water collected thirty feet above the bottom. In three sets of determinations no difference was found, therefore, if there is a layer depleted of oxygen it is very thin, perhaps less than 2 cm, or else the degree of oxygen depletion is low.

Figure 6 should be compared with Figure 7, which shows the stability fields for iron species. All of the Eh measurements of Lake Superior sediments are above the region of stability of iron sulfides, even for a total sulfur content of  $10^{-1}$  moles per liter. Therefore, the fact that definite, albeit scattered layers of black iron sulfide ("hydrotroilite") are found in many cores suggests that some of the Eh readings obtained are high, either because of the lack of equilibrium or because of electrode contamination. Nevertheless, one has only to compare the scattered sulfide of Lake Superior sediments with the abundant black sulfides of Lake Michigan sediments to see that sulfate reduction is a relatively unimportant process in Lake Superior.

Gray clay: pH and Eh measurements of gray clay must be corrected for the Donnan potential. A correction of +0.2 pH units and +12 mv is a convenient, albeit approximate adjustment.

The gray clays grade between two extremes of Eh and pH that are generally, although not exactly, correlative with depth. At one extreme the uppermost gray clays have Eh and pH values identical with the brown sediments at depth (pH about 6.9, Eh about +125 to +150 mv). At the other

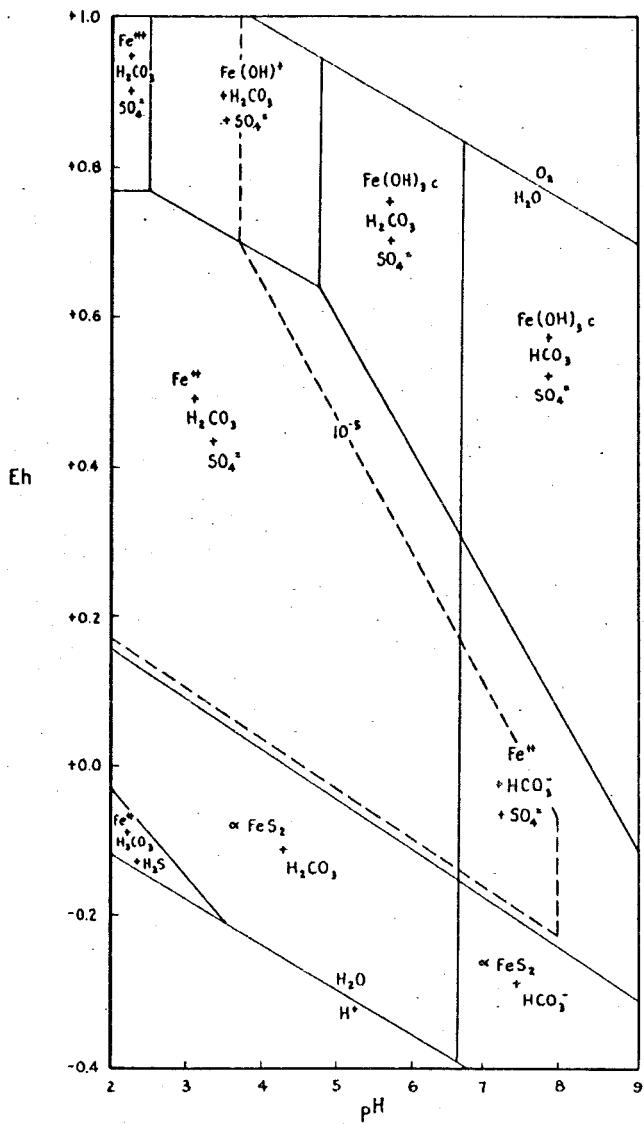


Figure 7. Eh-pH diagram for the system Fe-O-OH-S-CO<sub>2</sub> at 1 atm. and 25°C, showing metastable field of Fe(OH)<sub>3</sub>,  $\Sigma C = 10^{-3}$  m/l,  $2S = 10^{-6}$  m/l. Boundary between solids and ions containing iron drawn at an activity of  $10^{-3}$  m/l. Boundary for these activities at  $10^{-6}$  m/l shown as dashed lines.

extreme the deepest gray clays, those that are varved, have a pH of 7.9 to 8.4, and an Eh of +150 to +200 mv. Saturometer tests show that the gray varved clays are saturated with respect to calcite, thus the trend of an increasing pH with depth is thought to be an increase in the percentage of carbonate saturation. The simultaneous trend toward a higher Eh is thought to be due to a decrease in bacterial activity with depth.

Red clay and till: Like the varved gray clays, the varved and massive red clays and red clayey till are saturated with respect to calcite, and invariably have a pH between 8.0 and 8.6. The Eh of these clays is quite variable; readings both higher and lower than the readings in the gray clays have been recorded. The highest readings (near +300 mv) are usually, but not always, the deepest in the cores, and they include the measurement on till. The high readings are probably indicative of an extremely low rate of bacterial activity.

### Carbonates in Lake Superior Sediments

Red clayey till, red clay, varved red clay, and varved gray clay all contain considerable carbonate. Whereas the CaO content of more recent clays varies monotonously between 1.7 and 3.3 percent, the deeper sediments listed above contain 4 to 8 percent CaO, the additional calcium being present as carbonates. Carbonate saturation is shown by the saturometer tests. X-ray diffraction confirms the presence of calcite and dolomite in these sediments and their virtual absence in more recent sediments.

The high carbonate content of tills and glacial sediments has long been recognized (for example, see Clark, 1929, p. 511). The calcite and dolomite is finely-ground rock flour rather than a product of carbonate precipitation within the lake basin. This is particularly evident in Lake Superior in light of the following argument: Saturated tests show that the lake is considerably under-saturated at present. The data of Keller and Reesman (1963) show that glacial milks are undersaturated with respect to carbonates even when they are draining carbonate terrains. Therefore, it is unlikely that Lake Superior has ever been saturated with respect to carbonates, and even more unlikely that significant carbonate precipitation has ever occurred. Therefore, the carbonate in Lake Superior glacial sediments must be in the form of detrital fragments, the products of glacial corrosion.

The source of the carbonate must be the extensive carbonate terrain to the north and northeast of the Lake Superior basin, because there are no extensive carbonate source rocks in the basin itself. A portion of the carbonate might also be derived from rock flour ground from much closer

Paleozoic carbonate rocks south of Lake Superior that were subsequently carried north by streams into glacial Lakes Keweenaw and Superior, but confirmation of a major source to the north is found in the timing of the cessation of major detrital carbonate sedimentation. It is commonly held that varve deposition indicates the presence of a glacier within the basin of deposition (Flint, 1957, p. 294), and it is logical to postulate that the cessation of varving indicates retreat of the glacier out of the basin. The end of extensive carbonate deposition in Lake Superior occurs simultaneously with the end of varve formation, just at the time when the glacier could no longer supply sediment from north of the Lake Superior basin. Therefore milk from the glacial ice mass itself must have been the major source of detrital carbonate, and not streams bringing carbonate from Paleozoic carbonates to the south.

In the varved sediments of Lake Superior, both red and gray, the light layer is richer in carbonate than the dark layer as is shown both by qualitative dilute hydrochloric acid tests and by quantitative CaO analyses. Typical CaO concentrations are 7 percent in a light red layer and 4 percent in a dark red layer.

The light layer is interpreted as the "spring or summer layer," glacial flour dumped into the lake by rapid spring and summer melting of glacial ice. The dark layer is interpreted as the "fall or winter layer," the slower and thinner accumulation of particles settling out beneath the winter ice cover of the lake. Farrand (1963) finds that the summer layer of the deeper varves has a higher content of silt-sized particles than the winter layer, which suggests that carbonate was concentrated in the summer layer because it was of a slightly coarser grain size than the rest of the glacial milk. Another possible contributing factor is as follows:

In an undersaturated lake, solution of carbonate particles will be significant. As particle size decreases the importance of surface energy considerations increases (see for example Schmalz, 1963). The smaller the particle the more rapidly it will dissolve. If a carbonate particle of less than two microns diameter is not incorporated in the sediment immediately it will stand a good chance of being dissolved in the undersaturated lake water. Those particles from the spring and summer thaw that are immediately buried in the summer layer are less likely to be dissolved because the dissolving of only a little of the available carbonate will saturate the interstitial water.

Since the retreat of the glacier out of the Lake Superior basin the principal source of carbonate in lake water has been from the leaching of carbonate from till and other glacial deposits. Transport to the deep areas of the lake has been predominantly in solution and in the tests of organisms. No surface sediments examined contained sufficient calcite or dolomite to give a recognizable diffraction peak, thus the maximum percentage of well ordered inorganic calcite or dolomite must be less than the experimentally determined minimum of 0.2 percent for either phase.

## Colloidal Properties of Lake Superior Sediments

The fine-grained surface sediments of Lake Superior are flocculated "muds," whereas the sediments at depth are deflocculated, sticky "clays." A gradual transition downward from mud to clay occurs in the upper part of the sediment column, paralleling a significant downward decrease in water content of the sediments. Typical transitions have been observed in the hydroplastic cores, GS-26, GS-31, and GS-2. In some localities the contact between mud and clay is sharp, but usually such a sharp contact is a disconformity or diastem. For example, a sharp contact occurs in GS-10, between the lowest (JA) and second lowest (JB) Jenkins slices (Figure 12), and the striking contrasts in trace element content and color suggest that this is the contact between the gray clay and brown sediment units. Similarly, in GS-19 and GS-20 red, glacial lake clay is found covered by only a few centimeters of flocculated brown sediment, and the contact may very well be a diastem.

The flocculation and subsequent sedimentation of the terrigenous clays occurs despite the low total ionic concentration in Lake Superior possibly because of the high flocculating power of the divalent cations  $Mg^{++}$  and  $Ca^{++}$  (van Olphen, 1963, p. 96). Therefore, particle flocculation as well as particle size may be factors responsible for the concentration of recent sediments close to shore and the relative thinness of recent sediments over much of the central basin.

The deflocculation at depth in the sediment may be a diagenetic process associated with compaction and water loss. The mechanism by which it occurs in these sediments or in marine sediments is not well understood. Factors that may be important are summarized by van Olphen (1963,

pp. 111-115) and by Meade (1964). It is also possible that the glacial lake clays were originally deposited in a deflocculated condition, but this is not necessarily proven by their present state.

The "stickiness" at depth is to a first approximation an indication of water loss. Stickiness appears in dispersed clay-water systems when the water content becomes less than a critical value that has been referred to as the "stickiness limit." However, the exact water content at the stickiness limit varies from sediment to sediment, as it is a complex function of sediment mineralogy and the chemistry of pore solutions and exchangeable cations (Grim, 1962, pp. 52-71).

Supposed Oxidation-Reduction Phenomena

in Lake Superior Sediments

Red and gray sediments: The nature of the transition from predominantly red to predominantly gray sediments and the explanation of the change in color are matters of considerable geochemical interest.

The red clay, both massive and varved, is red because of the presence of finely divided ferric oxides and hydrated oxides (Murray, 1953). The gray clay, both massive and varved, is gray because clay minerals, unaltered rock flour, and organic matter predominate over ("mask") any ferric oxides and hydroxides present. Gray clay becomes brick red if heated at 400°C for 24 hours, but as this treatment destroys some of the clay minerals, oxidizes organic matter, and also promotes oxidation of inorganic compounds, nothing is proved about the relative importance of the masking agents. If a silty clay from the brown sediment is treated with hydrogen peroxide at room temperature until all gas evolution ceases, the sediment separates into a red silt and a brown floc of clay and oxidized organic matter.

In the sediments the transition from red to gray clay occurs during the period of varve deposition. The gray color appears first in the summer layer, and the red color persists longest in the winter layer. Thus there is a portion of each of the varve sequences in which gray summer layers alternate with red winter layers. In addition, isolated layers of red clay are found well up in the gray sediments (Farrand, 1963). All of the varved clays and other clayey lake sediments found above the present water level along the north (Ontario) shore of Lake Superior are gray (Farrand, 1960). In Lake Michigan, in a lengthy core from the

deepest part of the lake, a transition upward from red to gray sediment occurs 550 cm above the highest varves (Hough, 1958, p. 72).

Two hypotheses have been proposed to explain transitions from red to gray sediment. Hough has suggested that the transition in Lake Michigan is a diagenetic boundary, above which reduction of ferric iron has taken place (*ibid*, p. 74). Farrand (1965) has proposed that the color change in Lake Superior is a change in sediment provenance. The relative merits of the two hypotheses as applied to Lake Superior will now be considered.

According to the diagenetic hypothesis the red clay and gray clay have the same provenance. In the gray clay the ferric oxides have been reduced by bacterial action. The transition from red to gray would have occurred because the organic productivity of Lake Superior rose and the rate of inorganic detrital sedimentation decreased as the glacier retreated, until finally the amount of organic matter annually incorporated in the sediment was enough to support a level of bacterial activity that could reduce the ferric oxides and hydrous oxides present, or at least mask their presence.

This theory does not explain a number of the observed relationships. If the Lake Superior transitions are diagenetic, then one would presume that similar diagenetic changes ought to occur within the varve sequences in all of the Great Lakes, that is, at the same time relative to the retreat of the glacier from each particular lake basin. Therefore the fact that the transition is within the varve sequence in central Lake Superior but 550 cm above the highest varves in central Lake Michigan is perplexing.

Alteration of red clay to form gray clay by reduction of ferric phases does not seem to be a likely mechanism in Lake Superior, because

bacterial activity in the varved clays probably never attained a level high enough to effect extensive reduction of all of the ferric iron present. The reasoning behind this conclusion, admittedly indirect, is as follows:

- a) The present Eh and pH of red and gray varved clays are indistinguishable (Figure 6), suggesting that the varved clays of both colors were deposited in similar geochemical environments and have had similar diagenetic histories.
- b) Most of the Eh and pH readings in the varved clays are higher than readings in the overlying massive gray clays and brown sediments, exclusive of sediments very close to the sediment-water interface, suggesting (but not proving) that the Eh and pH of the diagenetic environment of the varved clays has always been higher than that of the overlying sediment.
- c) Figure 7 shows that ferric species are the stable phases at the present time. Thus if any process is now occurring it is probably oxidation rather than reduction.
- d) No hydrotroilite (ferrous sulfide) is present in red or gray varves, in contrast with the massive gray clay and brown sediment, which contain scattered bands of hydrotroilite. Supply of sulfate is a factor in the formation of hydrotroilite by sulfate reduction, but inasmuch as the present sulfate content of Lake Superior is little more than rainwater we may assume that the sulfate content has been constant. Therefore the absence of sulfides in the gray varved clay suggests that the redox potential of the gray varved clay was never low enough to support sulfate reducing bacteria, in which case it is improbable that

bacterial activity would have been sufficient to reduce the ferric oxides and hydrated oxides of the red clay.

In defense of the hypothesis of diagenetic reduction it should be pointed out that all the hypothesis requires is that the red color of ferric compounds be masked by other substances. Actual reduction of iron need not occur. We do not know how much organic matter it takes to "mask" the color of a given percentage of iron oxides, nor do we know what the role of other clay-sized phases may be in this masking process. It is known that dark-colored complexes of iron and organic matter are very common in argillaceous sediments, but no one knows the redox field of stability for these complexes, and it may be that the complexing can occur at redox potentials well above the stability fields of iron sulfides.

The interbedding of red winter layers and gray summer layers at the red-gray contact is not explained satisfactorily by the diagenetic hypothesis. Because Spring and Summer are periods of maximum production of microorganisms in the lake water, and thus periods of maximum use of organic matter, one would not expect them to be periods of maximum incorporation of organic matter into the underlying sediment. Rather, the period of maximum incorporation of organic matter into the sediment might be late Fall, when organisms that have been killed by the onset of colder weather settle to the lake bottom. Consequently, the fall and winter layer ought to be subject to more bacterial action than the summer layer. Reid (1962) has found that the present organic content, approximated by ignition loss on heating at 650 °C for 30 minutes, is higher in the winter layer than in the summer layer, although the difference is small (10.85 percent, as opposed to 9.89 percent). Welten (in Flint, 1957, p. 293) finds a similar relationship in a Swiss lake. But this relationship is

opposite to that which would be expected if the red-gray alternation were to be explained by diagenetic reduction, because a diagenetic hypothesis would require greater organic activity in the summer, gray, "reduced" layer.

Thus while we cannot deny outright the possibility of reduction by bacterial processes or deny the possibility of masking of ferric oxides and hydrous oxides by organic matter, the hypothesis of diagenetic change does not explain the observed temporal and spatial distribution of red and gray sediment, and on several counts conflicts with our intuitive picture of the nature of glacio-lacustrine sedimentation and accompanying organic activity, and it seems likely that some other factor is the major control of the distribution of red and gray sediment in Lake Superior.

In presenting the hypothesis of a change in provenance, Farrand (1965) notes that the source of most of the red and varved red lake clays may be sediments from Glacial Lake Keweenaw that were pushed along ahead of and incorporated in the glacier. However, he emphasizes that additional sources for red clay, and the ultimate source for the red sediments of Glacial Lake Keweenaw are the ferruginous sediments and metasediments common along the south and west (Minnesota) shores of Lake Superior. The iron in this source province is already oxidized. Varved clay is only gray on the north shore because there are no deposits of red Keweenaw clay and very few outcrops of oxidized ferruginous bedrock that far north. In central Lake Superior the red-gray transition occurs because after the glacier retreated north of the northernmost deposit of red clay it could only erode and redeposit gray clay derived from the North Shore and parts of Canada north and east of Lake Superior. The red-gray alternation at the red-gray contact is explained as follows: The winter layer, consisting

of particles of extremely fine clay size, remains red several years after the red clay detritus is no longer being supplied, because it takes several years for all of the fine red particles to settle. In contrast, the bulk of the summer layer is somewhat coarser, gray clay and settles more rapidly. Therefore, the summer layer becomes gray soon after the local supply of detritus becomes gray.

In Lake Michigan the red to gray transition did not occur during varve deposition because red clay of the Glacial Lake Keweenaw type mantled the Lake Michigan basin to its northernmost boundary. In Lake Michigan the eventual red-gray transition may very well be a diagenetic phenomenon, as Hough has suggested (1958, p. 74).

Thus the hypothesis of "changing source area" can explain the nature of the red and gray clays and the red-gray transition in Lake Superior much more satisfactorily than the hypothesis of diagenetic reduction. A sediment source with a high ferric/ferrous ratio has been superseded by a source with a lower ferric/ferrous ratio. Nevertheless, the general upward increase in organic activity and upward decrease in the rate of inorganic sedimentation imply that there ought to be an upward increase in the importance of diagenetic phenomena, perhaps not in the red varved and gray varved clays; but more likely higher.

Redox phenomena at the gray clay-brown sediment contact: Swain and Prokopovich (1957) say that at the base of the "red clay" (the brown sediment of this report) which overlies the gray clay of the Silver Bay area, western Lake Superior, "red clay" containing ferric oxides and hydrated oxides is being reduced to gray clay. They postulate a reduction process despite the high Eh values (+200 to +500 mv) they recorded

in the sediments. The experiences of this writer suggest that such high Eh values are not valid, and that they may be due to electrode contamination. Nevertheless, the question of the importance of reduction processes at this boundary is valid.

This investigation has found that the gray clay contains a higher percentage of very fine grained but unweathered rock fragments ("rock flour") than the brown sediments. Farrand (1963) has found that the transition from gray clay to brown sediment is marked by an abrupt increase in the median diameter of sediment grains. This suggests that, although the color change from gray to brown may very well be a redox phenomenon, the boundary is a sedimentary contact, and no brown sediment (the "red" of Swain and Prokopovich) is being currently altered to gray sediment.

## TRACE ELEMENTS IN LAKE SUPERIOR SEDIMENTS

### Zirconium

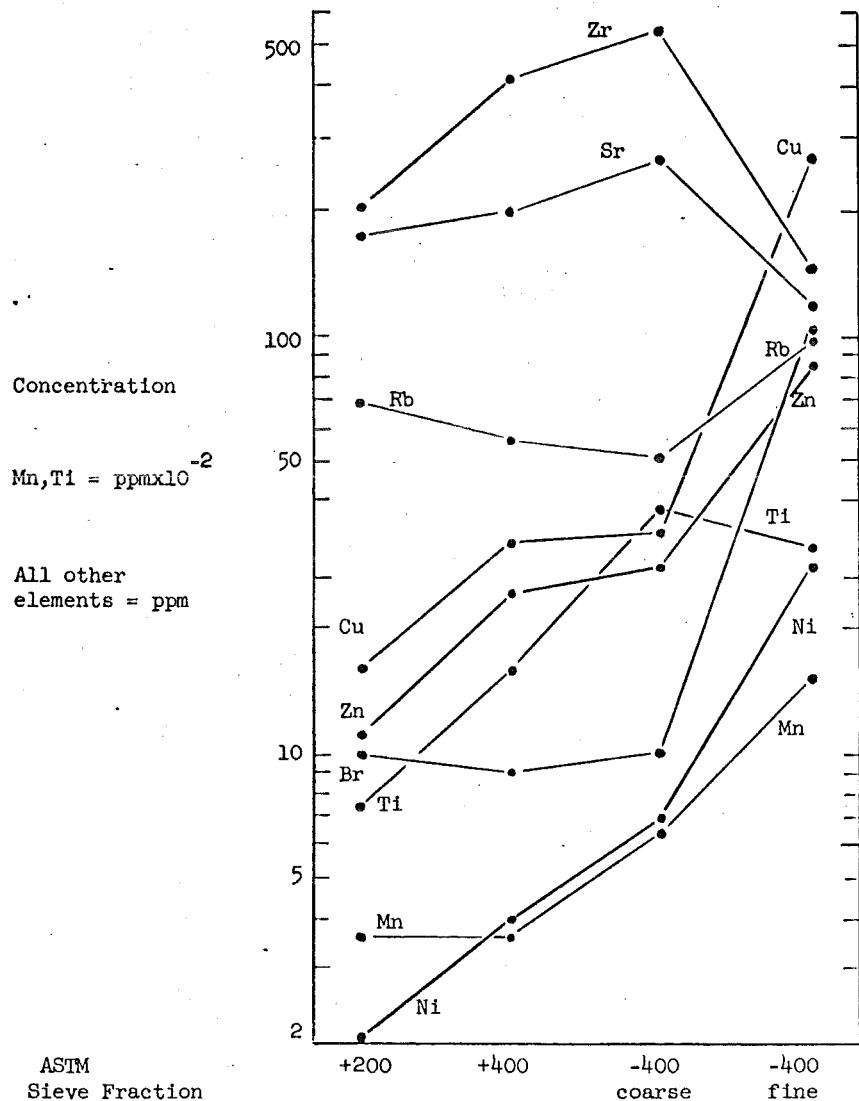
Analyses of the zirconium content of size fractions of sediments show that zirconium is concentrated in the fine silt fraction (Figure 8). The Zr content of all samples analyzed is  $184 \pm 81$  ppm (standard deviation of the mean = 7 ppm), slightly higher than the  $137 \pm 64$  ppm average for shales reported by Green (1959) from the work of Degenhardt (1957), suggesting the presence of a regional anomaly.

The distribution of Zr in the size fractions shows that much of the Zr is not bound in clay minerals, and leaves little room for doubt that it is present in detrital heavy minerals, principally zircon,  $ZrSiO_4$ . Farrand (1963) finds that zircon is one of the principal heavy minerals in all samples examined.

Because of the concentration in the fine silt fraction it is necessary to consider the particle size of samples whenever absolute zirconium concentrations are compared. For instance, the mean Zr content of Lake Superior surface sediments ( $192 \pm 67$  ppm, standard deviation of mean 10 ppm) and sediments at depth ( $167 \pm 89$  ppm, standard deviation of mean 8 ppm) are significantly different at the 99 percent level, but this is probably a reflection of the larger fine silt fraction of the average surface sediment collected in this study rather than proof of a change in source area. Likewise, although Lake Michigan and Lake Huron samples have an average Zr content of  $165 \pm 13$  ppm (standard deviation of the mean  $\pm 4$  ppm) which is significantly less than the mean of Lake Superior surface samples, the almost complete identity of this mean (165 ppm) with that of subsurface

FIGURE 8: TRACE ELEMENTS IN SIZE FRACTIONS OF

GS - 2 - 62 - OP



samples (167 ppm) suggests that this is also a particle size effect.

This effect is borne out in detail in the sediment analyses. For example, the samples from locality GS-2, silty clays, have a relatively high Zr content, about 206 to 360 ppm, while samples from GS-18 (152-170 ppm), GS-23 (148-167 ppm), both very fine grained, and GS-28, (89 ppm) and GS-29 (94 ppm), coarser grained, have a lower Zn content.

### Titanium

Grain size separations (Figure 8) show that titanium has a maximum concentration in the fine silt size fraction which is similar to but less pronounced than the maximum exhibited by zirconium. In particular, the percentage of titanium in the fine silt fraction is only slightly higher than the percentage of titanium in the clay size fraction.

The fine silt maximum is undoubtedly due to the presence of titanium in detrital heavy minerals (rutile, ilmenite, sphene, magnetite, orthopyroxenes, amphiboles), and the relatively high concentration in the clay-sized fraction shows the presence of titanium in several possible states (Migdisov, 1960):

- a) In the clay minerals  
(e.g. in clays formed from the alteration of biotite).
- b) As colloidal titanium oxides and loosely hydrated oxides (the so-called "leucoxene") formed by hydrolysis of  $Ti^{+4}$  released by the weathering of aluminosilicates.
- c) As clay-sized detrital heavy mineral particles.

Because of the relatively greater segregation of zirconium than titanium in the fine silt fraction one might expect that the Zr should show greater total variation in the sediment analyses. This is in fact true, the standard deviation for all analyses of Zr being 44 percent, that of Ti being 26 percent, a highly significant difference according to the F test ( $F_{120, 122} = 2.86$ ).

Figure 9 is a plot of the variation of Ti concentration with the zirconium concentration for samples at depth. Most of the samples have median diameters in the clay size, which minimizes particle size effects.

A positive correlation between the two elements is evident, although scatter is moderate. Figure 10 is a similar plot for surface samples, keyed geographically. Grain size and source area variations introduce considerably more scatter. The scatter is explained as follows:

The samples high in zirconium fall into two groups, based on their Ti content. A low-Ti group is largely composed of samples of sediment derived from the eastern shore of the lake. The predominantly granitic rocks of that shore should be lower in Ti-containing detrital minerals. A high-Ti group is largely composed of samples of sediment derived from the land surrounding Keweenaw Bay. The Precambrian basaltic rocks of that region contain many detrital heavy minerals of high titanium content, as shown by analysis Su-9.

Among the samples low in Zr the titanium concentrations cluster about the same line that was found in the deeper samples, but the scatter along the horizontal Ti axis is greater.

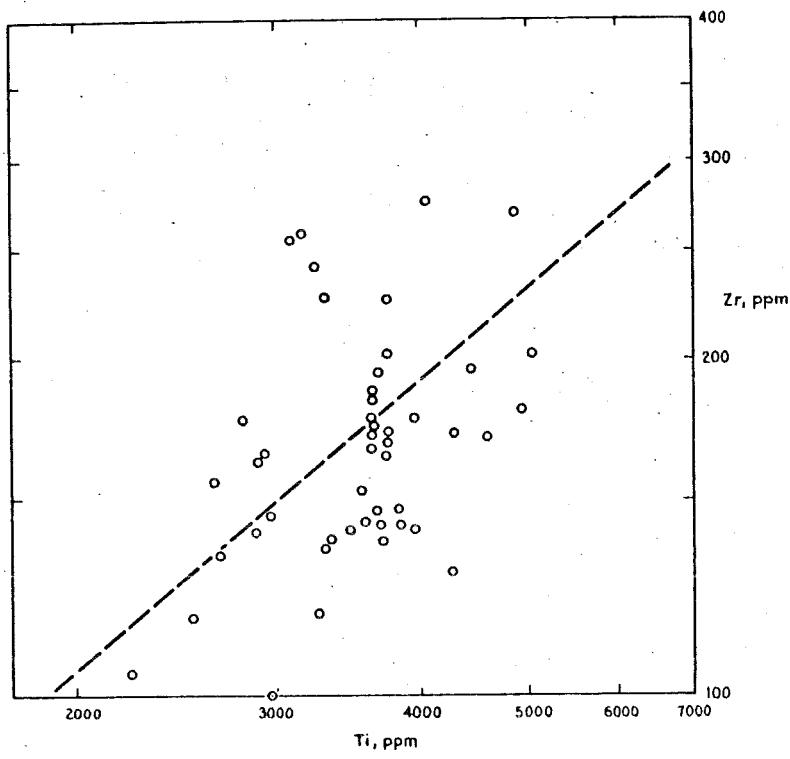


Figure 9. Variation of Zirconium with Titanium in Lake Superior sediments at depth.

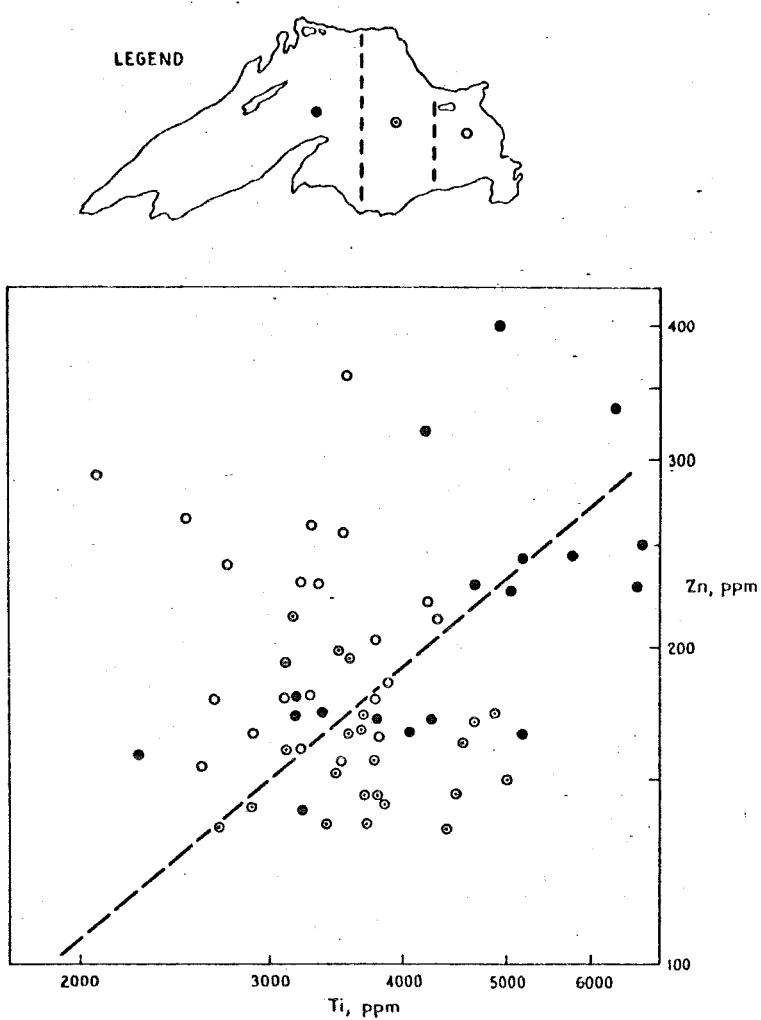


Figure 10. Variation of Zirconium with Titanium in surface sediments of Lake Superior. Dashed line is the trend observed in sediments at depth, as shown in figure 9.

### Manganese

General: Figure 8 shows that manganese is strongly concentrated in the clay size fraction of Lake Superior sediments.

In Figures 11 and 12 the trace element contents of two typical Jenkins profiles of the uppermost 20 cm of lake mud are shown. Similar profiles are found everywhere in the lake, and the profiles from Lakes Michigan and Huron analyzed suggest that the surface enrichments shown are typical of all of the Great Lakes. Manganese enrichment is present in the analyses made by Swain and Prokopovich (1957), although they are apparently unaware of the ubiquity of the phenomenon.

As shown by Figures 11 and 12 and the basic data in Appendix 3, manganese is enriched in Lake Superior sediments at the sediment-water interface, and strong enrichment does not extend to the depths that similar enrichment of copper and zinc does. The Mn content of the top Jenkins sampler slice exceeds that of the second slice in five out of seven vertical sequences analyzed, whereas near equality or a slight decrease of Cu and Zn from second to top slice is found in six out of seven profiles. Thus the Cu/Mn and Zn/Mn ratios characteristically rise to a maximum about seven cm from the surface and then decline (Figure 11 B). The rise in Mn concentration does not correspond proportionally to the rise shown by any other major or trace element or any major sediment fraction.

Previous studies (e.g., Krauskopf, 1957, and the summary of Rankama & Sahama, 1950) show that the Mn may be present in Lake Superior sediments in any of three forms: as species sorbed on inorganic and organic substrates, as Mn oxides and hydrous oxides, and as firmly bound components of detrital silicates. In the following sections the evidence from the

FIGURE 11: TRACE ELEMENTS IN A JENKINS SURFACE MUD PROFILE

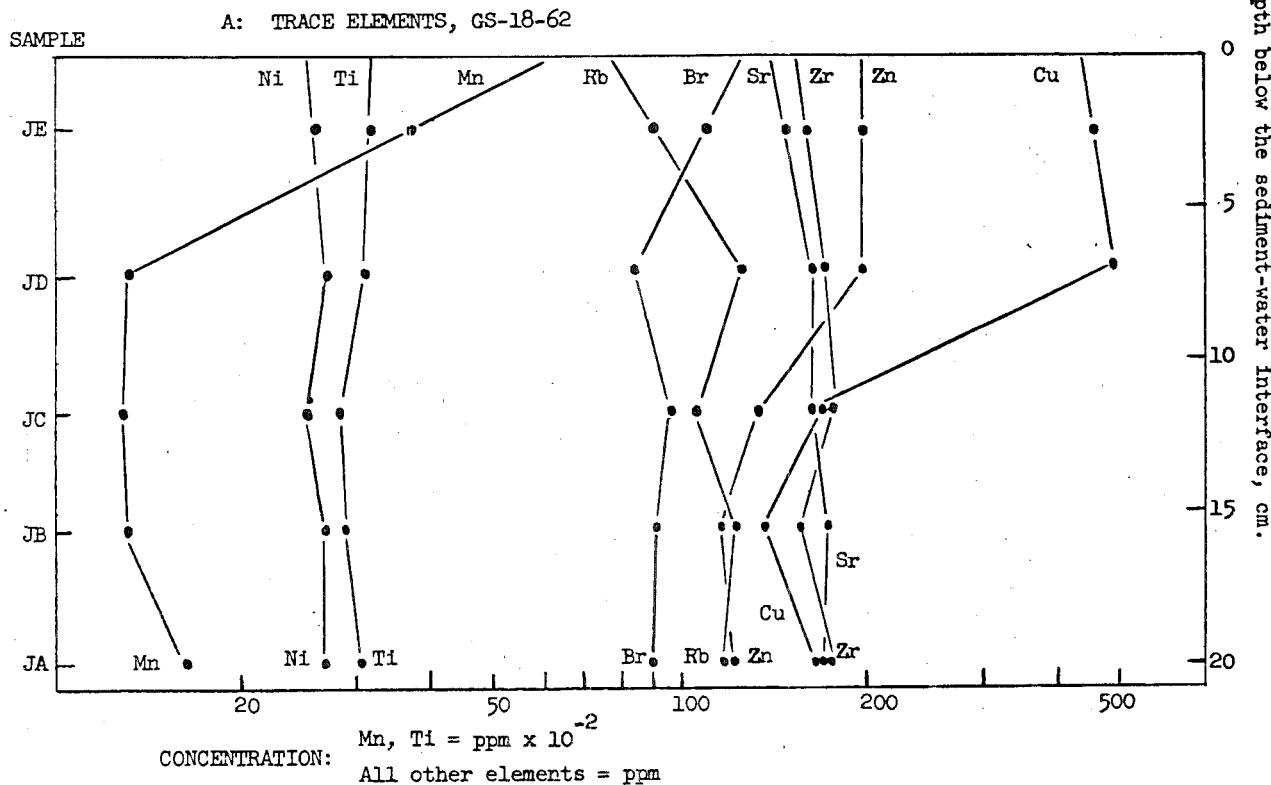


FIGURE 11: TRACE ELEMENTS IN A JENKINS SURFACE MUD PROFILE

B: ELEMENT RATIOS, GS-18-62

SAMPLE

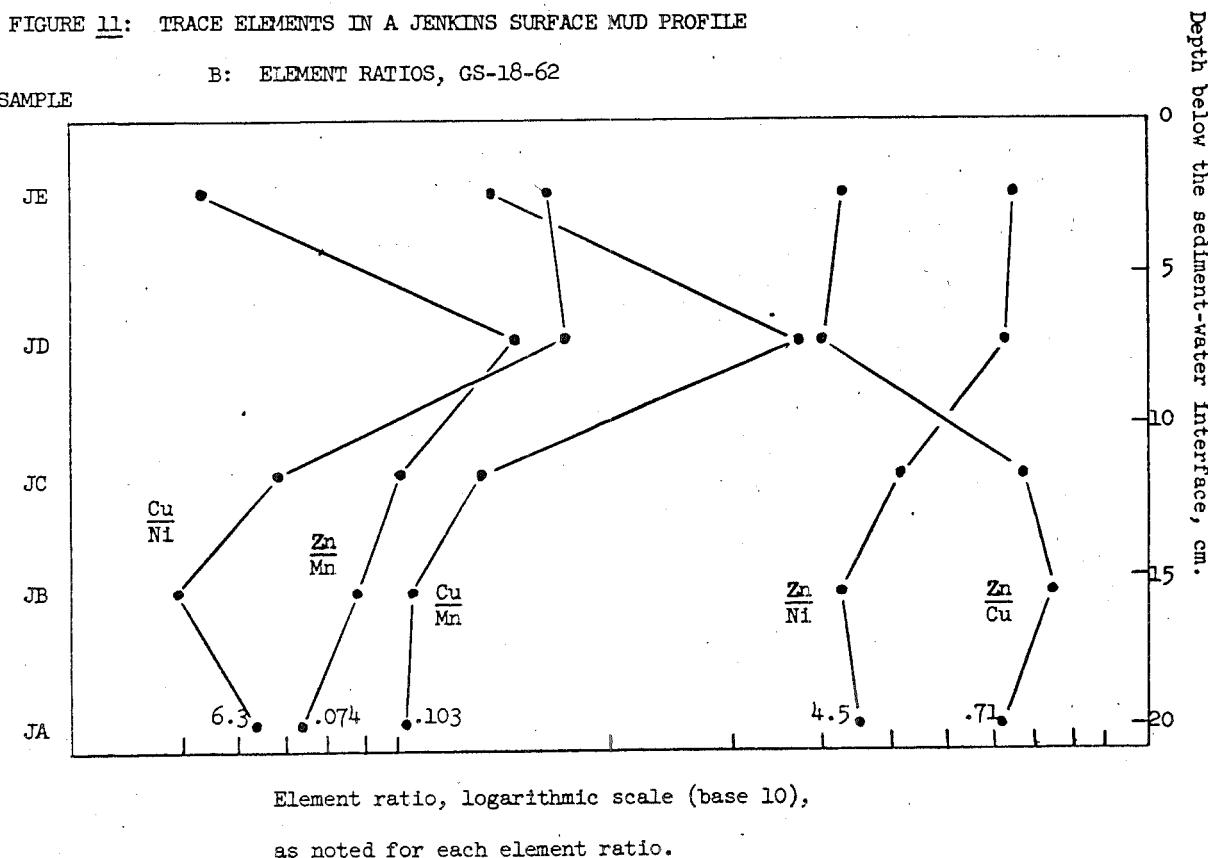
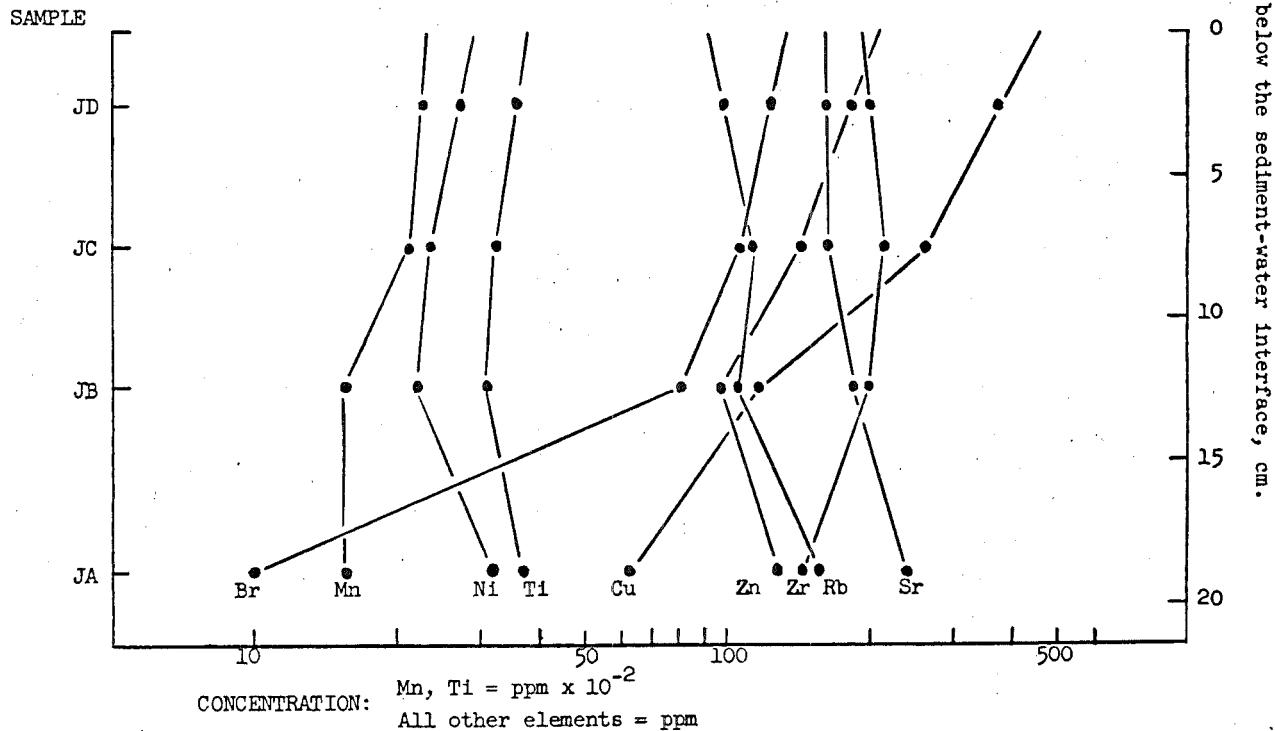


FIGURE 12: TRACE ELEMENTS IN A JENKINS SURFACE MUD PROFILE  
GS-10-62



literature will be compared with the evidence from Lake Superior in an attempt to determine the magnitude of each contribution.

Sorption of manganese: Murata (1953) has determined the percentage of exchangeable Mn in river muds, using the technique of ammonium acetate exchange. He finds that exchangeable Mn is always less than one percent of total Mn. The leaching experiments of this investigation, summarized in Appendix 4, also show very low percentages of leachable Mn. The quantity of Mn leached is roughly proportional to the amount present, which is in itself suggestive of a sorption mechanism, but the extremely low percentage leached suggests that most Mn is not now held in a sorbed state. The low values are not due to precipitation of Mn after exchange, because saturation with respect to Mn oxides was not even approached in the leaching solutions. The low results could be explained as unfavorable exchange coefficients or unfavorable exchange kinetics, but a more likely explanation is that much of the Mn is not sorbed at all, but is present in the sediment in some other form. This is particularly true in regard to the surface enrichment, where the Mn content is as high as 0.6 percent, far above concentrations that can be explained by sorption alone.

Detrital manganese silicates: Some of the Mn may be in the structural position of  $\text{Fe}^{++}$  in detrital silicates. Confirmation of this is suggested by the size fraction analyses (Figure 8), which show that Mn, although concentrated in the clay fraction, is not as restricted to that fraction as copper, zinc, and nickel, elements which are associated with clay minerals and organic matter. Although a large fraction of the manganese found at depth is probably detrital manganese bearing silicates, it is inconceivable

that the supply of those silicates richest in Mn could increase so dramatically in such a short time with so little a change in other components of the sediment. Therefore an increase in detrital manganese-ferous silicates is not the cause of the near-surface enrichment of manganese.

Precipitated manganese species: Figure 13 is an Eh-pH diagram for the manganese-hydroxide-oxide-carbonate-sulfide system, incorporating recent thermodynamic data determined by Bricker (1964) and quoted by Garrels and Christ (1965). Krauskopf (1957), Garrels (1959), Schmidt (1962) and Hem (1963), using older thermodynamic data, consider this and related systems at varying ionic concentrations and compare the theoretical calculations with experiments and natural observations.

The exact position of the boundary between the stability fields of manganous ion and the manganese oxides depends on the particular manganous ion concentration chosen to define the boundaries between solid and dissolved species. In Figure 13 the boundaries have been calculated for  $10^{-6}$  moles per liter, and dashed lines for  $10^{-4}$  m/l are added to show the magnitude and direction of the effects of changing manganous ion concentration.

Hem (1963) has studied complexes of manganous ion in aqueous solution, and finds two complexes,  $MnHCO_3^+$  and  $MnSO_4^0$  are important in natural waters. In Lake Superior less than five percent of the  $Mn^{++}$  will be complexed, and because this would entail only a small correction these complexes have been ignored in the construction of Figure 13.

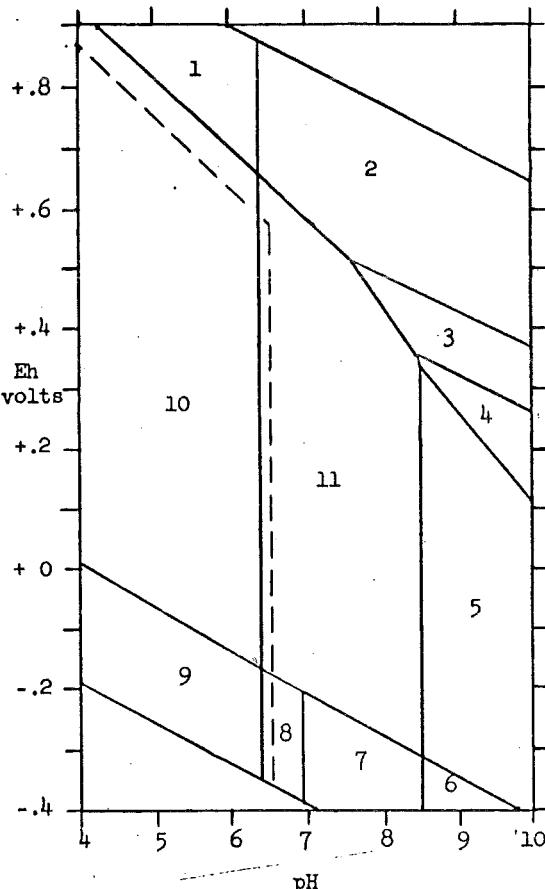
The concentration of Mn in true solution in Lake Superior is not well known. Swain and Prokopovich (1957) report an average  $Mn^{++}$  concentration

FIGURE 13: Eh-pH DIAGRAM OF THE SYSTEM  
 $\text{Mn-O-OH-S-CO}_2$  at 1 atm and  $25^\circ\text{C}$ .  
 $S = 10^{-3} \text{ m/l}$        $C = 10^{-3} \text{ m/l}$

Boundaries between solids and  $\text{Mn}^{++}$  at  $a_{\text{Mn}}^{++} = 10^{-6}$   
Contour of  $a_{\text{Mn}}^{++}$  at  $10^{-4}$  shown by dashed line.

#### FIELDS

1.  $\frac{1}{4}\text{MnO}_2 + \text{SO}_4^{=2-} + \text{H}_2\text{CO}_3^-$
2.  $\frac{3}{4}\text{MnO}_2 + \text{SO}_4^{=2-} + \text{HCO}_3^-$
3.  $\text{MnO(OH)} + \text{SO}_4^{=2-} + \text{HCO}_3^-$
4.  $\text{Mn}_3\text{O}_4 + \text{SO}_4^{=2-} + \text{HCO}_3^-$
5.  $\text{MnCO}_3 + \text{SO}_4^{=2-} + \text{HCO}_3^-$
6.  $\text{MnCO}_3 + \text{HS}^- + \text{HCO}_3^-$
7.  $\text{Mn}^{++} + \text{HS}^- + \text{HCO}_3^-$
8.  $\text{Mn}^{++} + \text{H}_2\text{S} + \text{HCO}_3^-$
9.  $\text{Mn}^{++} + \text{H}_2\text{S} + \text{H}_2\text{CO}_3^-$
10.  $\text{Mn}^{++} + \text{SO}_4^{=2-} + \text{H}_2\text{CO}_3^-$
11.  $\text{Mn}^{++} + \text{SO}_4^{=2-} + \text{HCO}_3^-$



of 0.15 ppm, and a range of .02 to 0.4 ppm for water of the Silver Bay area, Lake Superior, but it is not known whether the samples were filtered. The U. S. Public Health Water Quality Network reports (1960, 1961) find the Mn content to be below their detection limit of .005 ppm. However, the U. S. P. H. N. samples were composite samples analyzed up to six months after sampling, and changes might have occurred after sampling due to precipitation, sorption, or coprecipitation effects (Hem, 1963). Thus the exact concentration of manganese in Lake Superior is not known at this time. The data summarized by Livingstone (1963) suggest that the Mn content of most natural aerated waters is in the range of .001 to .025 ppm.

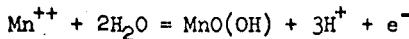
Figure 13 does not take into account solid solution of iron and manganese. However, most analyses of pyrolusite and manganite contain less than a third of a percent of  $\text{Fe}_2\text{O}_3$ , and only minor qualitative adjustments in the region of limnologic interest would result if iron solid solution were to be included in the figure (Palache et al, 1944, pp. 563, 647).

From Figure 13 it is evident that oxidation in the natural lakes will result in the formation of compounds containing  $\text{Mn}^{+3}$  or  $\text{Mn}^{+4}$ . The initial precipitates in this system are like the iron oxide initial precipitates in that they are poorly crystalline, metastable compounds of indefinite hydration that gradually lose water as they recrystallize. They are usually amorphous to X-rays (Hem, 1963), and none could be detected by X-ray examination of Lake Superior sediments. Hem (1963) has studied precipitates obtained upon oxidation of solutions initially containing 10 ppm Mn. Although he cannot identify the species precipitated he does find that the ratio of  $\text{Mn}^{+3}$  to  $\text{Mn}^{+4}$  in the precipitate decreases with decreasing pH, in qualitative agreement with Figure 13.

Also, from Figure 13, it is evident that an increase of pH favors the formation of manganeseous carbonate.

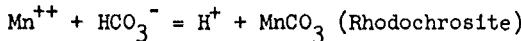
Comparison of Figure 13 with the pH-Eh relationships of Lake Superior sediments and water (Figure 6) shows that Mn<sup>++</sup> should be the stable species in all fine grained sediments, but that close to the sediment-water interface the upward increase in redox potential and pH reduces the quantity of Mn<sup>++</sup> that can remain in solution. In the overlying water still less Mn<sup>++</sup> will be stable. Therefore the observed surface enrichment of Mn can be interpreted as a precipitation of Mn oxides, hydrated oxides, or carbonate. Mn is being concentrated at the sediment-water interface because that interface is the boundary between two processes. On the one hand, detrital and recently precipitated oxides, hydrated oxides, or carbonates are sedimenting out of the lake water onto the sediment. On the other hand bacterial activity has reduced the Eh and pH of the sediment below, enabling previously precipitated Mn to go into solution again. The Mn<sup>++</sup> concentration gradient so produced results in the upward diffusion of Mn, terminating at the sediment-water interface by precipitation due to the relatively abrupt increase in Eh and pH. Mn is known to follow a similar cycle of upward migration and reprecipitation in eutrophic lakes during summer hypolimnetic oxygen depletion, except that in this case the surface, or more precisely, the volume in which Mn precipitation takes place is displaced upwards into the water mass, often corresponding with the thermocline (Hutchinson, 1957, p. 808-810). This type of a mechanism is only a concentration of previously sedimented Mn oxides or carbonates. The Mn is ultimately derived from the surrounding basin.

The two most relevant equilibria of Figure 13 are:



$$\text{Eh} = 1.495 - .177\text{pH} - .059\log(a_{\text{Mn}}^{++})$$

and:



$$K_{\text{eq}} = 3.22$$

A quantitative comparison of these equilibria with the individual measurements of Eh, pH, and bicarbonate in Lake Superior hypolimnetic waters suggests that it is actually the carbonate equilibrium that presently controls manganese solubility in all cases. However, the differences are slight, for assuming activity coefficients of 0.86 for  $\text{Mn}^{++}$  and 0.96 for  $\text{HCO}_3^-$  the average calculated equilibrium  $\text{Mn}^{++}$  concentrations are 1.4 ppm for the oxide equilibrium and 0.7 ppm for the carbonate equilibrium. This is not a significant difference in view of the uncertainty in Eh, pH, and alkalinity measurements and thermodynamic data. Both averages are slightly above the measurements and estimates of the actual  $\text{Mn}^{++}$  content of Lake Superior, but the difference is not large enough to warrant rejection of solubility control of the manganese concentration at this time.

Nevertheless, one ought to consider other possible mechanisms, which if operative would prevent attainment of equilibrium with solid manganese species. Two such mechanisms are as follows:

- a) Co-precipitation of manganese with iron. However, the manganeseiferous crusts, discussed below, are enriched in manganese but not significantly enriched in iron. Therefore if the mechanism of formation of the crusts and of the near-surface enrichment of manganese is the same, co-precipitation is probably not an important factor.

b) The effect of organisms. Organisms may play two roles in addition to that of regulating the pH and Eh gradient. One of them, that of acceleration of oxidation under favorable redox and pH circumstances, that is, where the solid species is already stable, would not affect ionic concentrations. In contrast, scavenging of manganese from the water by organisms might actually keep the concentration of manganese below the concentration that would be in equilibrium with solid species. If so, sedimentation of these organisms would be a major mechanism for transfer of manganese from water to sediment. The relative importance of this type of transfer has not been determined.

Could the Mn surface enrichment be caused by an increase in the rate of supply of Mn oxides and hydrous oxides? Even if such an increase in supply or decrease in dilution has occurred the mechanism of reprecipitation due to the Eh and pH gradient should be important. The writer feels that the latter is the major factor, and that all other factors are secondary. However, more study is needed, because observations to date do not categorically eliminate the possibility of changes in the rate of supply or dilution, but only limit the nature of the source of supply:

a) The Mn surface enrichments in western Lake Superior, close to the iron ore deposits of Michigan and Minnesota and to the basic and ultrabasic rocks of the region, are not greater than the Mn surface enrichments of eastern Lake Superior, where source rocks should be poorer in Mn. Moreover, the surface enrichments are found in Lakes Michigan and Huron. Therefore the Mn does not appear to be derived from any one geographically restricted source. If the surface enrichment has been caused by an increase

in the rate of sedimentation of Mn, the source of this additional detritus is some widespread process acting throughout the western Great Lakes region.

Manganese crusts: Moderate yellowish brown crusts containing very high concentrations of manganese have been found in only three Lake Superior localities. Data on the chemical composition of these crusts and adjacent sediments are summarized in Table 7. The comparative rarity of the crusts suggests that they are local developments, but their actual areal extent has not been determined. The three known occurrences are from two widely separated areas that do not have any obvious topographic or sedimentologic similarities. The one to three distinct crusts at each locality are each less than two millimeters thick, and are buried by two to eight centimeters of brown sediment. Therefore they probably were formed prior to the beginning of extensive mining and shipping activity in Lake Superior, and it is possible that they are near-contemporaneous.

The crust samples of Table 7 are mixtures of crust and up to 50 percent of adjacent sediment. The manganese contents of the crust samples are all over ten times the manganese contents of the adjacent sediments. This enrichment appears to be independent of the normal surface enrichment in manganese at these localities, as it occurs in distinct layers, and as the observed concentrations are twice the maximum observed surface concentrations.

In contrast, the iron content of crusts and adjacent sediment is not significantly different. However, both the iron and the manganese analyses of these crusts are less reliable than similar analyses of the majority of sediments, because the major element standard and the trace

TABLE 7: ANALYSES OF MANGANIFEROUS CRUSTS  
AND ADJACENT SEDIMENTS

Trace elements (Zr-B) in ppm dry weight

Major elements ( $\text{Fe}_2\text{O}_3$  -  $\text{Al}_2\text{O}_3$ ) in percent dry weight

	Al	Su-7-61 A2 (crust)	B	JE	Su-8-61 JF (crust)	JG	GS-4-62 JB1 (crust)	JB2 (crust)
Zr	159	321	158	166	163	167	161	99
Sr	169	199	157	160	108	166	110	134
Rb	110	104	78	135	144	106	127	74
Br	51	114	40	57	37	72	81	76
Zn	103	142	96	139	317	175	133	86
Cu				178	96	208	140	91
Ni				31	26	23	32	16
Mn	2540	29400	1700	2720	14800	3410	1740	31700
Ti	2270	4200	2440	5080	4020	3770	4610	2630
V	155	120	145					
Ga	7	10	10					
B	14	25	19					
$\text{Fe}_2\text{O}_3$	12.0	13.7	11.3	12.9	11.5	12.6		
$\text{K}_2\text{O}$	2.9	2.7	2.9	3.1	3.1	2.8		
$\text{CaO}$	2.7	2.8	2.7	2.1	2.2	2.2		
$\text{SiO}_2$	54	54	55	53	55	56		
$\text{Al}_2\text{O}_3$	13.9	12.8	13.9	14.1	14.0	12.7		

element "spike" used in the analyses were prepared for the analysis of sediments with smaller X-ray absorption coefficients and much lower manganese contents.

Copper, nickel, and probably vanadium are impoverished in the crusts relative to the adjacent sediments, and in this respect these crusts resemble the fresh-water crusts analyzed by Gorham and Swaine (1965). Other elements show no significant trends or show trends probably related to features other than the crust per se.

The crusts are probably sediment enriched with a manganese oxide, hydrous oxide, or carbonate. Similar crusts are thought to be deposited in areas of relatively slow deposition (Gorham and Swaine, 1965), and this may be true with regard to the Lake Superior crusts. The crusts, now buried, would be almost diastemic horizons that were later buried when the rate of sedimentation increased at the given localities. Re-solution and upward diffusion of manganese could be a factor in the formation of these crusts. The presence of a sharp layer of manganese enrichment implies a sharp, undisturbed sediment-water interface, with a clear differentiation between sediment of low redox potential beneath and water of high redox potential above. It implies that there has been no sediment mixing by organisms or currents, and no significant dilution of the precipitated manganese species by additional detrital sediment. If precipitation of additional manganese species derived from the overlying water was an additional source of manganese, the precipitation probably took place close to, if not immediately at the site of deposition, because a precipitate forming at more distant localities would be thoroughly mixed with normal detrital sediment before deposition. Definite conclusions concerning these manganiferous crusts cannot be made until more is known about their

occurrence and geochemistry.

Summary: Although a small fraction of the Mn of Lake Superior sediments is sorbed, most of the Mn is present as Mn-bearing silicates and heavy minerals and as precipitated Mn oxides and hydrated oxides. Surface enrichment in Mn is probably due to the reduction, upward migration, and reprecipitation of previously sedimented Mn minerals, although the evidence for this mechanism is circumstantial. In the opinion of the writer an increase in the supply of detrital Mn is a minor factor. Rare, slightly buried, manganese-rich crusts may be horizons of very slow deposition, but more study will be required before they are fully understood.

### Nickel

The average nickel content of Lake Superior sediments analyzed is  $27 \pm 8$  ppm (standard deviation of mean = 1 ppm). The size fraction analyses (Figure 8) show that nickel, like zinc, manganese, bromine, and copper is concentrated in the clay size fraction.

The difference between the average concentration of nickel in surface samples ( $28 \pm 2$  ppm) and the average concentration in sediments at depth ( $32 \pm 1$  ppm) is just significant at the 97 percent confidence level, and the difference is of the order of magnitude that might be expected from the slightly coarser grain size of the average surface sediment (slightly smaller clay size fraction of the surface sediment). In the Jenkins surface mud profiles (Figures 11, 12) nickel does not show the strong surface enrichment that is found in Zn, Cu, Mn, and Br. In some profiles the nickel content rises slightly, but in others the concentration of nickel varies little. If individual Jenkins profiles are examined the concentration of nickel is found to vary inversely with the concentration of silica. In the Jenkins profiles the shapes of the increases in Cu, Zn, and Mn are smoothed out if the ratios of Cu/Ni, Zn/Ni, and Mn/Ni are plotted rather than the absolute elemental concentrations, and for samples from below the region of surface concentrations the ratios vary less than the absolute elemental concentrations.

The leaching experiments (Appendix 4) show that some nickel is exchangeable. Because of the extremely low concentration levels involved the results of the exchange experiment are only approximate in the case of Ni, but they apparently show that the percentage of exchangeable Ni is slightly less than the percentage of exchangeable Cu and Zn, and also that

the percentage of exchangeable Ni is higher close to the sediment-water interface than at the bottom of Jenkins cores. Thus it is believed that the percentage of exchangeable Ni in the surface slice is the minimum percentage of Ni in the sample that was incorporated by sorption and exchange mechanisms, and that the decrease in exchangeable Ni with depth is indicative of fixation of the Ni. An alternate explanation is that Ni sorption has accelerated recently, but this does not explain why the total quantity of Ni has remained constant.

Hirst (1962) conducted similar leaching experiments on the sediments of the brackish water Gulf of Paria, Venezuela, using 25% acetic acid instead of 1 normal ammonium acetate. Despite the harsh treatment only 12 to 15 percent of the nickel could be leached from his muds and clays. Although the remaining 85 to 88 percent of Ni could be interpreted as being extremely fixed Ni it is more likely that most of the 85 to 88 percent of unremoved Ni was present as structurally bound components of detrital silicates.

There is no statistically significant difference between the Ni content of surface sediments from eastern Lake Superior and surface sediments from Keweenaw Bay and western Lake Superior, even though source rocks in the predominantly basic western area probably contain more nickel than source rocks from the predominantly granitic eastern area (Table 8). This suggests that the detrital Ni-bearing components of the clay size fraction of Lake Superior sediments are weathering products rather than rock fragments, and that the source rock differences have been obliterated by the weathering processes.

Because of the behavior outlined above this investigator uses the convenient postulate that the concentration of nickel in the clay size

fraction is constant, and then compares the behavior of other elements concentrated in the clay size fraction with Ni. As shown above the postulate is a fair first order approximation, but it does not completely specify what components of the clay size fraction contain the Ni. The inorganic fraction of Jenkins cores decreases upward, as the Ni content remains constant or increases slightly, and the interpretation will vary depending on the partitioning of the Ni between organic and inorganic fractions of the clay size fraction. Because the Ni remains constant or increases slightly it is most likely divided between the two fractions in proportion to the mass of the fraction, that is, its concentration in the separate fractions is about equal.

Analyses of Ni from the literature are shown in Table 8. Although the low nickel content of Lake Superior sediments may at first glance suggest that the source rocks of the region are low in Ni, it is more likely that the low Ni content is an indicator of the non-marine character of Lake Superior and Lake Superior sedimentation. The higher Ni content of marine sediments is interpreted as the gradual incorporation of more non-detrital Ni in the sediment (Turekian & Carr, 1960). The extreme examples of this trend are the deep sea red clays, in which the Ni content averages 127 ppm (Green, 1959). The non-marine sediments contain a lower percentage of non-detrital Ni because of more rapid rates of sedimentation.

TABLE 8: NICKEL CONTENT OF VARIOUS EARTH MATERIALS

Data in ppm	
Recent marine argillaceous sediments (Potter et al, 1963)	40
Recent nonmarine argillaceous sediments (Potter et al, 1963)	26
Shales (marine?) (Turekian & Carr, 1960)	71
Devonian pelites (marine?) (Shaw, 1954)	64
Average basalt (Taylor, 1964)	150
Average granite (Taylor, 1964)	0.5
Lake Superior sediments (this study)	26.5

### Zinc

Figure 8 shows that Zn, like Ni and Cu, is strongly concentrated in the clay size fraction of Lake Superior sediments.

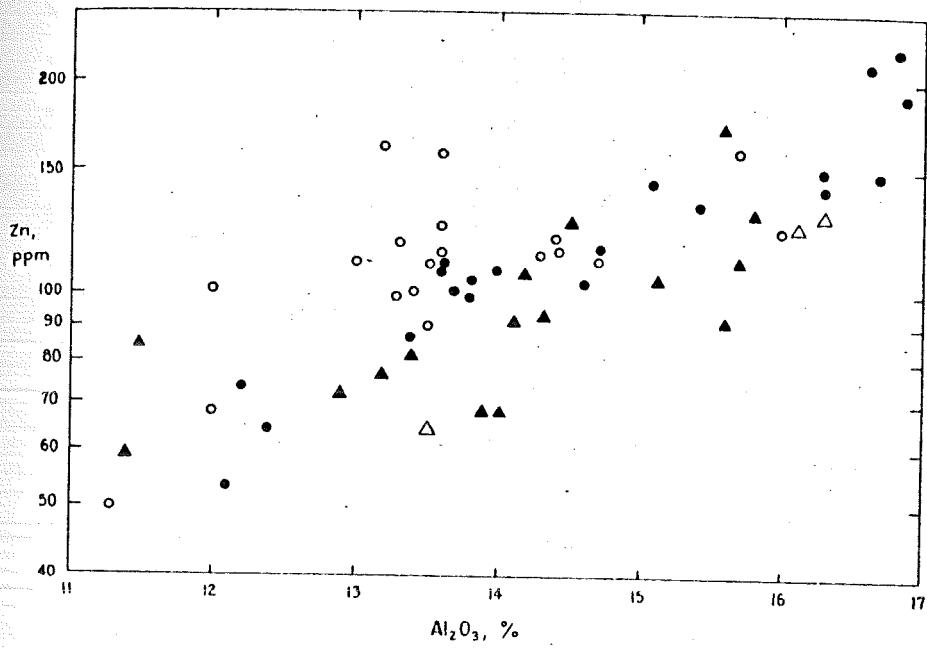
In Jenkins surface mud profiles (Figures 11 and 12) the sediment concentration of Zn, as well as that of Mn and Cu, rises toward the sediment-water interface. The surface enrichment of Zn is smaller in terms of percentage increase than the increases in Mn and Cu, but it is just as predictable in its occurrence. Moreover, it begins at a greater depth. The mean of Zn/Ni ratios at depth is  $4.13 \pm 0.13$ , that of the lower two slices of Jenkins cores is  $4.61 \pm 0.17$ , and that of the higher Jenkins slices is  $6.39 \pm 0.57$ , which shows that gradual Zn enrichment commences below the lower limit of Jenkins cores.

The maximum Zn concentrations occur in a 3 to 8 cm layer at the top of the sediment column, in contrast with Mn, which is almost always highest in the uppermost 3 cm. This is shown by the fact that the Zn content of the topmost Jenkins slice is little higher than that of the second slice, and in five out of nine cores the ratio of Zn to Ni actually decreases from the second to the topmost slice. The average depth at which the Zn concentration is the average of the concentrations in the topmost and lowermost Jenkins slice is 9 cm.

Appendix 4 shows the behavior of Zn in the ammonium acetate leach experiments. The greater the concentration of Zn in the sediment the greater the quantity of exchangeable Zn, but more significantly, the percentage as well as the absolute quantity exchanged increases toward the surface. Nevertheless, no more than ten percent of the Zn is leached. Note that considerable Zn is leached by both the second and third aliquots,

suggesting either very unfavorable exchange coefficients or extremely slow exchange equilibria are important. The latter is probably the case, although no proof is inherent in the Lake Superior studies.

Figure 14 is a plot of the zinc concentration as a function of the  $\text{Al}_2\text{O}_3$  concentration for sediments below the surface. Here, where the effects of the surface concentration of Zn are at a minimum, a correlation of Zn and  $\text{Al}_2\text{O}_3$  is evident. This correlation could have been predicted from the known enrichment of Zn in the clay size fraction. Note, however, that sediments of low Br content tend to have lower Zn than might be predicted from their  $\text{Al}_2\text{O}_3$  content. It is shown later in this paper that the Br content is probably indicative of the organic activity of the lake at the time of deposition, and suggested that the Br concentration will also be proportional to the organic content if a uniform state of decay has been attained. Therefore one might assume that this diagram shows that most of the Zn is combined in the inorganic clay fraction, but that even with the low concentration of organic matter that probably exists in these samples at depth, a significant amount of the Zn is combined with the organic matter, resulting in the Br-dependent scatter shown in the graph of Zn versus  $\text{Al}_2\text{O}_3$ . Although this is certainly possible, it is by no means a proven fact, for what is lacking is evidence that there is a cause and effect relationship between Zn and the organic matter, or evidence that the Zn and Br distributions are controlled by the same factor. The samples of low Br content are, with few exceptions, the deeper gray clays and the varved gray and red clays, and as they contain more rock flour and less clay minerals, the fraction of their  $\text{Al}_2\text{O}_3$  that represents minerals capable of Zn uptake might be less. This would produce the Br-dependent scatter, but the only relationship between Br and



## LEGEND

Sediments more than 35 cm below the sediment-water interface {

- more than 20 ppm bromine
- ▲ less than 20 ppm bromine

Sediments 10 to  
35 cm below the  
sediment - water  
interface {

- more than 20 ppm bromine
- △ less than 20 ppm bromine

Figure 14. Variation of zinc with  $\text{Al}_2\text{O}_3$  in non-surface sediments of Lake Superior.

Zn/Al<sub>2</sub>O<sub>3</sub> ratio would be the time of deposition. Note that the ratio of Zn to Ni increased slightly (4.13 to 4.61) over the same interval. Because both Zn and Ni are strongly confined to the clay size fraction it is clear that the Br-Zn/Al<sub>2</sub>O<sub>3</sub> trend is unrelated to the slight increase in the silt size fraction noted earlier.

Zinc sorption: The possible role of sorption and ion exchange in producing the surface Zn enrichment that is suggested by the leaching experiments must be considered in the light of previous studies. Many investigations of Zn sorption are of little use because the Zn concentration of solutions used is far above that of natural waters. Bachman (1961, 1963) comes closest to using Zn concentrations found in natural waters, although his solutions are still 5 to 50 times the natural concentrations. His data are shown in Table 9. The higher sorption capacity of formalin-killed than live algae is consistent with the observation that the Zn content of the organic matter of sediments may be considerably higher than the Zn content of living organisms (Rankama and Sahama, 1950, p. 713). Because Zn uptake always followed the Freundlich adsorption isotherm, and because the uptake of dead organisms was still high, Bachman postulated that the uptake was sorptive rather than metabolic, at least in the range of Zn concentrations studied. By using the value of k for Whitmore Lake sediment it is possible to extrapolate to the percentage of Zn that would be sorbed by the sediment at the Zn concentrations found in natural waters. For a Zn concentration of 1 ppb, 30.8 ppm Zn will be sorbed, and for a lake water concentration of 10 ppb, 123 ppm will be taken up by the sediment. It is apparent that sorption of Zn could account for the presence of a significant fraction of the Zn contained in Lake Superior

TABLE 2: ZINC SORPTION

Data from Bachman, 1961, 1963

For the Freundlich Adsorption Isotherm

$$x = m k c^n$$

where:  $x$  is the amount sorbed

$m$  is the mass of adsorbing material

$c$  is the concentration of the element  
in the solution

$k$  and  $n$  are constants

For all systems studied,  $n = 0.6$

The following values of  $mk$ , the "sorption capacity,"  
were determined ( $m$  in mg):

living Golenkina	$mk$
(a green alga)	0.0174

Formalin-killed Golenkina	0.0530
---------------------------	--------

Whitmore Lake sediment	0.0308
------------------------	--------

N. B. For the Golenkina,  $m$  is one cubic millimeter  
of cells, assumed density of  $1 \text{ mg/cm}^3$  wet  
weight.

For Whitmore lake sediment,  $m$  is one mg dry  
weight. This sediment is a black muck with  
37 percent ignition loss, attributed to  
organic matter.

sediments.

It is a common observance that sorbed ions become more and more immobile as the sorbate "ages," and this phenomenon, generally termed "fixation," (Carroll, 1959, p. 767), is particularly well documented in the case of Zn. The mechanism of fixation of Zn in clay minerals has been studied by Elgabaly (1950). In dioctahedral phyllosilicates Zn enters the octahedral positions that are not occupied by Al, resulting in a decrease in the cation absorption capacity and an increase in the anion absorption capacity of the clay, whereas in trioctahedral phyllosilicates the Zn replaces Mg, equally charged, and no changes in exchange capacities occur. In either case the lattice substitutions are far from reversible even if drastic leaching with concentrated solutions of Mg or Al is undertaken within hours after initial Zn uptake.

Fixation processes are slower than surface adsorption (Carritt and Goodgal, 1954). Because Bachman's experiments were usually terminated at the end of 24 hours they do not reflect all of the Zn uptake which could occur if the sediment were left in equilibrium with the solution for longer periods of time. Tiller and Hodgson (1962) did not attain equilibrium in thirty days, showing that the process of sorption and subsequent fixation and sorption of more Zn could account for an even larger fraction of the Zn than suggested by Bachman's sorption capacity data. The Zn concentration in Lake Superior should be between 5 and 10 ppb; therefore it is possible for sorption and fixation on organic and inorganic substrates to account for all of Zn uptake by Lake Superior sediments.

Precipitation: The possible role of precipitation of Zn minerals in the

regulation of Zn in lakes can be studied by constructing an Eh-pH diagram similar to those constructed for Mn and Cu in this report, but the results are of less significance because of the absence of some thermodynamic data, particularly with respect to the relationship of Zn and Si. For instance, as the pH of natural waters increases, the solubility of Zn should be limited by the precipitation of one of several chemical species, not all of which are well known thermodynamically. Precipitation of  $ZnSiO_3$  is a possible limiting factor, but the position of a  $Zn^{++}$ - $ZnSiO_3$  boundary depends not only on the  $Zn^{++}$  concentration but also on the as yet unknown amount of unpolymerized  $H_3SiO_4^-$  present in natural waters. Furthermore,  $ZnSiO_3$  is not known as a natural mineral, and for this reason alone, "intuition" suggests that  $ZnSiO_3$  should not have a stability field under normal limnologic conditions. Precipitation of hemimorphite,  $Zn_4(OH)_2 \cdot Si_2O_7 \cdot H_2O$ , is another possible phase that could limit Zn solubility, but its Gibbs free energy is not known, and its association with sulfides in limestones suggests more alkaline (and possibly more reducing) conditions than those found in Lake Superior surface sediments. Smithsonite,  $ZnCO_3$ , and hydrozincite,  $Zn_5(OH)_6(CO_3)_2$ , are still other possible limiting species, and their Gibbs free energies are known, but neither will be significant below a pH of 8.0 for the  $CO_2$  partial pressures and total carbonate contents that might occur in Lake Superior. Smithsonite, hemimorphite, or hydrozincite solubility may limit the  $Zn^{++}$  concentration in the carbonate-saturated clays at depth, but the Zn content of these sediments is low, and sorption phenomena may prevent attainment of saturation.

None of the complexes listed by Yatsimirskii and Vasilev (1960) and Bjerrum et al (1957) should be important in Great Lakes limnologic

environments, therefore  $Zn^{++}$  should be the predominant species in true solution.

The Eh of lake and sediment waters should have no effect on the solubility of Zn except at very low potentials, where sphalerite,  $\propto$  ZnS, will be the phase limiting solubility. The  $Zn^{++} - \propto$  ZnS boundary is almost identical to the "sulfide fence" in the Cu-Fe-S system shown in Figure 15. Thus, where iron sulfides are found, Zn sulfide may also be present. However, because of the Eh - pH relationships in Lake Superior sediments sulfide precipitation should not be a significant factor in water to sediment transfer of Zn.

Regional aspects of zinc distribution: The samples from Lake Michigan and Lake Huron show that there is a surface enrichment of Zn in the two lakes that is similar to that in Lake Superior. The Lake Michigan surface sample has the second highest Zn concentration (303 ppm) and the highest Zn/Ni ratio found in this study. Braidech and Emery, in their classic study of trace elements in water supplies (1935) found that the 200 to 300 ppb Zn content of their Lake Michigan samples was higher than that found in any other body of water studied. Moreover, Ostrum (1957) found that the shales of the Illinois basin contained  $200 \pm 100$  ppm Zn, which is considerably higher than the 95 ppm of the average shale (Turekian and Wedepohl, 1960). Thus, while no firm conclusion can be based on the single Jenkins sequence analyzed, there is a strong possibility that Zn is anomalously high in Lake Michigan sediments, and such an anomaly would be easily explained by the high Zn content of Lake Michigan water. The excess Zn may be ultimately derived from the source rocks of the lake sediment, but it can just as easily be explained by industrial and urban

contamination in the heavily populated Lake Michigan basin.

Conclusion: In summary, although the evidence with regard to precipitation mechanisms is unsatisfactory, the adequacy of sorption is established, and it is likely that most of the Zn of Lake Superior sediments, particularly that in the surface concentrations, is sorbed zinc and structural zinc that entered the sediment via sorption and fixation.

## Copper

General: Copper is concentrated in the clay fraction of Lake Superior sediments, as shown by Figure 8. It is strongly enriched in the near-surface sediments (Figures 11 and 12), the Cu enrichment resembling the Zn enrichment in several important respects:

- a) Copper, like Zn, has maximum enrichment in a 3 to 8 cm zone at the top of the sediment column, unlike Mn, which is almost always highest in the top 3 cm.
- b) Leaching experiments (Appendix 4) show that, like Zn, only a small percentage of the Cu can be leached. The absolute amount of Cu leached and the percentage of Cu leached increase toward the sediment-water interface. Again like Zn, considerable Cu is leached in both the second and third aliquots, suggesting either very unfavorable exchange coefficients or extremely slow exchange equilibria are important. The exchangeable Cu from sediments at depth is nil. Hirst (1962), in leaching with 25 percent acetic acid, also found wide variations in the percentage of leachable Cu in the sediments of the Gulf of Paria (0.5 to 45 percent), but did not explain the great variation.

Copper may be present as sorbed ions, as precipitated copper minerals, and as firmly bound constituents of detrital minerals. The relative contribution of each state to the total Cu content of Lake Superior sediments will now be considered.

Sorption: Sorption of copper has been studied quantitatively by Hydeman (1959). She shows that uptake of copper by clays follows the Freundlich

isotherm (Table 2), and is not a function of the concentrations of other ions for solutions of low to moderate ionic strength. From her graphs the constants k and n may be calculated. For illite H-36 (Morris, Illinois), at pH = 6.8, n is 0.5 and k is 519. The average Cu concentration of Lake Superior waters is 3.8 ppb (Table 6). Thus Morris Illite in equilibrium with an infinite supply of water containing 3.8 ppb Cu will adsorb ions until the copper concentration in the solid phase is 726 ppm, over 200 ppm higher than the highest concentration observed in Lake Superior sediments! The sorptive capacity (n) of Lake Superior sediments and copper as the cation is not known. Carritt and Goodgal (1954) determined the pH dependence of Cu sorption on recent argillaceous sediments, but they do not give enough information to determine a value for n. However, the total sorptive capacity of the sediment might not be much lower than that of illite, because the sediments contain some clays with higher sorption capacities than illite as well as components with lower capacities. Thus sorption is an adequate mechanism to explain the uptake of copper by Lake Superior sediments, even at present levels of Cu concentration, and even more Cu might be sorbed if concentrations were to become higher.

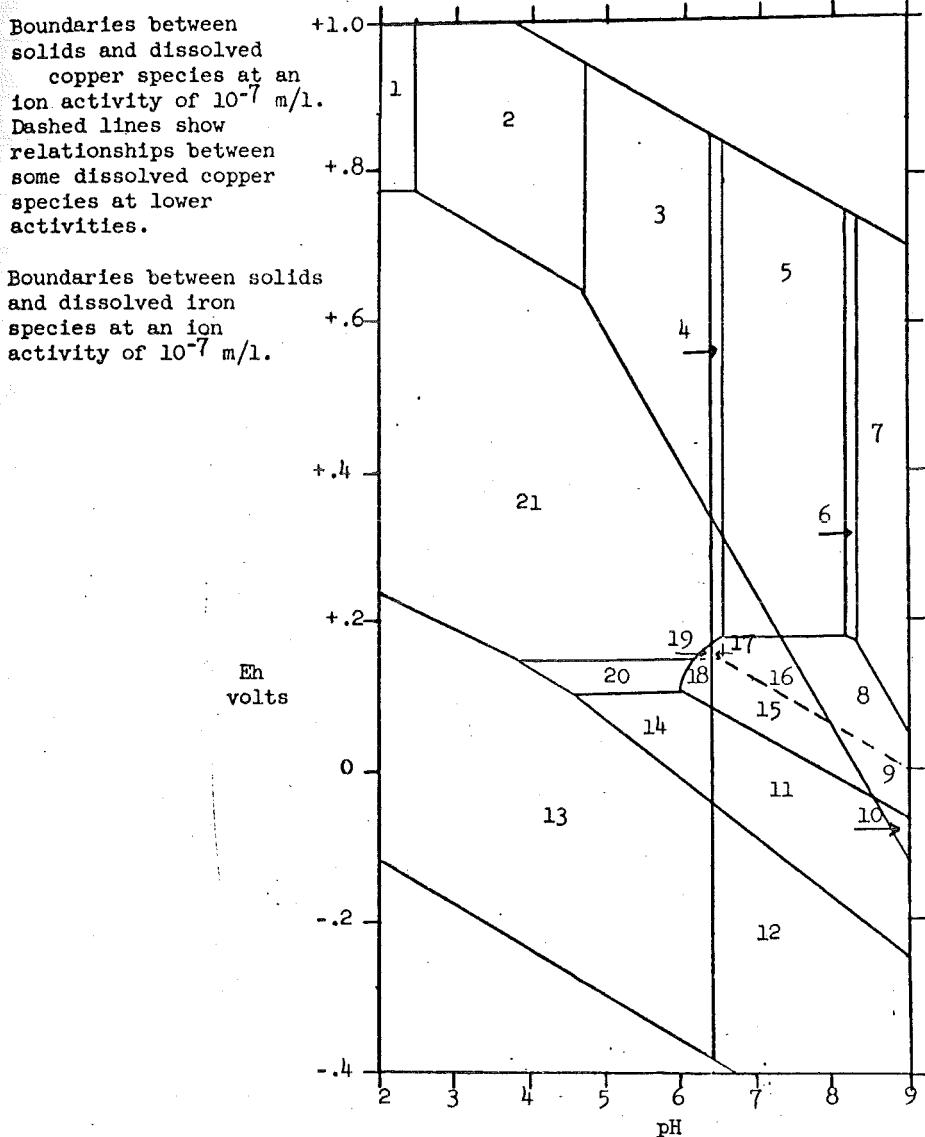
Precipitation: The role of precipitation mechanisms in the uptake and retention of copper in the sediments may be studied with the aid of an Eh-pH diagram and comparison of the theoretical diagram with observations of the natural environment. For the construction of Figure 15, a Cu concentration in solution of  $1 \times 10^{-7}$  m/l, slightly higher than the concentration of Cu in Lake Superior (Table 6) has been used to fix the boundary between solid and dissolved species. Total sulfur and total

STABILITY FIELDS OF FIGURE 15

(Parentheses indicate species whose activity is less than  $10^{-7}$  m/l in the indicated field)

1.  $\text{Fe}^{+++} + \text{Cu}^{++} + \text{H}_2\text{CO}_3 + \text{SO}_4^- =$
2.  $\text{Fe(OH)}^+ + \text{Cu}^{++} + \text{H}_2\text{CO}_3 + \text{SO}_4^- =$
3.  $\text{Fe(OH)}_3 + \text{Cu}^{++} + \text{H}_2\text{CO}_3 + \text{SO}_4^- =$
4.  $\text{Fe(OH)}_3 + \text{Cu}^{++} + \text{HCO}_3^- + \text{SO}_4^- =$
5.  $\text{Fe(OH)}_3 + \text{CuCO}_3^{\circ\text{aq}} + \text{HCO}_3^- + \text{SO}_4^- =$
6.  $\text{Fe(OH)}_3 + \text{CuO} \text{ (tenorite)} + \text{HCO}_3^- + \text{SO}_4^- =$
7.  $\text{Fe(OH)}_3 + \text{Cu}_2(\text{OH})_2\text{CO}_3 \text{ (malachite)} + \text{HCO}_3^- + \text{SO}_4^- =$
8.  $\text{Fe(OH)}_3 + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{CuCO}_3^{\circ\text{aq}})$
9.  $\text{Fe(OH)}_3 + \text{Cu}_2\text{O} + \text{HCO}_3^- + \text{SO}_4^- (+\text{Cu}^+)$
10.  $\text{Fe(OH)}_3 + \text{Cu} \text{ (native copper)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{Cu}^+)$
11.  $\text{Fe}^{++} + \text{Cu} \text{ (native copper)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{Cu}^+)$
12. Various Cu and Cu-Fe sulfides +  $\text{HCO}_3^-$
13. Various Cu and Cu-Fe sulfides +  $\text{H}_2\text{CO}_3$
14.  $\text{Fe}^{++} + \text{Cu} \text{ (native copper)} + \text{H}_2\text{CO}_3 + \text{SO}_4^- (+\text{Cu}^+)$
15.  $\text{Fe}^{++} + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{Cu}^+)$
16.  $\text{Fe}^{++} + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{CuCO}_3^{\circ\text{aq}})$
17.  $\text{Fe}^{++} + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{HCO}_3^- + \text{SO}_4^- (+\text{Cu}^{++})$
18.  $\text{Fe}^{++} + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{H}_2\text{CO}_3 + \text{SO}_4^- (+\text{Cu}^+)$
19.  $\text{Fe}^{++} + \text{Cu}_2\text{O} \text{ (cuprite)} + \text{H}_2\text{CO}_3 + \text{SO}_4^- (+\text{Cu}^{++})$
20.  $\text{Fe}^{++} + \text{Cu}^+ + \text{H}_2\text{CO}_3 + \text{SO}_4^- =$
21.  $\text{Fe}^{++} + \text{Cu}^{++} + \text{H}_2\text{CO}_3 + \text{SO}_4^- =$

FIGURE 15: Eh-pH DIAGRAM OF THE SYSTEM Cu-Fe-S-O-OH-CO<sub>2</sub>  
 at 1 atm and 25 °C    C = 10<sup>-3</sup> m/l;    S = 10<sup>-5</sup> m/l  
 Shows metastable fields of Fe(OH)<sub>3</sub> and Fe(OH)<sup>+</sup>



carbonate have been fixed at  $10^{-5}$  m/l and  $10^{-3}$  m/l, respectively, again close to Lake Superior concentrations. Free energy values used in the construction are those compiled by Garrels (1959), except that of  $\text{CuOH}^+$ , which was calculated from the instability constant tabulated by Yatsimirskii and Vasilev (1959).

In Lake Superior the predominant copper species in solution will be  $\text{CuCO}_3^{\circ\text{aq}}$ . Ten percent of the Cu will be present as  $\text{CuOH}^+$ , however, as the reaction  $\text{HCO}_3^- + \text{CuOH}^+ = \text{CuCO}_3^{\circ\text{aq}} + \text{H}_2\text{O}$  is independent of Eh, and also essentially independent of pH in the bicarbonate field, with  $(\text{CuCO}_3^{\circ\text{aq}})/(\text{CuOH}^+) = 9.0$ . The dissolved ions will be somewhat different in the sediments, as  $\text{Cu}^+$  is the stable ion at lower redox potentials. The boundary between  $\text{Cu}^+$  and  $\text{CuCO}_3^{\circ} + 10\% \text{CuOH}^+$ , shown as a dashed line in Figure 15, bisects the region in which many lake sediment measurements lie, so that all three ions will be present, the relative proportions of each depending on the exact redox potential and pH.

With respect to the stability of solid species, comparison of Figures 15 and 6 shows that the brown sediments lie in the region of stability of solid Cu minerals - cuprite at higher redox potentials, and native copper at lower Eh values. The Cu-CuFe sulfide "fence" coincides roughly with the iron sulfide "fence," therefore those sediments containing hydro-troilite might also contain copper or copper-iron sulfides. The red and gray clays that are carbonate saturated lie close to or even in the stability field of malachite or  $\text{CuO}$ , but these same red and gray carbonate-saturated clays have low copper contents.

If the conditions of construction of Figure 15 are changed slightly the relative size of the  $\text{CuO}$  and malachite fields are altered. Azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ , is almost stable in the system plotted, and the rate of

alteration of azurite to malachite or  $Cu_2O$  to malachite might be very slow.

Proof or disproof of the actual presence of copper minerals in the Lake Superior sediments is difficult. Even if all the Cu present existed as a single copper mineral its concentration would be far below the detection limits of X-ray diffraction. No copper mineral has been identified in the sediments examined by X-ray techniques. The behavior of Cu in the acetate leaching experiments is suggestive of the presence of some sorbed copper, but some of the Cu leached could have come from solution of precipitated copper minerals. Thus all that can be said is that some Cu might be present in the Lake Superior sediments of low redox potential as cuprite, native copper, and possibly as Cu-Fe and Cu sulfides in the strata containing hydrotroilite. This would happen if the concentration of dissolved Cu species in equilibrium with sorbed Cu exceeded the concentration of dissolved copper species that would be in equilibrium with the copper mineral stable at the prevailing Eh and pH. If this happens, the copper mineral will precipitate, and sorbed Cu will be desorbed, until the remaining sorbed Cu is in equilibrium with the dissolved Cu concentration that is in equilibrium with the Cu mineral. Fixation of Cu will remove Cu from this equilibrium, decreasing the mass of precipitated Cu mineral, and thus increasing the proportion of sorbed and fixed copper.

A separate question is whether precipitation of cuprite could be the mechanism by which Cu is originally incorporated in the sediment. The Eh of Lake Superior waters and the topmost centimeter of the sediments are too high to admit of this possibility, unless all of the intermediate Eh values in the sediment close to the sediment-water interface are due to mixing of water and sediment during sampling. In particular, the redox potential of the sediment at Su-1 is too high for the top three centimeters,

yet the Cu analyses of this interval are 490 and 691 ppm, two of the highest Cu concentrations in the lake. The possibility that downward diffusion of copper takes place is considered in a later chapter.

Firmly bound components of detrital minerals: Because the chemical processes of sorption and precipitation probably were less important in glacial time than during later periods, the percentage of the Cu in the glacial sediments that is present as firmly bound constituents of detrital minerals should be higher, and the total Cu in the glacial sediments should be a reasonable maximum for the amount of Cu present in most recent sediments in that form. The glacial sediments have Cu contents ranging from 9 ppm in one light carbonate-rich layer of a varve to 114 ppm in one dark non-carbonate rock flour-rich layer of another varve, and many analyses of mixtures of light and dark varve layers are under 50 ppm. These sediments should contain some sorbed Cu. Even after correction to a carbonate-free basis the Cu content is low. Because most Cu is sorbed or goes into solution on weathering, the absolute concentration of Cu in more recent sediments that is present as firmly bound constituents of detrital minerals should be even less. Hirst's data on Gulf of Paria sediments confirms this: none of the argillaceous sediments that he analyzed had over 45 percent of 25%-acetic acid-leachable Cu, and several had less than one percent.

Some detrital ore mineral fragments may be incorporated in sediments rapidly deposited close to the ore deposits of the Keweenaw peninsula or Isle Royale. This might be true in the case of some of the samples from Keweenaw Bay, in particular, the sample from GS-14 at 46-48 cm depth. Reid (1961) found particles of azurite and malachite in the fine sand

fraction of a core from a nearby locality.

Regional aspects: The Cu content of Lake Superior sediments is unusually high. Morita (1954) found 14 to 260 ppm Cu in the sediments of Japanese lakes. He also finds the average Cu/Zn ratio of Japanese and European shales is 0.4 to 0.55. The average Cu/Zn ratio for surface sediments of Lake Superior is  $1.73 \pm .13$ , three times as high. Moreover, the average Cu/Zn ratio for Lake Superior sediments at depth is  $0.675 \pm .046$ , still above Morita's shale averages, suggesting that the anomalously high Cu content is a regional phenomenon that is long lasting, and not just a surface feature.

The analyses of samples from Lakes Huron and Michigan are too few to be of statistical reliability, but examination of the individual ratios is worthwhile. The Cu/Zn ratios of the Lake Huron Jenkins samples are independent of depth, and average 0.785. In the Lake Michigan Jenkins core the ratio decreases toward the surface from .45 to .22, just the opposite of what happens in Lake Superior. These ratios from Lake Michigan, considerably below Morita's averages, are further evidence for a Zn anomaly in Lake Michigan, as suggested above.

The absolute Cu percentage, like the Cu/Zn ratio, is high in Lake Superior. Potter et al. (1963) find the average Cu content of marine argillaceous sediments to be 37.3 ppm, and the average content of nonmarine argillaceous sediments to be 27.0 ppm. The average Cu content of Lake Superior sediments at depth is 71 ppm, and that of the surface sediments is 230 ppm. Potter et al. list three Cu analyses of Lake Michigan sediments of 24, 72, and 31 ppm, of the same order of magnitude as the 46 and 63 ppm found in this investigation (the surface Cu concentration of 104 ppm found

by this investigation is omitted from this comparison because many samplers miss the sediment at the sediment-water interface, and Potter's only "surface" sample was listed as being from "0-10 cm").

The geographic distribution of high Cu concentrations within Lake Superior is irregular, but not entirely random. In Figure 16 those localities where the Cu/Zn ratio of surface samples is over 3.1 or under 1.2 are noted.

The higher Cu/Zn ratios are found in Keweenaw Bay and the region between Keweenaw Bay and the lake outlet, whereas lower ratios occur to the north and northeast. The Cu deposits of the Keweenaw peninsula are the obvious source of sediments and waters of high Cu concentration. Mining operations on the Keweenaw peninsula have gone on continuously since 1845. Tons of stamp mill refuse have been dumped into streams, and even into Keweenaw Bay itself. Su-9 is a stamp mill "sand," taken from a dumping ground in Keweenaw Bay. Although this is a "waste" product it still contains Cu in excess of 0.1 percent.

In Keweenaw Bay the strong Cu anomaly is not limited to the surface sediments. The sample from GS-14 at 45 cm depth has 674 ppm Cu. Because a sediment at 45 cm depth is pre-mining in age of deposition by any estimate of sedimentation rates it must be concluded that natural processes are capable of at least some Cu enrichment of Lake Superior sediments.

Isle Royale, on the opposite side of the Lake Superior syncline from the Keweenaw peninsula, contains cupriferous strata of the same age. The repeated glaciation of the island has doubtless contributed considerable Cu and Cu-bearing detritus to the Lake Superior system. In this study no samples of sediment from close to the island were available, therefore this must remain as conjecture.

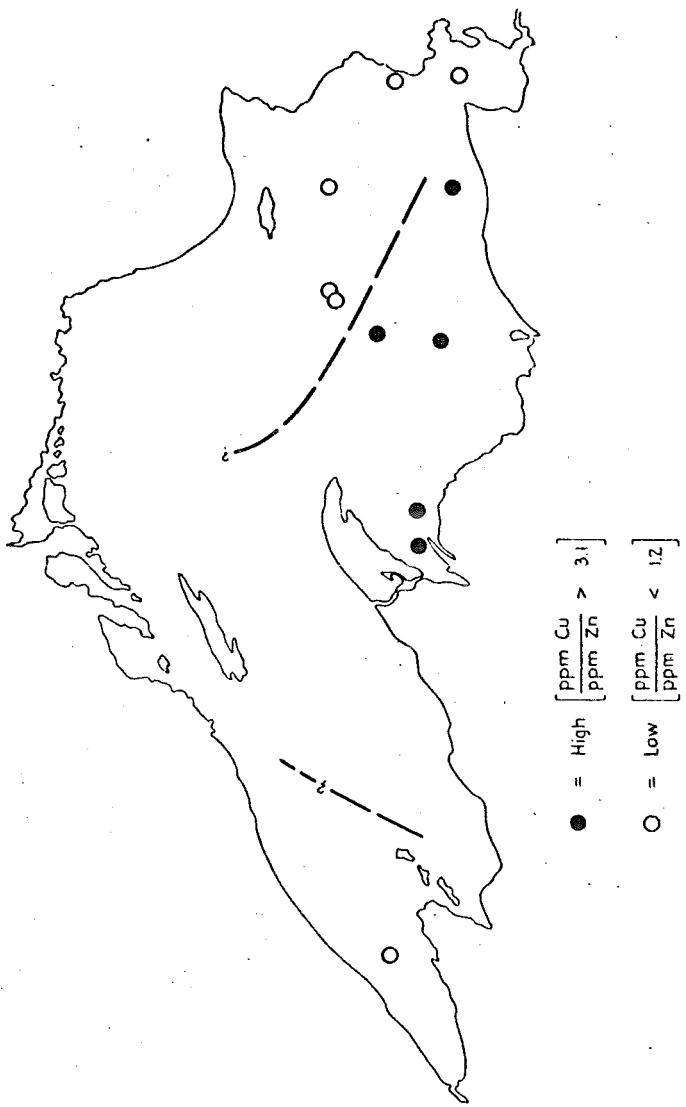


Figure 16. Anomalously high and low  $\text{Cu}/\text{Zn}$  ratios in surface samples in  
Lake Superior

### Lead

Ten analyses for lead have been made to determine if further study is warranted. Sediment samples from the upper 6 cm of sediment of Jenkins surface mud cores in both Lakes Superior and Michigan contain 20 to 35 ppm lead, averaging 29 ppm, whereas sediment samples from lower parts of the same Jenkins cores and from glacial Lake Superior sediments at depth contain 8 to 15 ppm lead, averaging 11 ppm.

Wedepohl (1956) shows that clay minerals contain most of the lead of sediments, because lead is easily sorbed. Therefore, the surface concentration of lead in Lakes Michigan and Superior is most likely an increase in the concentration of sorbed lead, resembling the surface enrichments of zinc and copper.

Table 10 is a compilation of relevant abundance data from the literature. Note that the lead content of the glacial lake sediments of Lake Superior is lower than that of average argillaceous sediments. This cannot be explained solely by the high carbonate and non-carbonate rock flour content of these sediments because the three samples of recent mud from the lower parts of Jenkins cores that contain less rock flour and considerably more clay minerals also contain very little lead.

Because lead is so easily sorbed, most natural lead should enter the basin of deposition as a sorbed constituent rather than as ions in true solution. On the other hand, the surface concentration of lead may be the result of industrial contamination, including lead from the exhaust fumes of internal combustion engines, and lead from industrial sources might enter the Great Lakes in rainfall as well as in runoff from land and effluent dumped directly into streams and lakes.

TABLE 10: LEAD CONTENT OF VARIOUS EARTH MATERIALS

Data in ppm

14 Modern marine argillaceous sediments (Potter et al., 1963)	20.8 $\pm$ 4
19 Modern fresh water argillaceous sediments (Potter et al., 1963)	21.2 $\pm$ 4
Modern non-pelagic clays (Wedepohl, 1956)	20
13 Devonian shales (Shaw, 1954)	16.1 $\pm$ 9.3
20 Ancient marine argillaceous sediments (Potter et al., 1963)	13.3
13 Ancient fresh water argillaceous sediments (Potter et al., 1963)	12.7
Limestones (Wedepohl, 1956)	7
Limestones (Graf, 1960)	8 $\pm$ 4
Sandstones (Wedepohl, 1956)	7
Average basalt (Turekian & Wedepohl, 1961)	5
Average granite (Turekian & Wedepohl, 1961)	20
All Great Lakes sediments analyzed (this study)	18.3
Argillaceous sediments, upper 6 cm, Lakes Superior & Michigan (this study)	29
Argillaceous sediments, below 6 cm, Lakes Superior & Michigan (this study)	11

A more detailed study of the geochemical behavior of lead in the Great Lakes region may be of great help in interpretation of the behavior of lead in all limnologic environments. Determining whether the surface concentration of lead is a natural or man-made phenomenon and estimating the capacity of the sediments to remove excess lead from the lake waters will be practical byproducts of such a study.

### Vanadium

The vanadium content of sediments from eastern and central Lake Superior is  $117 \pm 34$  ppm (s of mean = 8 ppm), whereas the vanadium content of sediments from Keweenaw Bay and western Lake Superior is  $136 \pm 23$  ppm (s of mean = 8.6 ppm), just significantly higher at the 90 percent confidence level. The average V content of sediments from Lakes Michigan and Huron is 132 ppm. At any given locality the V content of sediments at depth is the same as that of the sediments close to the surface. There is a tendency for the V content to decrease slightly in the upper part of Jenkins surface mud cores, and also a tendency for the silty Jenkins cores (GS-2, 7) to have less V than the Jenkins cores with very little silt (GS-18, 23). K and Al behave similarly, which suggests that V is more concentrated in the inorganic clay-sized fraction than in the organic or sand-sized fractions of the sediment. However, these V trends are not always present, nor is their intensity related to the intensity of the trends in Al or K, and the lack of a good correlation of V with any other single sediment parameter indicates that V is relatively abundant in several sediment fractions.

Table 11 summarizes relevant abundance data from the literature. Note that the average basalt contains over ten times as much V as the average granite. This suggests that the higher V content of the sediments of Keweenaw Bay and western Lake Superior reflects local derivation from the basaltic rocks of that region, thus paralleling the behavior of Ti and Sr in this respect. That the difference in the V content of the derived sediments is so much less than the probable difference in the V content of the source rocks suggests that weathering and transport processes must

include powerful "leveling" processes, and again suggests that the V is relatively abundant in several sediment fractions, only one of which is unweathered rock flour. There may be considerable loss as well as redistribution of V in weathering.

It is not obvious why the V content of Lakes Michigan and Huron should resemble western rather than eastern Lake Superior. Some factors other than provenance may be involved. The sedimentary geochemical behavior of V is not well understood. Several authors (Rankama & Sahama, 1959, Le Riche, 1959) find a positive correlation between V and organic matter, yet Le Riche (*ibid*) found on detailed analysis that the V was associated with the clay minerals of the sediment, and the studies of Sugawara et al (1956) show that V is not accumulated by live plankton, suggesting that organisms are probably not responsible for water to sediment transfer of V. Considerable V is thought to be incorporated at the site of weathering, and Hirst (1962) found that the acid soluble fraction of V in argillaceous sediments from the Gulf of Paria was only 2.8 to 15 percent of the total V. On the other hand, Potter et al. (1963) found V to be a reliable discriminator of fresh water and marine sediments, which suggests that there must be some sediment - water exchange taking place within the basin of deposition. The results of this investigation do not prove or disprove any of these partly conflicting hypothesis, but rather, suggest that the truth lies somewhere in between.

The V analyses of Lake Michigan sediments made in this study are 30 percent higher than the V analyses of similar Lake Michigan sediments reported by Potter et al. (1963). If the discrepancy is the result of systematic analytical bias the actual V content of all of the Lake Superior sediments is closer to the average V content of the nonmarine

sediments than to the average V content of the marine sediments analyzed by Potter et al. However, the provenance-related distribution of V within Lake Superior shows that use of the absolute V content of sediments as a discriminator of fresh water from marine sediments is not without its inherent risks. In other basins, anomalies in the V content of source rocks might easily lead to misinterpretation.

TABLE 11: VANADIUM CONTENT OF VARIOUS EARTH MATERIALS

Data in ppm

14 modern marine argillaceous sediments (Potter et al, 1963)	$125 \pm 7$
19 modern fresh water argillaceous sediments (Potter et al, 1963)	$79 \pm 4$
20 ancient marine argillaceous sediments (Potter et al, 1963)	116
13 ancient fresh water argillaceous sediments (Potter et al, 1963)	74
63 Devonian pelites (Shaw, 1954)	$120 \pm 38.5$
14 Mn shales (Mohr, 1955)	164
18 Ordovician phyllites (Goldschmidt, 1954)	200
14 black shales (Spencer, 1957)	262
Carbonate rocks (Graf, 1960)	$15 \pm 8 ?$
Basalt (Turekian & Wedepohl, 1961)	250
Granite (Turekian & Wedepohl, 1961)	20
Argillaceous sediments, Lakes Superior, Michigan, and Huron (this study)	$125 \pm 19$

### Gallium

The Gallium content of Lake Superior sediments is  $13.2 \pm 5.4$  ppm. There is a slight upward increase in the Ga content of Jenkins cores, hardly greater than the analytical uncertainty, but possibly significant, because it occurs in most of the Jenkins sequences analyzed. Some of the lowest Ga analyses are from sediments at depth, but the average Ga content of sediments at depth cannot be distinguished statistically from the average Ga content of surface sediments. The correlation of Ga and Al, Ga and V, Ga and Zn, or Ga and Ni is poor, and there is no single element closely correlated with the reported Ga analyses of the Lake Superior sediments.

The factor most responsible for this seeming independence is the fact that the standard deviation of all Ga analyses for the lake,  $\pm 5.4$  ppm, is probably of the same order of magnitude as the standard deviation of the analytical technique, because the Ga content of these sediments is close to the analytical limit of sensitivity. Under these circumstances no correlation would be shown by the analytical results even if a correlation did in fact exist.

The lack of strong correlations is also explained by previous studies of the geochemical behavior of Ga. Gallium substitutes for aluminum in silicates. Like V, some Ga is incorporated in clay minerals at the site of weathering, but Potter et al. (1963) show that another fraction of the Ga apparently goes into solution and is incorporated in argillaceous sediments in basins of deposition. Table 12, which summarizes relevant abundance data from the literature, shows that the Ga content of igneous rocks is similar to that of argillaceous rocks, and the Ga content of

granites is little higher than that of basalts. Because of clay mineral formation the difference between the Ga content of argillaceous sediments derived from granitic provinces and derived from basaltic provinces should be even less than the differences between parent rocks. Thus, we may conclude that:

- a) Sediments at depth and near-surface sediments have similar Ga contents probably because the rock flour prevalent at depth has nearly the same Ga content as the clay minerals prevalent near the surface.
- b) There is no geographic trend in Ga distribution within Lake Superior because weathering processes probably reduce the small difference in Ga content of the two major petrologic provinces.

Reference to Table 12 shows that the Ga content of Lake Superior sediments is similar to that of most fresh-water argillaceous sediments, suggesting that the content of non-detrital Ga, incorporated in the sediment in the basin of deposition, is low. The slight surface enrichment in Ga observed may be an increase in non-detrital Ga.

In contrast, the three Lake Michigan samples analyzed would be categorized as marine sediments on the basis of their high Ga content (19 to 22 ppm). The excess Ga may be inherited from marine Paleozoic argillaceous sediments of the Lake Michigan basin, but neither the present writer nor Potter et al. (1963), who first noted the Lake Michigan anomaly, have conclusive evidence as to the source of the anomalous Ga.

TABLE 12: GALLIUM CONTENT OF VARIOUS EARTH MATERIALS

Data in ppm

14 modern marine argillaceous sediments (Potter et al., 1963)	20.0 $\pm$ 4
19 modern fresh water argillaceous sediments (Potter et al., 1963)	13.7 $\pm$ 4
20 ancient marine argillaceous sediments (Potter et al., 1963)	25.3 $\pm$ 9.5
13 ancient fresh water argillaceous sediments (Potter et al., 1963)	16.2 $\pm$ 5
Carbonate Rocks (Graf, 1960)	2.5 $\pm$ 1.5
63 Devonian Pelites (Shaw, 1954)	18.8 $\pm$ 6.3
Average Basalt (Burton et al, 1959)	12
Average Granite (Burton et al, 1959)	18
29 Lake Superior argillaceous sediments, this study	13.2 $\pm$ 5.4

### Bromine

General: Figure 8 shows that bromine is concentrated in the clay size fraction of Lake Superior sediments. The bromine content of the sediments increases upward toward the sediment-water interface, but the increase is not regular, and the magnitude of the increase and the depths at which it can be detected are dependent on sediment type.

The Br content is highest in the brown sediments, where two types of upward increases occur. First, the uppermost three to ten centimeters often have a higher concentration of Br than the sediment immediately below. Examples are shown in Figures 11 and 12 (note that sample JD in Figure 12 is probably a sample of gray clay). An example of an exception is GS-23 (Appendix 3) in which there is no significant change in Br content within the Jenkins sequence. Second, a more gradual increase in the Br content occurs over one or two meters of brown sediment, between the greatest depths cored and the depths at which the more rapid increase close to the surface occurs. For example, in GS-7 HPC, brown sediment at 160 to 190 cm contains 76 to 78 ppm Br, whereas brown sediment from 30 to 75 cm contains 87 to 92 ppm Br.

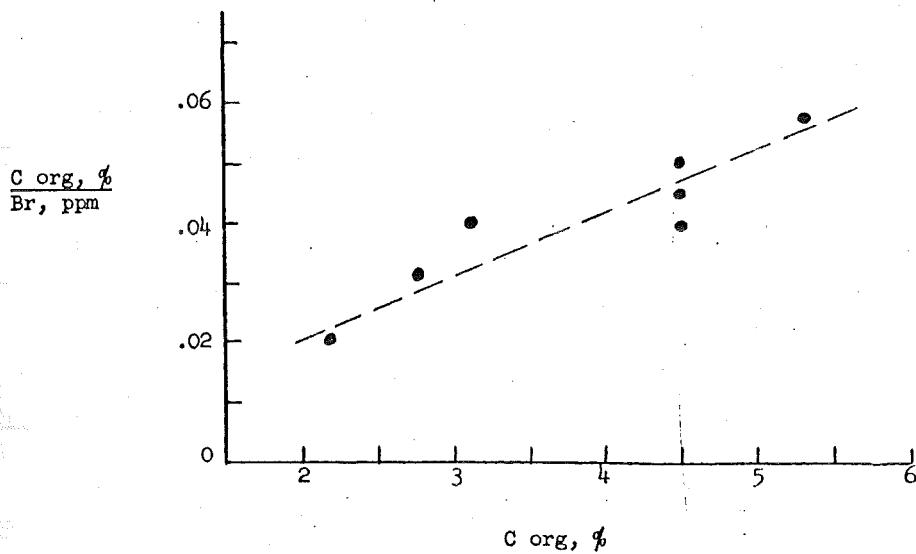
The Br content of massive gray clay is less than that of overlying brown sediment but greater than that of underlying varved gray or red clay. As in the brown sediment, a gradual upward increase in the bromine content is often observed. For instance, the gray clay between 150 and 215 cm at GS-13 contains 26 to 41 ppm Br, whereas higher gray clay samples, between 30 and 95 cm, have 44 to 59 ppm Br. The overlying brown sediment has 141 ppm Br, and the underlying varved gray clay (the HPB sample) has 4 (?) ppm. An unusually low Br content for massive gray clay occurs in GS-31,

where the gray clay between 64 and 80 cm contains no detectable Br (less than the analytical limit of sensitivity of 1 to 2 ppm).

The Br content is least in varved gray or red and massive red clays, where about all that can be said is that the Br content is always less than 4 ppm, and may be considerably less because of analytical uncertainty. In Figure 17 the Br and organic carbon content of Jenkins samples are compared. The analyses of organic carbon were made by Dr. J. A. Borchardt. C org increases toward the surface, and Br increases slightly toward the surface or remains relatively constant within the uppermost 20 cm of the sediment in the two localities analyzed. Consequently, Figure 17 shows that the C org/Br ratio increases as C org increases, that is, the rate of increase in C org is higher than the rate of increase of Br.

Evidence from the literature: Information on the distribution of Br in non-evaporitic recent sediments is not extensive. The study of Mun and Bazilevich (1962) shows that the content of Br in sediments increases with the concentration of C org. This paper is particularly relevant because it is a study of lacustrine muds whose organic content is similar to that of Lake Superior sediments. Uptake of Br by organisms and organic matter is accomplished by a variety of mechanisms, but it is convenient to follow the lead of Mun and Bazilevich and refer to this uptake as sorption, inasmuch as only part of the uptake seems to be metabolic. Part of the evidence for the connection of organic matter and Br is the purely negative observation that there is just no other fraction of the sediment that can take up the anion. Clays are known to have an anion exchange capacity, mostly associated with the edges of phyllosilicate sheets (van Olphen, 1962), but the capacity is small. Br minerals per se are found only in

FIGURE 17: VARIATION OF BROMINE CONTENT WITH  
BROMINE/ORGANIC CARBON RATIO IN  
SOME JENKINS SURFACE MUD CORES



supersaline residues. Thus the evidence for organic "sorption," both from the standpoint of this and previous investigations, is reasonable.

Cause of the near-surface enrichment often observed in Jenkins cores: In Lake Superior the interpretation of the increase in Br concentration just below the sediment-water interface and the increase of C org/Br ratio with increase in C org in Jenkins cores depends on the interpretation of the increase in C org. If the near-surface upward increase of C org is caused by continuing decay processes wherever organic C is present, then we might expect the C org/Br ratio to change as it does, provided the decay products escaped more readily than Br. If this is the case, then the concentration of the less mobile component, Br, would be a better indicator of changes in the primary productivity of the lake than the more mobile component, C org. On the other hand, if the near-surface increase in C org is due to an increase in the organic productivity, then the change in the C org/Br ratio might be indicative of a limited supply of Br in the lake. As the productivity increases a greater percentage of available Br is utilized for essential organic processes, and less is passively "sorbed." The writer favors the explanation of continuing decay to explain the change of the C org/Br ratio in the Jenkins cores.

A further cautionary word is necessary in regard to the statement that Br is "less mobile." Mun and Bazilevich (1962) find that the Br content of pore solutions is always 2 to 10 times that of the corresponding surface lake water, and that the absolute Br content in the pore solutions increases with depth. This shows that whatever may be the relationship between the mobility of Br and organic decay products, Br is in itself a relatively mobile element, likely to migrate in time if water movement or

concentration gradients are present. Therefore, the near-surface increase in Br observed in Jenkins cores may be due to escape of Br as decay proceeds, and the change in C org/Br ratio only defines a minimum for the amount of organic decay that has taken place.

Explanation of the behavior of bromine at depth: In the light of the above it is not difficult to interpret the variation in Br content at depth in a qualitative sense. The upward increase in the concentration of Br observed in the sediment sequence varved clay-massive gray clay-brown sediment and the gradual upward increases observed both in the gray clay and in the brown sediment are the results of the interaction of three processes:

- 1) Organic productivity has increased since glacial time.
- 2) The rate of sedimentation has decreased since glacial time.
- 3) In older sediments more organic decay has occurred, and a greater percentage of Br has escaped.

### Lithium

Ten lithium analyses were made in order to evaluate the importance of further study. The average lithium content of six surface sediments analyzed is 45 ppm, whereas the average lithium content of four red and gray varved clays is 96 ppm. Li does not vary systematically within the two Jenkins surface mud profiles, nor is there a systematic variation between light and dark layers of varves.

Thus the behavior of Li is antipathetic to that of the organic and the clay mineral fractions of the sediments, and the high Li content of the glacial sediments must be indicative of an anomalously high Li content of either the carbonate or the non-carbonate rock flour fractions of the sediments.

Table 13 summarizes relevant abundance data from the literature. Although carbonates apparently have as much Li as igneous rocks, some of the Li of carbonate rocks is probably bound in the argillaceous insoluble residue (Graf, 1960). Why the carbonate and its associated insoluble residue or the igneous rocks of the Lake Superior region would have an anomalously high Li content is far from obvious, and further study must be made if this distribution is to be adequately explained.

Lithium is not sorbed in clays, but enters the vacant octahedral positions in the dioctahedral magnesium clay minerals at the site of weathering (Horstman, 1957). For this reason there may be little sediment-water exchange of lithium within Lake Superior itself.

TABLE 13: LITHIUM CONTENT OF VARIOUS EARTH MATERIALS

Data in ppm

Carbonate rocks (Graf, 1960)	20 $\pm$ 17
Average Basalt (Heier & Adams, 1964)	10
Average Granite (Heier & Adams, 1964)	30
Devonian Pelites (Shaw, 1954)	55
Shales (Horstman, 1957)	66
Shales (Greene, 1959)	72
Lake Superior surface sediments (this study)	45
Lake Superior glacial sediments (this study)	96

### Boron

The boron content of Lake Superior sediments is  $25.9 \pm 15$  ppm ( $s$  of mean = 2.2 ppm). This average is based on only 35 determinations, most of which are surface samples, but there is no apparent difference between the B content of surface samples and samples at depth. In Jenkins surface mud cores the B content of successive slices shows no consistent behavior. Some sequences could be interpreted as being a decrease toward the surface; others suggest an increase toward the surface, especially if the deepest Jenkins sample is ignored. No correlation of B and Si, B and K, or B and Al is apparent, sediments of high Si and low Al and K (high silt content) (e.g., GS-2-62-Jenkins) having as high or higher boron contents as finer grained sediments of lower Si and higher Al and K (e.g., GS-23-62-Jenkins).

The average B content of 26 ppm is even lower than the 45.6 ppm average found by Potter et al. (1963) for 19 recent non-marine sediments, and is considerably lower than the 89.6 ppm found by the same authors for 14 modern marine sediments. This is consistent with the studies of Landergren (1945) and Harder (1959) which show that the B content of argillaceous sediments is proportional to the salinity (i.e. boron content) of the waters in the basin of deposition. The B is both sorbed on the clay minerals and fixed in the clays as a structural constituent, substituting for aluminum (Harder, 1961). Therefore, the low B content of Lake Superior sediments is indicative of the fresh water environment of deposition.

The independence of B content and grain size shown in the Lake Superior sediments by the lack of correlation between B and Si, Al, and K,

suggests that a significant fraction of B may be in the silt and sand fractions, as well as in the clay fraction. In the coarser fractions the most probable host is tourmaline, which has been found in the preliminary heavy mineral studies (Farrand, 1963). The ratio of boron in heavy minerals to boron in clay minerals is not known, but an estimate might be made by first assuming that the B concentrations in the weight fractions are equal, as suggested by the analyses. In Lake Superior, where low salinities minimize the concentration of sorbed B it is not surprising that other forms should be significant.

The average B content of Great Lakes waters and sediments and marine waters and sediments are listed in Table 14. The correlation of B in sediments and B in overlying water is qualitatively excellent, but quantitatively perplexing. If the Superior and oceanic sediment and water concentrations are used to determine the constants of the Langmuir adsorption isotherm it is found that the B content of Lake Huron and Lake Michigan sediments is too high, which shows that something besides sorption equilibria is important here. The B content of Lake Michigan sediments is particularly high considering the difference between the B content of marine and Lake Michigan waters. The three analyses of B made by Potter et al.(1963) on Lake Michigan sediments and included in Table 14 were by far the three highest non-marine B analyses found in that study. Therefore it is probable that the excess B of Lake Michigan sediments is not sorbed, but is present in some other state. The bedrock of the Lake Michigan basin is composed entirely of sedimentary rocks, most of which are marine in origin. The excess B may be in part tourmaline, in part B substituting for Al in the structure of clays formed or altered in the marine environment. In this respect it is interesting to note that the average B

TABLE 14: AVERAGE BORON CONTENT OF GREAT LAKES  
SEDIMENTS AND WATERS

(sources in parenthesis)

Lake	Number of analyses	Sediment B, ppm	Number of analyses	Water B, ppb
Superior	35	26(1)	6	38(2)
Huron	6	51(1)	6	53(2)
Michigan	6	73(1,3)	6	64(2)
Ocean	14	90(3)		4,650(4)

Sources:

- (1) This study
- (2) U. S. D. H. E. W. National Water Quality Network Data Compilations, 1959-60, 1960-61.
- (3) Potter, et al, 1963, 3 analyses of B in sediments of Lake Michigan are 73, 95, 99. The 14 marine sediments are a representative suite.
- (4) Sverdrup et al, 1942.

content of Illinois Pennsylvanian shales, 130 ppm (Ostrum, 1957), is higher than the average of 90 ppm found by Potter et al. (1963) for marine argillaceous sediments. It is apparent that the B content of Lake Michigan may be strongly affected by the nature of its basin geology.

### Rubidium

Figure 8 and Appendix 5 show that rubidium is concentrated in but not limited to the clay size fraction of Lake Superior sediments, as the coarser size fractions have about half as much Rb as the clay size fraction.

The Rb of Lake Superior surface sediments is  $114 \pm 41$  ppm, and that of sediments at depth is  $147 \pm 40$ . The standard deviations of the means are 6 and 5, respectively, therefore the means are significantly different, although there is an overlap in the concentration ranges. In some Jenkins cores there is a 10 to 30 percent upward decrease in Rb, but more often the Rb content of the Jenkins sample does not change significantly in the interval cored.

There is a positive correlation between K and Rb. The average Rb/K ratio of surface sediments,  $4.0 \times 10^{-3}$ , is statistically indistinguishable from the average Rb/K ratio of sediments at depth, which is  $4.2 \times 10^{-3}$ .

The distribution of Rb among the size fractions of the sediment implies that Rb is contained in several mineralogic fractions. Rb, slightly larger than K, substitutes for the latter in most potassium-bearing minerals (capture). Therefore the Rb of the coarse fractions is most likely contained in potassic feldspars, and the Rb of the clay size fraction must be contained both in potassic feldspars and in clay minerals. The surface sediments of Lake Superior contain more clay minerals than the sediments at depth, therefore the constancy of the Rb/K ratio shows that the Rb/K ratios of rock flour and clay minerals must be similar.

The average absolute concentrations of Rb and K of the surface sediments are slightly less than those of sediments at depth because, as

TABLE 15: RUBIDIUM CONTENT OF VARIOUS EARTH MATERIALS

	ppm
Average Limestone (Graf, 1960)	$70 \pm 40$
Average Basalt (Taylor, 1964)	30
Average Granite (Taylor, 1964)	150
Average Shale (Turekian & Wedepohl, 1960)	140
Average surface sediment, Lake Superior (this study)	$114 \pm 6$
Average subsurface sediment, Lake Superior (this study)	$147 \pm 5$

stated above, quartz (often of silt size) is a larger fraction of the average surface sediment.

Table 15 summarizes abundance data from the literature. The Rb as well as the K content of igneous rocks increases with progressive magmatic differentiation (Horstman, 1957). Note that although Rb is 5 times as abundant in the average granitic rock as in the average basaltic rock, there is no apparent difference in the Rb content of surface sediments derived from the granitic eastern province and the basaltic western province of Lake Superior source rocks. This is evidence for considerable chemical "leveling" during the weathering processes in which clay minerals are formed. In weathering K and Rb are still linked, although K moves out of the weathering profile somewhat more rapidly than Rb. Rb should be sorbed more readily than K, but this has not been documented in nature (Horstman, 1957). Note in Table 15 that shales, and also Lake Superior sediments, are not enriched in Rb with respect to granitic igneous rocks.

### Strontium

The concentration of strontium in the surface sediments of Lake Superior is  $154 \pm 42$  ppm (s of mean = 7 ppm). Figure 8 shows that although there is a Sr maximum in the fine silt fraction the element is relatively abundant in all size fractions, and one would not expect the Sr content of surface sediments to vary much with variation in median diameter. Such is the case, as shown by the random scatter in a plot of the variation of Sr with  $\text{SiO}_2$  in surface sediments.

The Sr content of Jenkins cores does not decrease toward the surface, showing a parallelism of Sr and Ca and divergence from K, Al, and often Si in this respect. The writer interprets this as an increase in the proportion of organic Ca and Sr bound in the tests of plankton and other organisms, compensating for a concomitant decrease in the inorganic fraction and its Ca and Sr. An alternate interpretation would be that there has been an increase in sorption of Ca and Sr by the inorganic fraction or that considerable Ca and Sr are sorbed by the organic fraction, but this is not supported by the size distribution of Sr shown in Figure 8. The sample analyzed is an orange peel sample from close to the surface. In it considerable Sr is bound in fragments larger than clay size. Moreover, increased sorption by the inorganic fraction would imply that the Ca and Sr concentrations in Lake Superior water have increased, and this is improbable in the light of the history of carbonates in the lake as outlined above. Also, most uptake of Ca and Sr by organisms is metabolic (Marshall, 1961), which suggests that the latter of the two alternatives is also unlikely.

The concentration of Sr in surface samples from Lake Michigan and

Lake Huron is  $145 \pm 21$  ppm (s of mean = 8 ppm). Although this is virtually identical to the surface average of Lake Superior it does not necessarily follow that the distribution of Sr among the sediment components is the same.

Figure 18 is a plot of the variation of Sr with Ca for all samples analyzed for both elements. Several trends shown are significant.

In the sediments of low Ca content from the eastern half of the lake Sr is positively correlated with Ca, the trend being shown by the dashed line. The slope of the line is not a constant Sr/Ca ratio, however, as Sr/Ca increases slightly as Sr increases. If some of the Sr present is sorbed this might be explained by the known preferential sorption of Sr over Ca.

In the sediments of low Ca content from Keweenaw Bay and the western half of the lake, Sr is positively correlated with Ca, but the average Sr/Ca ratio is lower than in the samples from the eastern half of the lake, primarily because the Ca content is higher. Both Keweenaw Bay and the western half of the lake receive detritus from the basalts and other basic and ultrabasic rocks of late Precambrian age on both limbs of the Lake Superior syncline. In these basic igneous rocks calcium-bearing silicates that are low in Sr are common; therefore the lower Sr/Ca ratio of the sediments of these areas is explained as the admixture of detrital, Ca-bearing, Sr-poor, silicates.

The varved clays from any part of the lake, high in Ca, vary widely in Sr content and in Sr/Ca ratio. The average Sr content is 247 ppm, almost 100 ppm higher than the average of surface sediments, but there is considerable overlap in the ranges, and the average atoms Sr/1000 atoms Ca ratio of the varved clays, 1.8, is much lower than the average ratio

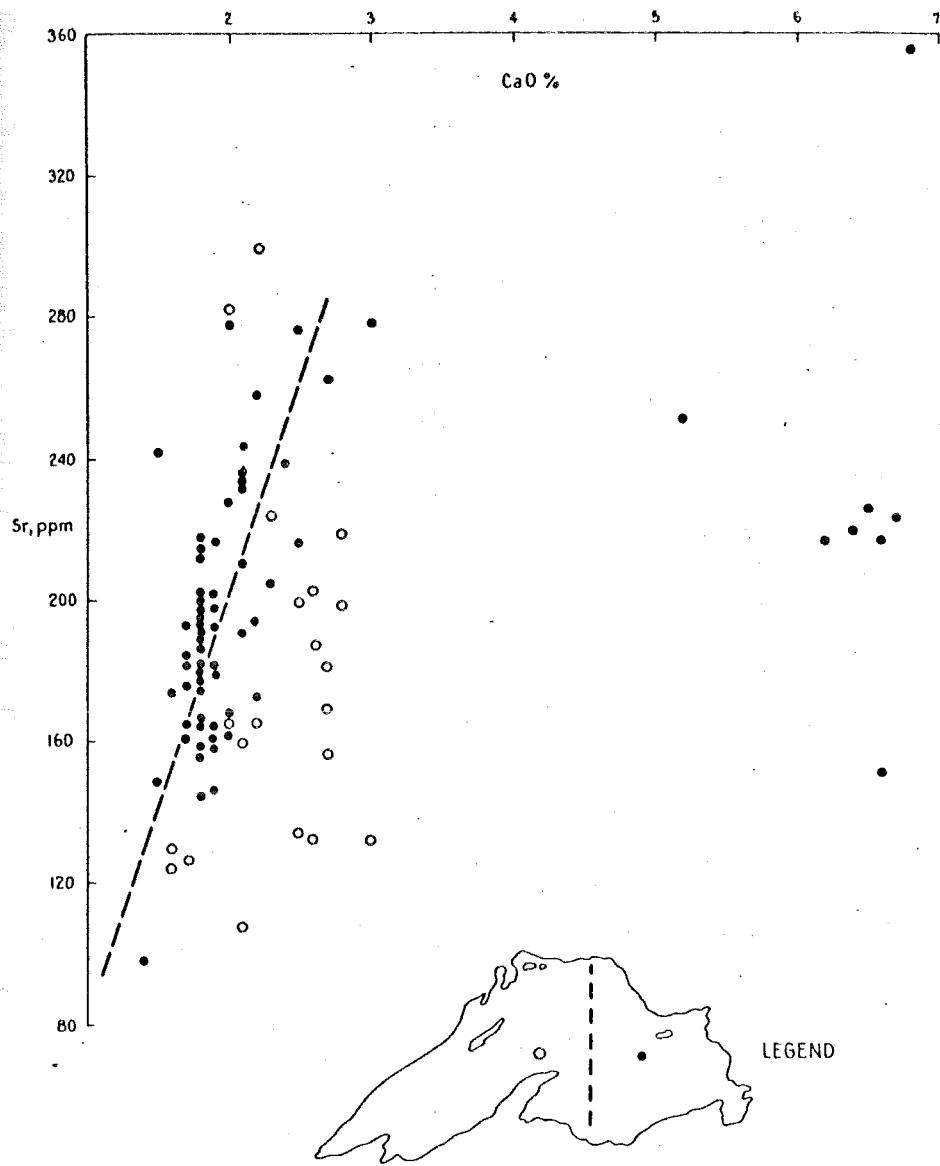


Figure 18. Variation of Strontium with Calcium in Lake Superior sediments.

for low-Ca sediments, which is 3.5. Nevertheless, when the light and dark layers of a varve are compared the Sr content is higher in the carbonate-rich light layer than in the carbonate-poorer dark layer.

The following is a likely explanation for the trends noted immediately above: The Paleozoic carbonate rocks north and northeast of the Lake Superior basin, from which the carbonate of the varved clay has been derived, should have a low Sr/1000 Ca ratio, because the Sr content of carbonates decreases with increasing age as Sr is expelled from the carbonate structure during recrystallization. Kulp et al. (1952) find that the average atoms Sr/1000 atoms Ca ratio for North American Paleozoic carbonates is 0.60. In contrast, Kleerekoper (1961) has found that the ratio in plankton from Lakes Simcoe, Ontario, and Huron is 1.37. Clays, on a carbonate-free basis, have an even higher ratio (Turekian & Kulp, 1956). Therefore the varved clays have a lower ratio because their principal Sr-bearing component, Paleozoic carbonate, has a lower ratio. Even though other sediment fractions in the varved clays have higher ratios, the concentration of Sr is directly proportional to the abundance of carbonate, because the absolute amount of Ca and Sr bound in carbonate is large compared to that in other fractions. That the ratios for Lake Superior sediments, both surface and at depth, are higher than the ratios for carbonate and plankton probably shows that some of the Sr is in the clay fraction, but caution should be used in making quantitative comparisons. We infer that the Paleozoic rocks to the northeast have a ratio similar to the average for North American carbonates. We infer that plankton from Lake Superior has the same ratio as plankton from Lakes Simcoe, Ontario, and Huron. But it is known that the sorption of Sr in clays is a function of the Sr/Ca ratio in solution as well as of the

absolute concentrations of Ca and Sr in solution (Robinson, 1962), and similar but by no means identical equilibria that govern the metabolic uptake of Sr and Ca by organisms have been defined quantitatively by Marshall (1962). Now that the basic mechanisms are understood, a detailed study of Ca and Sr and their interrelationships, taking into account both organic and inorganic mechanisms, and making further analyses of sediment fractions, source rocks, and water chemistry should be made.

In summary, the distribution of Sr is best explained by considering the sediment to be composed of independent, Sr-bearing fractions, detrital Paleozoic carbonate, clays (sorbent), organogenic carbonate, and detrital Ca-bearing silicates. The Sr/Ca ratios of these fractions differ considerably, leading to variations in the Sr/Ca ratios of sediments deposited in different areas and in the same area at different times.

THE ROLE OF ORGANISMS AND ORGANIC MATTER  
IN THE DISTRIBUTION OF TRACE ELEMENTS IN  
LAKE SUPERIOR

Theoretical

General: The role of organic matter in the distribution of trace elements in Lake Superior and its sediments has been considered in detail so far only in connection with the distribution of bromine. In this section some general considerations will be followed by an appraisal of the relationship between organic matter, organisms, and other trace elements in Lake Superior.

Organisms and organic matter play three significant roles in the distribution of trace elements to and in sediments:

- a) They act as intermediate hosts in the transfer of trace elements from water to sediment (scavenging effect).
- b) They act as chemical regulators of the sediment environment.
- c) Organic matter is a sediment component, to which trace elements may be attached by sorption, chelation, or other bonds.

Scavenging effect: Organisms take up trace elements from both the particulate and dissolved matter in lake water, then carry the trace elements down to the substrate as they molt or die. This has been called the "scavenging effect" by Goldberg (1954) and others. Uptake may be metabolic or sorptive in nature. For example, Bachman (1963) found Zn uptake to be sorptive at the concentration levels of his studies, but suggested that a greater percentage of the Zn uptake might be metabolic.

at lower Zn concentrations. Marshall (1962), on the other hand, found that uptake of Sr was at least 95 percent metabolic.

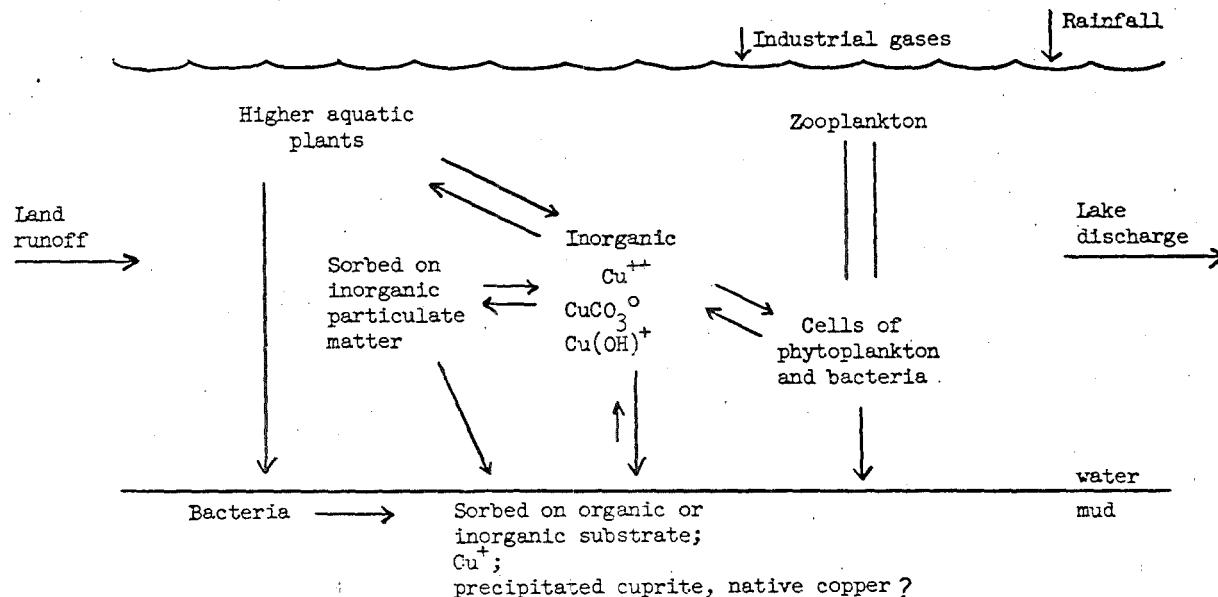
Sedimentation follows death or molting. The efficiency of trace element removal depends in part on the rate of decay of the test or organism. Kleerekoper (1953) finds that plankton begin to decay long before they reach the sediment-water interface, and additional decay will take place at the sediment-water interface, because of the relatively high concentration of microorganisms found in that environment. Bacterial action in the mud itself will promote decay processes after burial, raising the trace element concentrations in interstitial waters, favoring sorption, fixation, precipitation, chelation, and at the same time establishing a concentration gradient that favors upward migration and escape of most trace elements.

The cycle of a trace element within Lake-water-sediment systems has been diagrammed by many authors (e.g., Hays and Phillips, 1958, Bachmann, 1961), and Figure 19 is such a diagram for copper. The distinction between sorbed and metabolic Cu has not been made; probably the types of organisms noted contain both. With minor modifications, Figure 19 will illustrate the cycle of almost all of the moderately soluble trace elements studied in this investigation.

Organisms as environmental controls: Both the Eh and pH of sediments are partially dependent on organic activity in the sediment. Release of  $\text{CO}_2$  by bacterial decay of organic matter and release of  $\text{H}^+$  by sulfate reducing bacteria lower the pH. The Eh of a sediment is dependent on the balance of downward diffusion of oxygen and the metabolic activity of bacteria, which is dependent on the amount of organic matter present

FIGURE 19: DIAGRAMMATIC SUMMARY OF THE COPPER CYCLE IN LAKES

After Hayes & Phillips, 1958; Bachman, 1961



(Baas Becking and Moore, 1959).

Organic matter as a chemical "host:" As shown in the previous sections covering individual elements the literature contains many examples of the capacity of organic matter to take up trace elements in non-metabolic processes. The division of this trace element uptake into "sorbed" and "fixed" fractions depending on the rapidity of exchange is a useful oversimplification. Because it is not likely that all the sorptive or fixative uptake by a sediment will be limited to sorption or fixation by one sediment fraction it is important to consider the relative importance of the various components as substrates.

One approach to this problem is that of Morita (1954), who examined the distribution of Cu in Japanese lakes. He determined the Cu content of algae in a lake, assumed that the organic matter of the sediment below had the same percent Cu by dry weight, and then divided the sediment Cu into an organic and an inorganic fraction on that basis. The sediments he studied had 5 to 26 percent of the total Cu present in the organic fraction. However, Bachman (Table 9) has shown that the uptake of Zn by cells of a dead alga is greater than the uptake by living organisms, and it has been observed that the Zn uptake by the organic matter of sediments is apparently even greater (Rankama and Sahama, 1950, p. 713). It is likely that this is true for elements other than Zn as well, and the method of Morita probably gives low results for the percentage of an element contained in the organic fraction.

Another approach to the problem is that of Rapport (in van der Molen, 1957, p. 37), who studied the adsorptive properties of soils. He found empirically that the exchange capacity of soils correlated well with the

soil content of "active matter," where "active matter" is defined by:

$$\text{active matter} = \text{clay-sized fraction} (> 2\mu) \text{ plus } 3 \times \text{organic matter.}$$

Note that the clay size fraction is used in the definition. Because the clay size fraction contains much of the organic matter the equation for active matter implies that the organic matter is actually more than three times as capacious a sorption substrate per unit weight than the inorganic matter of the clay size fraction. Other investigators arrive at essentially similar results, shown in Table 16. This approach is basically sound, as it recognizes that there will be a distribution of the exchangeable element between the substrates present in proportion to their masses and sorption capacities. It is still only an approximation, because it is primarily a determination of rapid sorptive processes rather than long-term fixation processes, and also because it is based on the total exchange capacity of the sediment. The relative sorption and fixation by organic and inorganic matter will be different for different cations because of the great variety of specific mechanisms, differing from element to element, which are responsible for ion uptake by a sediment.

TABLE 16: CATION EXCHANGE CAPACITY OF CLAY MINERALS AND  
ORGANIC MATTER

Data from Grim, 1953, p. 132, except as noted.

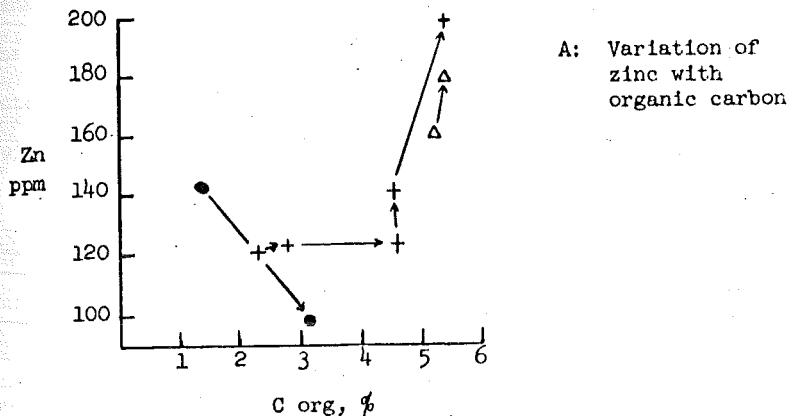
<u>Mineral</u>	C.E.C., m.e./100 g at pH 7
Kaolinite	3-15
Montmorillonites	70-100
Illites	10-40
Vermiculite	100-150
Chlorite	10-40
Glauconite	11-20
Organic Matter	150-500
Organic Matter (Australian soils - Hosking, J. S., 1948)	120-190, avg 170

### Evidence from Lake Superior Sediments

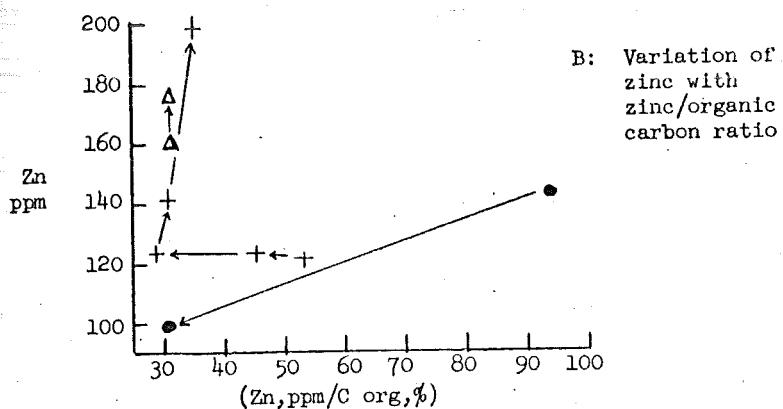
We are concerned not only with the problem of determining what fraction of a trace element is now sorbed on an organic substrate but also with the problem of determining whether the element was initially incorporated in the sediment by uptake and sedimentation of organisms. Another related question is whether the amount of organic matter in the sediment or the level of organic productivity in the water above are the major controls of the trace element concentration in the sediment. These questions have been considered previously in relation to the distribution of Br, and some of the problems encountered there are evident in the discussion below.

Zinc: The Zn concentration is plotted against C org in Figure 20A, and against the Zn/C org ratio in Figure 20B for the three Jenkins cores analyzed for C org by Dr. J. A. Borchardt. Figure 20A shows that Zn and C org are generally correlated, but in Figure 20B a marked reversal in trend is evident. In the lower portions of the Jenkins cores, where both C org and Zn are low, the increase in C org is not accompanied by an increase in Zn, and the Zn/C org ratio decreases as the surface is approached. In the higher portions of the Jenkins cores the Zn/C org ratio is relatively constant, but Zn increases at a rate slightly higher than that of C org, therefore the Zn/C org ratio increases. One does not feel very confident merely on the basis of this limited data, but these plots, especially Figure 20B, do suggest that some factor in addition to the total amount of organic matter present in the sediment influences the Zn concentration.

FIGURE 20: ZINC AND ORGANIC CARBON IN  
JENKINS SURFACE MUD CORES



A: Variation of zinc with organic carbon



B: Variation of zinc with zinc/organic carbon ratio

Legend:

- $\Delta$  GS-7-62 Jenkins
- $\bullet$  GS-10-62 Jenkins (JA, JB)
- $+$  GS-23-62 Jenkins

Arrows indicate "up" in sediment column

It was suggested above that the Br content might be a better indication of the organic productivity than total organic matter. Figure 21 is a plot of the variation of zinc with the Zn/Br ratio for four of the Jenkins cores. As Zn increases the ratio of Zn/Br increases. However, the Zn/Br ratio is not a regular function of depth below the sediment-water interface, particularly in GS-7, where it fluctuates wildly. Evidently no straightforward relationship applies here either.

Figure 13 and the accompanying text showed that in the deeper cores the Zn was largely bound by the inorganic clay fraction, but that a definite contribution related to the bromine content, and by inference, to organic activity, was also present. Because the Br content of the surface sediments is much higher it is probable that the contribution related to the bromine is also much higher. What is lacking, however, is a clear cut cause and effect relationship that would prove this.

Bachman's studies of Zn show that the scavenging effect should be important in the Zn cycle, and that some of this Zn should be incorporated in the organic fraction of the sediment. One also feels intuitively that as bacterial decay occurs in the sediment a greater fraction of the Zn should eventually be bound in the inorganic fraction, especially in view of the known mechanism of Zn fixation by clays.

Copper: Much the same considerations apply in the case of Cu. The Cu distribution is like that of Zn in that the increase in concentration is gradual in the lower part of Jenkins cores and more precipitous in the upper half. However, the percentage increase is greater, and as a consequence, plots of Cu versus C org, Cu versus Cu/C org, and Cu versus Cu/Br show similar trends, but with an even greater definition of the

LEGEND

- 65-10-62 Jenkins above postulated unconformity
- 65-7-62 Jenkins
- ◎ 65-18-62 Jenkins
- + 65-23-62 Jenkins

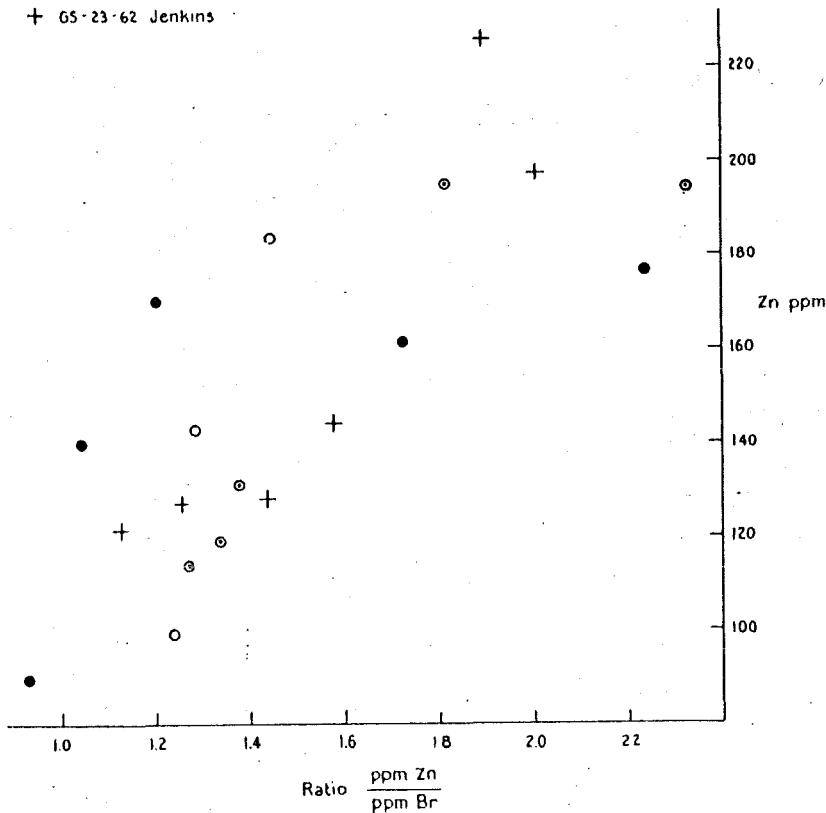


Figure 21. Variation of zinc with zinc/bromine ratio in Jenkins surface-mud cores.

trends. The conclusions with regard to the distribution of Cu are much like the conclusions with regard to Zn, except for the following factors:

- a) The percentage of total Cu in the inorganic fraction is most likely greater than the percentage of total Zn in the inorganic fraction because of the extraordinary specificity of the reaction whereby Cu is sorbed by clays, and possibly also because of the formation of cuprite or native copper at the low redox potentials created by organic activity in the sediment.
- b) The obvious source of Cu in the Keweenaw copper bearing strata and the extensive mining activity in the area make it even less likely that the surface increase in Cu is primarily due to a change in the activity of organisms or in the percentage or nature of the organic matter of the sediment.

Strontium: Literature cited in the section on Sr shows that metabolic uptake of Sr by organisms and their subsequent sedimentation is probably a major mechanism for water-sediment transfer of Sr. Much of this Sr should remain in the sediment, as organogenic carbonate, and as sorbed Sr on clays and organic matter. Re-solution of carbonate is also important.

Manganese: The bacterial lowering of the sediment Eh and pH, coupled with bacterial catalysis of oxidation, is probably the major cause of the surface enrichment of Mn. Oborn (1964) shows that aquatic plants may also play a scavenging role in water to sediment transfer of Mn. However, in Lake Superior the surface increase of Mn occurs closer to the sediment-water interface than the upward increase in organic matter. Therefore, even if part of the surface enrichment is attributed directly to an

increased scavenging by organisms there has been subsequent separation of that Mn and the organic matter, and an upward reconcentration of the Mn, by the re-precipitation mechanism outlined above.

Lead: The analyses of Pb made for this investigation are not sufficient evidence for an independent conclusion. Inasmuch as organisms and organic matter do not seem to be the major controls of the concentration and distribution of Zn and Cu, they are probably not the major controls of Pb.

Lithium: Although only a few analyses for Li have been made, C org and Li are apparently inversely related, and it is evident that the relationship of organisms and organic matter to Li is at the very most a matter of environmental control.

Zirconium and titanium: The distribution of Zr and Ti is unrelated to the activity of organisms and the distribution of organic matter in Lake Superior. Like silicon, Zr and Ti do not show consistent decreases toward the surface as organic matter increases, probably because the proportion of detritus of silt and fine sand size increases.

Other elements: The abundances of Ga, B, V, Ni, and Rb are not functions of the abundance of Br or C org, and are, therefore, by inference, not primarily controlled by organisms. The scavenging effect may be a significant factor in the water to sediment transfer of all the elements, but inorganic processes should also be considered. The Eh and pH gradients produced by organic activity should have only minor effects on solubility and exchange equilibria of these elements.

Summary: There is no trace element of those studied whose concentration in the sediment is simply and directly related to C org or to Br content, and therefore probably no trace element whose concentration in the sediment is directly and primarily controlled by the abundance of organisms and organic matter. This is not really a surprising conclusion, for one would have suspected that in Lake Superior, an oligotrophic body of water, relatively low in all dissolved ions, the abundance of trace elements in the sediment and sediment organic matter would be to a great extent a function of supply.

Organisms and organic matter are an important but indirect control of the distribution of Mn, by virtue of their creation and maintenance of the Eh-pH gradient.

The importance of organisms in the transfer of trace elements from water to sediment cannot be determined from the type of analyses made during this investigation, but the literature suggests that they should be important in the transfer of many of these elements.

The present distribution of trace elements between inorganic and organic components can only be inferred from correlations of analyses of the entire sediment (or size fractions) with quantities like C org and Br, and it is evident that a method for separating the organic from the inorganic fraction without disturbing sorbed elements is sorely needed. The literature suggests that the two fractions should differ in their sorption and fixation capacities, but that the differences are moderate. The evidence from Lake Superior, while not conclusive, shows that for most elements, if atoms in all types of positions are considered, there may be almost no difference in the trace element concentration of the two fractions.

## THE NATURE AND CAUSES OF SURFACE ENRICHMENTS

### Introduction

The mechanisms by which the observed enrichments of trace elements at or near the sediment-water interface might be created have been considered briefly in the discussion of the individual elements, and in the section on organic matter. In this section further considerations of a general nature will be outlined.

A surface enrichment could be caused by any of the following:

- a) An upward decrease in the rate of detrital inorganic sedimentation, and resultant unmasking of chemical processes that continue to take place at a constant rate.
- b) An upward increase in the rate of chemical or organic sedimentation.
- c) Upward migration of trace elements because of diagenetic processes.
- d) An upward change in the composition of the detrital inorganic fraction.

## A Decrease in the Rate of Detrital Inorganic Sedimentation

The overall trend in Lake Superior has been a gradual decrease in the rate of deposition of lake sediments, as shown by measured rates of sedimentation in varved red clay and varved gray clay, and the calculated average rates for post-varve time.

If the rate of detrital inorganic sedimentation was to decrease and the supply of organic matter was to remain constant, the percentage of organic matter in the sediment would increase, although perhaps not in full proportion to the inorganic decrease, because the lengthened exposure at the sediment-water interface would promote greater decay of organic matter. The concentrations in the sediment of elements selectively sorbed by this increased percentage of organic matter would then increase. Likewise, if an element was incorporated in the sediment by means of a precipitation mechanism a decrease in detrital inorganic or organic sedimentation would result in an increase of the concentration of the precipitate, as long as the total sedimentation rate decreases.

The concentration of a sorbed element in the inorganic fraction might also rise, even if the concentration of the element in the lake water remained constant, because longer exposure before burial promotes additional fixation of sorbed elements, thereby promoting further sorption.

In Lake Superior the upward increase in Br concentration observed in the sequence varved clay-massive gray clay-brown sediment is probably related to the upward decrease in the rate of detrital inorganic sedimentation observed in these sediments, but the relationship is not simple. Both an increase in the rate of organic sedimentation and re-solution of Br at depth are also probable contributing factors. There is no unequivocal

method for determining the relative importance of these three factors.

A separate question is whether a decline in the rate of sedimentation of the uppermost 3 to 10 cm of brown sediment is the cause of the many variations in major and trace element concentrations observed in Jenkins surface mud cores. The widespread existence of such a decline cannot be demonstrated on the basis of the physical characteristics of the sediments. Moreover, all of the trends in element distribution observed in Jenkins cores can be explained in other more plausible ways. For instance, it has been shown above that the near-surface behavior of Ca, Sr, Br, C org, and Mn are at least in part explained by early diagenetic redistribution.

Similarly, the section on organisms and organic matter above concludes that because of the nature of the variation of the Zn/C org, Cu/C org, Zn/Br, and Cu/Br ratios in Jenkins cores it is unlikely that a decrease in the rate of detrital inorganic sedimentation close to the sediment-water interface, and a resultant decrease in the dilution of organic matter is the sole cause of the surface increases of Cu, Zn, and by analogy, Pb.

And yet it is important to note that all of the near-surface enrichments observed in the Jenkins cores are in a sense caused by the documented decrease in rate of sedimentation over the past 10,000 years or so! Processes other than detrital inorganic sedimentation are now important because their products are no longer swamped by a relative superabundance of the products of detrital inorganic sedimentation.

### Increase in the Rate of Organic Sedimentation

If the productivity of an oligotrophic lakes rises because of an increase in the availability of nutrients, a rise in average temperature, or other factors, the amount of organic matter incorporated in the sediment will rise. This will have several effects on trace element behavior. Those elements selectively sorbed by organic matter will be enriched in the sediment by virtue of the increase in organic sorption substrate, unless the supply of the elements is extremely limited. The increased amount of organic matter in the sediment will support higher levels of bacterial activity. The rate of downward diffusion of oxygen will not balance bacterial consumption of oxygen, and the redox potential at any given level below the sediment-water interface will decrease, promoting the reduction, solution, and upward migration of manganese, but in contrast, limiting the solubility of copper, and possibly forming copper oxides or native copper. Where bacterial action lowers the Eh still more, sulfate reduction occurs, and Cu, Zn, and Fe sulfides may be formed.

The effects of decreasing detrital inorganic sedimentation, previously outlined, and the effects of increasing organic sedimentation might appear to be the same, and indeed have not been differentiated by this study. In theory there would be two major differences: in the former the exposure at the sediment-water interface will be lengthened, and organic decay will be more complete, while the opposite will be true in the latter: in the former the ratio of sorbate to sorbent will increase, while in the latter it will decrease.

It is logical to assume that the organic activity of Lake Superior has increased since glacial time, but it is difficult to determine what

part of the increase in Br or of C org is attributable to such an increase and what part is attributable to the known decrease in detrital inorganic sedimentation.

If the surface increase of manganese is indeed a redox process as outlined above, then any change which accentuates the reduction-controlling redox gradient favors the formation of a surface enrichment in manganese. Thus the decrease in detrital inorganic sedimentation and the probable increase in organic sedimentation are at least in part, and may be entirely, responsible for the observed surface concentration.

The arguments for and against creation of surface enrichment of Cu, Zn, and Pb by an increase in organic sedimentation will not be repeated here. The writer concludes that an increase in the rate of organic sedimentation can be no more than a minor factor.

### An Increase in the Supply of Ions in Solution

Any of the observed increases in the concentration of sorbed or precipitated ions could be attributed to an increase in the concentration of the dissolved ion in waters of the Lake Superior basin. We cannot determine the ionic concentrations in the lake water in the past without making assumptions about sorption and precipitation equilibria. The calculations that follow, based on such equilibrium assumptions, are therefore circumstantial evidence, but the model they generate does resemble nature, which is most heartening.

The surface enrichment in copper in Lake Superior is of particular interest because the deposits of native copper in the Lake Superior region are a possible source of the metal, and mining activity is a possible explanation for the presence of excess copper close to the sediment surface. A possible source of zinc and lead is the increased use of these two metals in the growing industry of the Great Lakes Region (vis. the Zn of galvanized metals, and the Pb of internal combustion exhaust vapors). Can the surface enrichment of these three elements be interpreted as contamination of the lake water and sediment by man, or are they a natural geochemical anomaly?

A critical factor is the depth to which surface enrichment extends. For instance, copper mining began in the Lake Superior region in 1845, if we choose to neglect the sporadic activity of Indians, who did little more than "scratch" the land surface. If we assume an average sedimentation rate of .017 cm per year, which Table 1 and the accompanying text shows should be a maximum rate for recent sedimentation, then the maximum thickness of sediment deposited in the past 120 years, since mining began, is

2.0 cm, which is considerably less than the average thickness of surface enrichment of copper found in Jenkins cores, inasmuch as the average depth at which the copper surface enrichment reaches half its maximum is 8 cm. Lead and zinc from exhaust fumes and industry are for the most part a phenomenon of the 20th century, which makes the disparity between rate of sedimentation and depth of surface enrichment even greater for these elements.

Mixing of the underlying sediment by organisms may explain a small part of the disparity. The sole benthic organisms present in sufficient number are the Pontoporeia, who do not mix more than the top two or three centimeters of sediment (J. C. Ayers, 1964, pers. comm.).

Wave energy should not move sediment at the water depths from which most of the Jenkins cores were taken. Whether there are bottom currents capable of disturbing the bottom sediments is not known, but the surface enrichment appears to be ubiquitous, whereas bottom currents, if they exist, are probably local, and closely related to the bottom topography. Therefore bottom currents are probably a minor factor in the explanation of the disparity.

The possibility of downward diffusion of trace elements enriching sediment that had been deposited prior to initial "human" contamination is strong. The chemistry and mathematics of diffusion through sediments are considered in Appendix 2. Although the formulation of a suitable model is not difficult, some critical constants are not available, and only an "order of magnitude" calculation can be made at this time. Nevertheless, the calculations show that the rate of downward diffusion of trace elements is high enough to account for the depth of surface enrichment, and the rate would be sufficient even if it is in fact an

order of magnitude less than that calculated for the model assumed.

None of the mechanisms for downward migration are mutually exclusive. It is obvious that if continued sedimentation, mixing by organisms, bottom currents, and downward diffusion are combined, the thickness of the zone of enrichment in Cu, Zn, and Pb is readily correlable with contamination by man.

Could the surface concentrations of Cu, Zn, and Pb be explained just as well by natural enrichment? Near-surface ore deposits are often accompanied by hydrochemical anomalies. One might expect an increase in the intensity of the anomaly as erosion progressively removes more of the blanket of glacial debris, and waters come into greater contact with cupriferous bedrock. The high copper content in GS-14 at 45 cm depth, presumably deposited many centuries ago, shows that indeed there is a natural geochemical anomaly in copper within Keweenaw Bay, close to the source of copper. The generally high levels of Cu in all sediments of Lake Superior, glacial and recent, is interpreted as a natural geochemical anomaly.

But there is no known recent natural event that could have increased the supply of Cu as suddenly and as strongly as that shown by the surface enrichments observed. In the cases of Zn and Pb the rapidity and intensity of the surface enrichments are equally significant features. Moreover, there is no obvious natural source of Zn or Pb in the Lake Superior basin that would be a source for a natural anomaly, as neither the copper nor the iron mining districts of the basin have significant Zn or Pb mineralization. Therefore it does not seem likely that the Cu, Zn, or Pb surface enrichments are natural geochemical anomalies.

### Upward Migration of Trace Elements

An upward decrease in the concentration of an element in the interstitial water is a necessary and sufficient condition for net upward migration. Because of the depth of Lake Superior, bottom currents are probably even less effective than organisms in mixing bottom sediment, and diffusion alone must be the mechanism for ionic migration below a depth of 2 to 3 cm.

Where an upward increase in redox potential or pH favors precipitation of an element, upward diffusion is promoted. In Lake Superior sediments this is true in the case of Mn, as shown in detail above.

In sorption any decrease in the sorptive or exchange capacity of the sediment will increase the interstitial concentration of the sorbed element. An increase in pH, as observed in the carbonate-saturated clays, and decay of organic matter both do this. An increase in the ionic strength of the medium and concomitant increase in the percent saturation of sorption sites favors desorption, but this should not be a significant factor for the doubly charged, highly sorbed cations of present interest.

Because no analyses of the interstitial waters of Lake Superior sediments have been made we can only infer the presence or absence of concentration gradients.

In the case of manganese, the surface concentration coincides with the redox and pH boundary at which rising manganese ions would be precipitated, and the redox potential and pH at depth is favorable to reduction and solution of manganese. Therefore, upward migration of manganese is quite probable.

In the case of copper the redox gradient favors downward diffusion.

In the cases of Zn and Pb the redox gradient has no effect on ionic diffusion.

In the case of bromine, the study of Mun and Bazilevich (1962) suggests that solution and upward migration of bromine might be expected. In particular, the upward increase in Br content sometimes observed in the upper parts of Jenkins cores may be a decrease with time due to particularly rapid decay of organic matter close to the sediment-water interface.

Similarly, the enrichment of organogenic Ca and Sr in the upper 3 to 10 cm of the sediment column may not be incorporated permanently into the stratigraphic column because of continued solution of carbonate and upward diffusion of  $\text{Ca}^{\frac{+}{2}}$ ,  $\text{Sr}^{\frac{+}{2}}$ ,  $\text{Mg}^{\frac{+}{2}}$ , and  $\text{HCO}_3^-$  toward the undersaturated lake water.

An Upward Change in the Composition of the Detrital

Inorganic Fraction

A surface enrichment of an element could be caused by an increase in the rate of sedimentation of a detrital mineral or group of minerals that contain the element as a firmly bound major or trace component or as a sorbed constituent.

The surface enrichment in manganese might possibly be explained solely by an increase in the supply of dissolved Mn and detrital colloidal Mn oxides, hydrous oxides or carbonates, but, as shown in the section on Mn, this is unlikely. Moreover, upward diffusion and reprecipitation of Mn should take place in either the presence or the absence of an increase in the detrital supply, therefore an increase in the detrital supply is a minor factor.

It is not likely that the surface enrichments of Zn, Cu, or Pb are caused by an increase in the rate of sedimentation of any detrital mineral or mineral group. The clay minerals are the only species present in the Lake Superior basin in quantity approaching that needed to explain a near-surface enrichment for these elements by this method. An upward increase in the percentage of clay minerals in the detrital inorganic fraction does occur, but evidence cited above shows that this increase takes place below the trace element surface enrichment phenomena, and therefore the two increases, clay mineral and trace element, are unrelated. Exceptions to the statements above are the sediments of Keweenaw Bay and Isle Royale, close to the copper deposits, that may contain some fragments of copper-bearing ore minerals.

### Summary and Conclusions

It is evident that the near-surface enrichments are probably caused by the interaction of several processes of change, but the correlations observed do not always enable us to determine uniquely the relative importance of each process. The writer feels that the following summary is the best explanation of the data at hand, but acknowledges that further study is needed.

The decrease in the rate of detrital inorganic sedimentation shown by the sequence red varved clay-gray varved clay-post varved gray clay sediments is not the immediate cause of the near-surface enrichment of many elements observed in Jenkins surface mud profiles. Nevertheless, the near-surface enrichments are observable because processes other than detrital inorganic sedimentation are no longer swamped by a superabundance of inorganic detrital sediment. The surface enrichment of Mn is caused by reprecipitation of Mn oxides, hydrous oxides, or carbonates, controlled by the Eh and pH of sediment and water, and thus ultimately controlled by organisms and bacterial decay processes. If there has been an increase in the rate of supply of detrital Mn it is a minor factor. The surface enrichment of Cu, Zn, and by inference Pb, are primarily caused by "human" contamination of Lake Superior, that is, by a man-made increase in the supply of dissolved ions, and a concomitant increase in sorption. High concentrations of organogenic Ca and Sr observed in the uppermost 3 to 10 cm will not become permanent buried components of the stratigraphic column because the Sr and Ca is contained in carbonates that are being dissolved in the undersaturated waters. Similarly, the near-surface upward increase of Br concentration may be due largely to relatively rapid

release of Br from the sediment because of rapid decay of organic matter close to the sediment-water interface. However, the more gradual variation of Br at depth is due to the documented decrease in the rate of detrital inorganic sedimentation, with a concomitant inferred increase in the rate of organic sedimentation and organic decay processes also contributing to the observed trend.

## TRACE ELEMENT PROVENANCE

### Theoretical: Detrital and Non-detrital Provenance

A trace element may be transported to the basin of deposition (Lake Superior) in any or all of the following fractions of the load of a river:

- 1) Undecomposed rock and mineral fragments
- 2) Minerals and colloids formed at the site of weathering or subsequently in water transport.
- 3) Particulate and colloidal organic matter, both living and dead.
- 4) Particulate and colloidal matter introduced by man, generally belonging to one of the above categories, but listed separately so as to emphasize the unique origin and in some cases the unique composition of the detritus of human civilization.
- 5) Chemical species sorbed on any of the above.
- 6) Chemical species in true solution, whether organic or inorganic, natural or man made.

Of these, the first five comprise the "suspended load" and "bed load," corresponding to the classic "detrital" fraction of sedimentation, whereas the sixth is the "dissolved load," or "non-detrital" fraction. Several investigators have assessed the relative importance of the solid and dissolved load in the transport of trace elements by making direct measurements of the two fractions (e.g., Nesterova, 1960). A similar but by no means equivalent partitioning is being made by Hirst (1962) and others, leading to some confusion. Hirst's theoretical definition of detrital and non-detrital fractions follows classic concepts. The detrital fraction "entered the basin of deposition in the solid state," whereas the non-detrital fraction "entered in solution" (*ibid*, p. 1148). Analytically, however, he defines the non-detrital fraction of an element in a sediment as that fraction which can be leached by 25% acetic acid, and the detrital

fraction as the remaining unleached portion. The theoretical and analytical definitions above are not the same in practice! Sorbed chemical species are detrital by the theoretical definition, whereas they are non-detrital by the analytical definition! Thus Hirst's analytical definition comes closer to differentiating transport modes 1 through 4 from 5 and 6. This is certainly a significant classification, as one feels justified in considering the sorbed species as being more closely related to the ions in true solution than to the sorption substrate because of dynamic equilibria. Perhaps what is needed is a redefinition of the terms "detrital" and "non-detrital," eliminating the correspondence with solid and dissolved load, respectively. Note also that leaching with 25% acetic acid is not a perfect differentiation of 1 through 4 from 5 and 6 because not all authigenic minerals are dissolved (e.g., sedimentary pyrite), and the acid dissolves some readily soluble detrital minerals. Also, sorbed ions that have been subsequently fixed are not quantitatively leached. For the present we may avoid genetic redefinition by using the terms "leachable" and "non-leachable," modified by adjectives indicating the nature of the leaching solution, to describe Hirst's analytical fractions.

Provenance of Lake Superior Trace Elements

It is evident from the discussion above that by the classic definition there is no completely "non-detrital" trace element in Lake Superior. For instance, it is quite probable that much of the copper now sorbed on Lake Superior sediments entered the lake sorbed on clay minerals or other components of the detrital fraction of river load. However, the widespread extension of the copper surface anomaly beyond the area of bedrock enrichment, particularly the extension toward the lake outlet, suggests that even if much of the copper from tributary streams enters the lake as ions sorbed on detritus, redistribution of the copper can and has taken place within the lake basin because of dynamic equilibria with the overlying water.

Similarly, a large fraction of the Zn and Pb now present in Lake Superior sediments may have entered the lake in sorbed state, but considerable redistribution may have taken place subsequently.

Although some of the Mn entering Lake Superior is in true solution, most Mn enters as colloidal hydrous oxides and hydroxides, precipitated at the site of weathering or in transport. Thus its origin is detrital with respect to Lake Superior. However, as re-solution followed by upward migration and re-precipitation takes place, the ultimate product of sedimentation is a non-detrital species of similar composition.

Sr, V, Ga, B, and Ni are an intermediate group. A substantial fraction must have entered the structure of clay minerals at the site of weathering, but another, variable fraction of each entered Lake Superior in solution or in sorption equilibrium with dissolved species.

Ti and Zr are the most detrital of the elements studied. A

significant fraction of these elements is incorporated in the sediment as undecomposed mineral fragments, and most of the remainder is incorporated in structural positions in clay minerals or is immediately precipitated as colloidal oxides at the site of weathering.

## Sedimentary Trace Element Provinces in Lake Superior

The distribution of many trace elements has been shown to be closely related to the two major petrologic provinces within the Lake Superior basin. The sedimentary expression of these petrologic provinces is best shown by those elements of which a significant fraction is incorporated into the sediment as unweathered minerals, that is, Sr, and Ti and Zr of coarser-grained sediments. In the fine-grained sediments, richer in the clay mineral products of weathering, the differentiation with respect to Ti and Zr is less marked, presumably because the weathering processes have reduced the disparity in concentration.

The petrologic provinces are also delineated by some of the elements of the intermediate group (V, Ga, B, Ni) defined above. However, for these elements the difference in trace element concentration in the derived sediment is far less than the difference in trace element concentration in the parent rocks, and in the cases of B, Ni, and Ga, no difference can be detected in the derived sediments. Here, then, is further evidence of the powerful leveling effect of the processes that occur during weathering.

Among the more non-detrital elements (Cu, Zn, Pb, Mn) only the distribution of Cu is geographically dependent within Lake Superior, and its distribution reflects not only the location of the source area but also shows the effect of distribution by currents and water masses within the Lake.

## THE LAKE SUPERIOR ENVIRONMENT

### The Role of Glaciation in the Distribution of Trace Elements in Lake Superior

Trace elements in the glacial sediments: The glacial sediments are characterized by the overwhelming predominance of physical, as opposed to chemical and biological, processes and products. There is an abundance of unweathered minerals (rock flour) and a low content of clay minerals, despite the high content of clay-sized particles. The trace element content of the glacial sediments reflects this composition. The content of Sr is high because it is present in unweathered rock particles. The content of Li is high, presumably because it too is more abundant in some component of the rock flour. The concentration of elements commonly sorbed on clay minerals (Zn, Pb, Cu) is low because the sorption capacity of rock flour is low and rapid burial allows little time for fixation. The concentration of these elements in the water was probably lower than at present also, because of the abundance of water, the relative unimportance of organic and chemical processes, and the absence of human contamination. The content of Br is low because rapid detrital inorganic sedimentation overwhelmed what little organic sedimentation was taking place at the same time. Other elements (e.g., V, Ni, Mn, Ga, B,) are present in unweathered rock particles and in the hydrolysate products of weathering in approximately equal amounts, and thus their abundance in the glacial sediments is normal for fine-grained sediments.

The source area for glacial Lake Superior sediments was a much larger area than the present Lake Superior basin, for it included the territory

north of the Lake Superior basin from whence the glacial advances came. Among the trace elements this is shown by the abundance of Sr in the glacial sediments, derived from the Paleozoic carbonates to the north.

Varves are differentiated into carbonate-richer light layers and carbonate-poorer (non-carbonate rock flour-richer) dark layers. The distribution of trace elements reflects this differentiation: Sr is more abundant in the light layers, while Ni, Zn, Ti, Zr, Cu, Rb, V, Ga, and B are more abundant in the dark layers.

Sequence of postglacial changes and trace element abundances: From the work of Farrand (1960, 1963) and this investigation, the sequence of post-glacial events in Lake Superior can be summarized as follows:

- a) The end of varve formation as the glacier left the Lake Superior basin.
- b) Rapid erosion of much of the fine-grained fraction of the superficial mantle of till, and consequent deposition of the gray clay unit in the lake.
- c) A gradual decline in the rate of inorganic detrital sedimentation, and a concomitant increase in the importance of the products of chemical weathering and organic sedimentation.
- d) The localization of detrital deposition to shoreline areas and bays, which are close to a source of supply.

As a consequence of this sequence of events the following trace element trends have occurred:

- a) There has been an upward increase in the percentage of Br, either because of the decrease in inorganic diluent of the products of organic sedimentation or because of an increase of the rate of organic sedimentation or, even more likely, both.
- b) There has been an upward increase in the percentage of manganese because of the onset of upward migration and reprecipitation and

the decrease in inorganic detrital diluent of such a chemical process.

- c) There has been an upward decrease in the percentage of lithium, possibly because of a decrease in the percentage of rock flour having a high Li content.
- d) There has been an abrupt decrease in the percentage of Sr because of the abrupt end to the supply of carbonate detritus.
- e) There have been abrupt increases in the percentages of Cu, Zn, and Pb, probably because of human contamination. These chemical enrichments are detectable because the rate of detrital inorganic sedimentation has declined.

Of the trace element trends listed above, (a) and (b) are trends which might be found in the sediments of many postglacial lakes. On the other hand, trends (c), (d), and (e) involve processes that might occur in many postglacial lakes, but it does not follow that the same elements will be involved in the same processes in other lakes.

Lake Superior as a Fresh Water Environment

Would prior empirical knowledge of trace element distribution in fresh-water and marine sediments enable us to determine that Lake Superior sediments are nonmarine in origin? This rather academic question is of considerable interest, inasmuch as the sediments of a lake as large as Lake Superior, if found in the geologic record, could easily be mistaken for marine deposits on physical evidence alone, in the absence of faunal criteria.

Conclusions based on the empirical approach, pioneered by Keith and Degen (1959) and Potter et al. (1963), have been noted in detail in discussion of the individual elements above. The following is a summary.

Boron: Lake Superior is "nonmarine," but Lake Michigan is "marine." The anomalous B in Lake Michigan may be derived from Paleozoic marine argillaceous rocks in the Lake Michigan basin.

Nickel: Both Lakes Superior and Michigan are "nonmarine." However, the work of Hirst (1962) suggests that a low nickel content indicates a more rapid rate of deposition rather than a lower salinity.

Copper: All Lake Superior sediments are "marine," Lake Michigan sediments at depth are "nonmarine," and Lake Michigan surface sediments are "marine." The erroneous conclusions are due in part to the man-made Cu anomaly and in part to the natural Cu anomaly of the Lake Superior basin.

Vanadium: Both Lakes Superior and Michigan are "nonmarine" if the V analyses of this study are adjusted to a level common with Potter et al. (1963), in Lake Michigan in order to be able to use their discrimination function.

Gallium: Lake Superior is "nonmarine," but Lake Michigan is "marine."

The cause of this anomaly is unknown, but may be related to derivation of the Lake Michigan sediments from marine argillaceous source rocks.

Thus the empirical approach is right more times than it is wrong, but it is far from infallible. Use of a multivariate discriminant function involving all of these trace elements, such as the function used by Potter et al.(ibid), will increase the reliability. The principal misclassifications are associated with anomalies in source rocks. Thus where source rocks are known it may be possible to refine the salinity criteria. Discrimination functions based on the variation of the leached trace element fraction may be more reliable in the case of partially detrital elements (e.g., B, V, Ni), but will probably be no improvement in the case of largely non-detrital elements like Cu, and fixation processes may make criteria based on the leachable trace elements useless for the evaluation of ancient sediments.

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## APPENDIX 1 : SAMPLE IDENTIFICATION

The following symbols are used to identify samples:

Initial Letters - designate the lake in which the sample was taken.

GS = Lake Superior (1962)  
Su = Lake Superior (1961)  
S = Lake Superior (1961, 1962)  
GM = Lake Michigan (1962)  
GH = Lake Huron (1962)

Numbers Following Initial Letters - designate the sample geographic locality, as shown on the index map, Figure 1.

eg, GS-23 (locality 23, Lake Superior 1962)  
SU-1 (locality 1, Lake Superior 1961)

Numbers Following the Locality Numbers - designate the year of sampling.

eg, GS-23-62 (sample collected in 1962)  
Because the year designation is not necessary  
for unique identification of all sediment  
samples discussed in this report, it is  
sometimes omitted.

Additional Letters - refer to the type of sample or the position of the sample in a sequence.

OP = Orange Peel sample (eg, GS-23-62-OP)  
OPSurf = sediment from an orange peel sample  
judged to be closest to the sediment-  
water interface.

HPC = hydroplastic core sample.

HPB = sample from the bit of the hydroplastic  
corer, hence, the lowest recovery from  
the hydroplastic core.

J = Jenkins surface mud sampler sample.

JA, JB, ... JF, JG = Sequential slices of a  
Jenkins core, A always being the lowest,  
and the highest letter at a given locality  
being at the sediment-water interface.  
The depth for each slice at each locality  
is given in Appendix 2.

Additional Numbers - refer to depth below the sediment-water interface,  
in centimeters.

APPENDIX 2: PHYSICAL DESCRIPTION OF SAMPLING  
LOCALITIES AND SEDIMENTS

GS-2-62.  $84^{\circ} 47.2'W$ ,  $46^{\circ} 44.1'N$ , 462' water depth, in the central north-south trending trough within Whitefish Bay.

Jenkins: 0-3 cm (JE) mud, silty, dark yellowish brown,  
10YR3/2  
3-11.5 cm (JD, JC, Part JB) mud, silty, dark  
yellowish brown, 10YR2/1  
11.5-19 cm (part JB, JA) mud, silty, dark yellowish  
brown, 10YR3/2

Orange Peel: identical; mixture of 10YR3/2 and 10YR2/1

GS-4-62.  $84^{\circ} 45.6'W$ ,  $47^{\circ} 06.5'N$ , 635' water depth, in the bottom of a north-south trending trough, less than two miles from shore at Mica Bay.

Jenkins: 0-3cm (JE) mud, silty, dark  
3-7cm (JD) yellowish brown,  
7-11cm (JC) 10-5YR3/1  
11-15cm (JB)  
15-18cm (JA)

HPC: identical; 135 cm of silty, dark yellowish brown mud,  
decrease in apparent water content with depth.

GS-5-62.  $85^{\circ} 00'W$ ,  $47^{\circ} 26.7'N$ , 200' water depth, on shoal west southwest of Leach Island, close to mainland east shore.

Orange Peel: Loam, with more sandy areas of moderate brown,  
5YR4/4, and more clayey layers of dark yellowish brown,  
10YR3/4.

GS-6-62.  $47^{\circ} 27.5'N$ ,  $85^{\circ} 08'W$ , 465' water depth, on north-south trending rise between two troughs.

Orange Peel: Loam, moderate brown, 5YR4/4.

GS-7-62.  $47^{\circ}29.5'N$ ,  $85^{\circ}12'W$ , 940' water depth, in center of long, linear, north-south trending trough.

Jenkins: 0-5.4cm (JE) Mud, slightly  
5.4-10.8cm (JD) silty, dusky  
10.8-16.2cm (JC) brown, 2.5Y3/2  
16.2-21.6cm (JB)  
21.6-23cm (Part JA)

23-28cm (Part JA) same, except dark yellowish brown, 10YR4/2

HPC: 230 cm core, all mud, slightly silty, dark yellowish brown, 10YR4/2. No laminations visible.

GS-8-62.  $47^{\circ}30.3'N$ ,  $85^{\circ}23'W$ , 520' water depth, on rise between two north-south trending troughs.

Jenkins: 0-5cm (JC, part JB) mud, dark brown, 10YR2/1  
5-10cm (part JB, JA) mud, moderate yellowish brown,  
5YR5/4

HPC: 0-17 cm clay, moderate yellowish brown, 10YR5/4 (presumed equivalent of 5-10 cm in Jenkins core).

17-226 cm clay, gray varved, 5Y5/1 and 5Y7/1

Orange Peel: Loam, 5YR5/4

GS-9-62.  $47^{\circ}27.6'N$ ,  $85^{\circ}38'W$ , 415' water depth, on rise between two north-south trending troughs.

Jenkins: 0-4cm (JB) laminated silt, loam, clay, disturbed in core recovery, dark, moderate, and dusky brown shades.  
4-5cm (JA) clay, gray, 5Y6/2

GS-10-62.  $47^{\circ}25.8'N$ ,  $86^{\circ}02.8'W$ , 1130' water depth, in north-south trending trough, near maximum depth at this longitude.

Jenkins: 0-6cm (JD, JC, JB) mud, very dark brown, 10YR2/2

6-9cm (JA) clay, light olive gray, 5Y6/2

GS-11-62.  $47^{\circ}25.0'N$ ,  $86^{\circ}05.4'W$ , 472' water depth, on rise southwest of trough sampled at GS-10.

Jenkins: 0-3cm loam, dark brown, 10YR2/1

3-3.5cm clay, sandy, light brown, 5YR5/4

GS-12-62. 412' water depth due west of locality GS-11, thus further up on rise southwest of trough sampled at GS-10.

Orange Peel: clay, gray, 10YR5/1, plus traces of a sandy loam similar to 0-3 cm at GS-11.

GS-13-62.  $47^{\circ}20.5'N$ ,  $86^{\circ}56.5'W$  (dead reckoning), 1020' water depth, near deepest part of the broad central Lake Superior basin.

HPC: 290 cm total length.

clay, gray, 2.5Y5/2, massive to faint horizontal laminations. Thin, scattered horizontal bands of black sulfide 0-228 cm. 228-254 cm has faint regular horizontal laminations that are not as distinct or as regular as typical varve laminations.

HPB: clay, as above, laminated.

Jenkins: 0-6.5cm mud, very dark brown, 10YR2/2

6.5-11cm clay, dark grayish brown, 10YR4/2

GS-14-62.  $47^{\circ}0.7'N$ ,  $88^{\circ}10.3'W$ , 338' water depth, on southeast slope of trough that extends along the axis of Keweenaw bay.

Jenkins: 0-2cm (JB) mud, gray, 5Y5/1

2-4cm (JA) clay, moderate reddish brown, 2.5YR4/4

HPC: 0-73 cm clay, silty, 5YR4/4, massive to faint thin horizontal bedding.

GS-15-62.  $47^{\circ}12.95'N$ ,  $87^{\circ}59.7'W$ , 300' water depth, on northwest slope of trough that extends along the axis of Keweenaw bay.

Jenkins: 0-4cm (JB) loam, sandy, grayish brown, 5YR3/2

4-5cm (JA) clay, moderate brown, 5YR3/4.

GS-18-62.  $47^{\circ}16.5'N$ ,  $86^{\circ}02.5'W$ , 1128' water depth, in deepest portion of north-south trending trough.

Jenkins: 0-5 (JE) mud, dark brown,  
5-9 (JD) 10YR3/2  
9-13 (JC)  
13-15 (part JB)

15-18 (part JB) mud, brown,  
18-24 (JA) 7.5YR4/4

GS-20-62.  $47^{\circ}14.0'N$ ,  $86^{\circ}08.0'W$ , on upper reaches of the western slope of a north-south trending trench.

Orange Peel: Surface-loam, gravelly, including pebbles of sandstone.

below surface - clay, light brown, 5YR5/4

GS-21-62.  $47^{\circ}06'N$ ,  $86^{\circ}19.0'W$ , ca 650' water depth, on broad rise between two north-south trending troughs.

Orange Peel: Surface-loam, sandy, dark brown, 10YR3/1

below surface - clay, moderate brown, 5YR4/4

GS-22-62.  $47^{\circ}06.4'N$ ,  $86^{\circ}26.5'W$  (dead reckoning), 750' water depth, on upper slope of the west side of a north-south trending trough.

Jenkins: 0-7cm (JC) mud, brown, 5YR3/2  
7-8cm (part JB)

8-8.5cm (part JB) mud, moderate  
8.5-11cm (JA) brown, 5YR4/4

GS-23-62.  $47^{\circ}06.4'N$ ,  $86^{\circ}22.3'W$  (dead reckoning), however the measured water depth of 1085' suggests that the locality is actually near the bottom of the trough just west of the designated coordinates.

Jenkins: 0-5cm (JF)  
5-9cm (JE) mud, dark brown,  
9-13cm (JD) 10YR3/2  
13-18cm (JC)  
18-22cm (JB)  
22-26cm (JA)

GS-24-62.  $46^{\circ}55.1'N$ ,  $86^{\circ}38.5'W$ , (dead reckoning), 1200' water depth, in north-south trending trough.

Jenkins: 0-8cm (JC, JD) mud, dark yellowish brown, 10YR3/2  
at 8 cm: 2 mm layer (JB2) clay, light brown, 5YR5/5  
8-15cm (JA, JB) clay, yellowish brown, 10YR5/2

GS-25-62.  $46^{\circ}43.6'N$ ,  $86^{\circ}36.1'W$ , 600' water depth, on broad eastern slope of a trough that heads close to south shore. The site of sampling is 8 mi. north of Grand Island, 13 mi. from mainland at "Pictured Rocks."

Jenkins: 0-3cm (JB) loam, dusky brown, 5YR2/2  
3-5cm (JA) silt, sandy, moderate brown, 5YR3/4

GS-27-62.  $46^{\circ}54.5'N$ ,  $85^{\circ}45.5'W$ , 510' water depth, on broad plain, 16 mi. north of the south shore mainland.

HPC: 0-220cm clay, gray, overlain by a thin layer of dark brown silt.

HPB: 220-226cm depth, clay, gray, 5Y5/1

GS-28-62.  $46^{\circ}54.5'N$ ,  $85^{\circ}22.5'W$ , 250' water depth, on shallow shelf west of a north-south trending trough.

Orange Peel: silt, brown, 5YR3 to 5/4, with darker silt, 5YR3/2 at surface.

GS-29-62.  $46^{\circ}56.8'N$ ,  $85^{\circ}12'W$ , about 240' water depth, on shelf east of a north-south trending trough.

Orange Peel: Sand, silty, brown, 5YR3 to 4/4, with darker silty sand, 5YR3/2, at surface.

GS-31-62. Probable locality  $46^{\circ}58.5'N$ ,  $85^{\circ}16'W$ , about 800' water depth, close to axis of a north-south trending trough.

HPC: 0-12cm loam, clayey, dark brown, 10YR3/2, with irregular silty and sandy laminae.

13-64 cm clay, moderate brown, 5YR4/3, with small whisps of black sulfide.

64-80cm clay, massive, gray, 5Y5/1

80-254cm clay, varved, gray, 5Y6.5to4/1

GH-1-62.  $45^{\circ}37.2'N$ ,  $83^{\circ}25.5'W$ , 510' water depth, in the deepest part of the northwest extension of Lake Huron toward the Straits of Mackinaw.

Jenkins: 0-4cm (part JE) mud, dark brownish gray, 5YR3/1

4-5cm (Part JE)	mud, dark gray,
5-10cm (JD)	N3, scattered
10-15cm (JC)	black sulfide
15-20cm (JB)	
20-25cm (JA)	

HPC: 0-155 cm clay, massive to faint, broad, horizontal laminae. Scattered specs of black sulfide, especially 0-24 and 50-58cm. color gray to olive gray near base (N3 to 5YR5/2).

GM-5-62.  $43^{\circ}21.5'N$ ,  $87^{\circ}32.5'W$ , 480' water depth, near western edge of broad depression near the west shore of Lake Michigan, northeast of Milwaukee.

Jenkins: 0-4cm (JF) mud, olive black, 5Y2/1,  
4-8cm (JE) sulfide rich.  
8-12cm (JD)

12-16cm (JC)	mud, olive gray, 5Y4/2
16-20cm (JB)	
20-24cm (JA)	

W

Su-1-61 = S-1-61.  $46^{\circ}59'55''N$ ,  $88^{\circ}12'12''W$ , 500' water depth, in deepest part of the trough running along the axis of Keweenaw bay.

Jenkins: 0-4cm (JH) mud, grayish brown,  
4-7cm (JC) 5YR3/2  
7-10cm (part JF)

10-11cm (part JF) mud, grayish brown,  
11-15.3cm (JE) 5YR4/2  
15.3-19.5cm (JC)  
19.5-23cm (JB)

S-2-61.  $47^{\circ}32'N$ ,  $88^{\circ}39'W$ , 870' water depth, between Isle Royale and the Keweenaw Peninsula; near axis of a sediment-filled trough, as shown by continuous sonic profiler ("sparker"). Deep coring penetrated gray varved clay, underlain in succession by red varved clay, red clay with silt layers, and red sandy till. The samples at 899'9" are separations of light and dark layers of thick varves, near the base of the varved section (red). (899'9" = 29'9" below the sediment-water interface). The sample at 940' (120' below the sediment-water interface) is a sample of red clayey till.

Su-4-61 (not the same as S-4-61)  $47^{\circ}40'00''N$ ,  $88^{\circ}36'30''W$ , ca 800' water depth, slightly south of midway between Isle Royale and Keweenaw Peninsula, on a relatively broad flat plain.

Orange Peel: mud, olive gray.

S-5-61.  $47^{\circ}08.9'N$ ,  $91^{\circ}18.0'W$ , .938' water depth, along deep axis of the western Lake Superior basin, 4 3/4 mi. southeast of Split Rock light. Deep coring penetrated brown sediment, underlain in succession by gray varved clay, red varved clay, red clay with silt layers, and alternating beds of red clay and clayey till (Farrand, 1962).

The samples at 965' (27' below the sediment-water interface) are separations of the light and dark layers of a thick varve near the base of the red varved section.

Su-7-61 (not S-7-61),  $46^{\circ}58.1'N$ ,  $91^{\circ}39.0'W$ , 600' water depth, in southwestern part of the broad western Lake Superior basin, three miles southeast of Agate Bay.

Core (small diameter drop core)

0-8cm	(A1)	mud, brownish gray,
8-15cm	(B)	5YR4/1
15-22cm	(C)	
22-29cm	(D)	
29-36cm	(E)	at 3cm (A2) two laminae,
36-43cm	(F)	each about 2 mm thick,
43-50cm	(G)	light brown, 5YR5/5
50-57cm	(H)	
57-65cm	(J)	
65-72cm	(K)	clay, pale red, 5R6/2
72-79cm	(L)	
79-86.8cm	(M)	
86.8-94.6cm	(N)	

Su-8-61 (=S-6-61).  $47^{\circ}03.6'N$ ,  $91^{\circ}11.1'W$ , 560' water depth, midway between shores in the broad western Lake Superior basin.

Jenkins:	0-6cm (JG)	mud, grayish brown, 5YR3/2
	6-9cm (JF)	as above, but faint
	9-10cm (part JE)	laminae of 5YR5/6
	10-13.5cm (part JE)	mud, dark yellowish
	13.5-18.5cm (JD)	brown, 10YR4/2
	18.5-23cm (JC)	

Su-9-61.  $46^{\circ}51.3'N$ ,  $88^{\circ}28.5'W$ , 1' water depth, a "black beach sand," one mile south of town of Keweenaw Bay, on Keweenaw Bay, at strand line. This is actually waste, from the stamp mill of a copper mill, that has been dumped into the Bay.

APPENDIX 3 : TRACE AND MAJOR ELEMENT ANALYSES OF  
BULK SAMPLES

Trace element analyses (Zr through Li) are given in parts per million dry weight. The analytical sensitivity for Br is about 1 ppm.

Major element analyses ( $\text{Fe}_2\text{O}_3$  through C org) are given in percent dry weight.

The  $\text{H}_2\text{O}$  is the so-called "plus" water, that is, weight loss at  $105\text{-}110^{\circ}\text{C}$ , and is given as percent of wet weight.







L67

	GS-10-62		GS-11	GS-12	GS-13-62-J and HPC		60-5	90-5	120-5	150-5	180-5	210-5
	JC	JD	OP	OP	JC	0-5	30-5					
Zr	213	197	121	142	134	136	137	133	143	138	143	148
Sr	161	160	277	210	160	234	232	159	228	236	259	243
Rb	111	99	74	143	111	151	148	90	143	129	162	161
Br	112	124	4	5	141	80	45	59	44	42	30	41
Zn	143	180	173	137	209	158	124	144	148	134	192	149
Cu	266	370	72	110	525	101	100	92	119	147	168	164
Ni	23	27	32	36	33	31	31	33	33	34	37	36
Mn	2100	2060	1570	1440	2510	1310	1010	1380	1450	1240	1480	1250
Ti	3190	3550		3870	4390	3220	3720	3710	3880	3360	3700	3830
Pb												
V												
Ga												
B												
Li												
Fe <sub>2</sub> O <sub>3</sub>	9.1	9.5	12.4		11.6	11.8	11.4	12.1	12.0	11.9	12.0	11.0
K <sub>2</sub> O	3.1	3.1	3.7		3.7	3.8	3.7	3.8	3.9	4.0	4.0	4.0
CaO	1.9	2.0	2.5		2.1	2.1	1.9	2.0	2.1	2.2	2.1	1.9
SiO <sub>2</sub>	61	62	55		56	56	55	52	52	54	52	54
Al <sub>2</sub> O <sub>3</sub>	13.4	13.5	16.4		15.7	16.0	15.1	16.3	16.3	16.9	16.7	16.8
C org												
H <sub>2</sub> O					86							

L-68

	GS-14-			62		GS-15-62			GS-18-62			GS-20-62			GS-21-			
	GS-13-62-HPC			HPB		62	HPC	JB	45-48	JB	JA	JB	JC	JD	JE	OP	OP	62
	240-5	270-5	290-300													Surf.	OP	
Zr	178	74	400	117	227	170	152	172	166	156	197	179	148					
Sr	257	242	293	86	154	98	167	179	165	165	145	87	116	211				
Rb	153	139	91	97	146	72	116	121	104	124	89		55	139				
Br	22	15	4	3	7	45	89	90	95	83	109	1?	39					
Zn	212	93		47	107	82	119	114	131	193	194	71						
Cu	119	225		64	674	219	168	134	169	487	450	122						
Ni	33	64		10	24	20	27	27	25	27	26	34						
Mn	1490	830		790	1420	1840	1610	1300	1290	1310	3670	4210	450	2700				
Ti	3970	5270		4960	2540	5010	3090	2900	2830	3070	3160	3530	1260	3760				
Pb																		
V							125			140	110	148						
Ga								13		16	11	13						
B							35			20	25	20						
Li																		
Fe <sub>2</sub> O <sub>3</sub>	12.5	8.2	8.8		10.0	6.9	10.0	9.9	9.6	11.3	9.6	10.2	11.9					
K <sub>2</sub> O	4.1	3.8	3.1		3.4	2.6	3.2	3.1	3.2	2.9	2.9		3.7					
CaO	2.7	1.5	7.2		6.5	1.4	1.8	1.8	1.8	1.9	1.8		2.1					
SiO <sub>2</sub>	52	62	47		49	72	60	59	62	62	62		55					
Al <sub>2</sub> O <sub>3</sub>	16.6	14.3	12.9		14.2	11.5	14.4	14.3	14.5	13.4	13.8		16.0					
C org																		
H <sub>2</sub> O				32							81		31					

### Sample

	GS-22-62		GS-23-62				GS-24-62		GS-25-62		GS-26-62-HPC			
	JC	JA	JB	JC	JD	JE	JF	JB	JB2	JB	0-5	20-2	29-33	45-50
Zr	172	160	167	167	166	148	147	161	99		134	141	146	150
Sr	158	193	187	173	193	180	160	110	134	73	149	219	222	223
Rb	120	139	124	169	142	112	148	127	74	77	94	114	132	130
Br	133	108	89	101	91	119	101	81	76	46	9	5	12	25
Zn	63	122	128	127	144	226	197	133	86	37	64		77	80
Cu	407	135	130	112	158	501	432	140	91	130	87	36	40	38
Ni	32	32	29	30	32	33	34	32	16	7	18	25	24	22
Mn	2340	1480	1510	1520	1740	3910	1690	1740	31700	530	1000	1240	1740	1500
Ti	4860	3130	3780	3610	4620	4430	4990	4610	2630	1750	2660	2900	2960	3050
Po		8				35								
V		125		145			90	115						125
Ga		15		19			7	33						15
B		40		19			26	30						30
Li		55					65							
Fe <sub>2</sub> O <sub>3</sub>	10.6	10.8	10.7	10.9	10.7	10.8	11.5				6.8	8.3	8.2	
K <sub>2</sub> O	3.2	3.8	3.8	3.9	3.5	3.2	3.0				3.4	3.0	3.0	
CaO	1.8	2.2	2.1	2.2	1.9	1.9	2.0				1.5	6.2	6.4	
SiO <sub>2</sub>	60	61	61	60	58	60	59				69	54	53	
Al <sub>2</sub> O <sub>3</sub>	14.4	17.8	17.7	17.3	15.7	15.1	14.0				13.5	13.6	13.2	
C org		2.3	2.86	4.6	4.6	4.6	5.4							
H <sub>2</sub> O	83	79	81	80	83	83	88	75						







	Su-8-61	SU-9-61	GH-1-62			GH-1-62-HPC			GM-5-62				
	JG	OP	JA	JB	JC	JD	JE	46-8	53-5	58-60	JA	JE	JF
Zr	167	184	151	165	155	161	162	185	129	156	156	159	147
Sr	166	169	148	173	146	158	171	268	300	282	124	114	123
Rb	106	13	108	130	102	115	122	148	157	141	128	99	96
Br	72	0?	68	70	58	59	86	5	12	6	73	80	84
Zn	175	83	124	173	136	188	241	103	113	108	94	269	303
Cu	208	3340	92	150	105	147	183	138	128	131	46	63	104
Ni	23	41	28	32	24	32	43	28	38	26	21	21	23
Mn	3410	1400	2620	3380	2130	2750	6300	1260	1160	1010	1720	1960	5400
Ti	3770	5640	3200	3940	2650	3540	3840	4310	3240	3120	3350	3410	3480
Pb											12	31	32
V			165			120	150	132	130	125	150	107	112
Ga			15			9	19	11	9	19	19	19	22
B			63			47	55	63	28	47	90	35	47
Li													
Fe <sub>2</sub> O <sub>3</sub>	12.6		9.6	9.6	9.5	9.4	9.8	9.1	10.9	9.9	8.4	8.3	8.3
K <sub>2</sub> O	2.8							3.8	4.1	4.4	4.0	3.5	3.2
CaO	2.2							5.5	2.2	2.0	3.7	4.7	5.7
SiO <sub>2</sub>	56							56	55	56	59	59	59
Al <sub>2</sub> O <sub>3</sub>	12.7							14.6	16.3	16.9	13.8	12.8	12.0
C org													
H <sub>2</sub> O			76	77	80	79	82				79	82	80

APPENDIX 4: TRACE ELEMENT ANALYSES OF  
LEACHABLE CATIONS

Format for the tabulation of results

Although all four elements (Cu, Zn, Mn, Ni) were analyzed from the same aliquots, the results are listed here by the individual elements. The columns of data are as follows:

Column 1. Locality and sample number.

Column 2. Sequence of acetate leaches of the same sediment sample.

Column 3. Milliliters of 1 N ammonium acetate used in leaching.

Column 4. Grams of sediment being leached (dry weight, determined after all leaching was concluded.)

Column 5. Micrograms of the element leached.

Column 6. Column 5, converted to ppm on the basis of Column 4.

Column 7. Concentration of the element (ppm) in the unleached sediment, as determined from analysis of a separate aliquot.

Column 8. Percentage of Column 7 that was leached.

Analytical Techniques: The method for leaching and analysis is explained in detail in the text section on analytical techniques.

Part A. Copper

	1	2	3	4	5	6	7	8
GS-2-62-JA		1	250	17.5	0			
"		2	250		10			
"		3	250		0			
Total JA			750		10	.57	19	3.1
GS-2-62-JB		1	250	22.4	15			
"		2	250		10			
"		3	250		0			
Total JB			750		25	1.11	38	2.9
GS-2-62-JC		1	250	20.4	62			
"		2	250		87			
"		3	250		50			
Total JC			750		199	9.7	221	4.4
GS-2-62-JD		1	250	12.1	100			
"		2	250		98			
"		3	250		68			
Total JD			750		266	22	267	8.2
GS-2-62-JE		1	250	8.0	70			
"		2	250		63			
"		3	250		38			
Total JE			750		171	21.4	273	7.8
GS-10-62-JA		1	300	4.95	63	12.7	63	20
" JB		1	300	15.01	46	3.06	117	2.6
" JC		1	300	5.47	160	29.3	266	11.0
" JD		1	300	7.34	199	27.1	370	7.5
GS-23-62-JA		1	400	11.0	13	1.18	135	0.87
" JB		1	400	11.3	14	1.24	130	0.95
" JC		1	400	11.4	15	1.32	112	1.22
" JD		1	400	10.5	34	3.22	158	2.04
" JE		1	400	10.1	190	18.8	501	3.76
" JF		1	400	11.8	99	8.4	432	1.95
GS-26-62-HPC								
" 5-10cm		1	400	23.19	27	1.2	87	1.4
" 50-55cm		1	400	18.43	55	3.0	nd	
" 126-130cm		1	400	30.63	53	1.7	21	8.1
GS-31-62-HPC								
" 27-36cm		1	400	33.51	23	0.68	112	0.6
" 95-102cm		1	400	36.80	17	0.46	77	0.6

Part B. Zinc

	1	2	3	4	5	6	7	8
GS-2-62-JA		1	250	17.5	10			
"		2	250		7			
"		3	250		6			
Total JA			750		23	1.3	50	2.6
GS-2-62-JB		1	250	22.4	17			
"		2	250		10			
"		3	250		8			
Total JB			750		35	1.6	61	2.6
GS-2-62-JC		1	250	20.4	18			
"		2	250		15			
"		3	250		18			
Total JC			750		51	2.5	110	2.3
GS-2-62-JD		1	250	12.1	54			
"		2	250		54			
"		3	250		15			
Total JD			750		123	10.2	123	8.3
GS-2-62-JE		1	250	8.0	15			
"		2	250		20			
"		3	250		16			
Total JE			750		51	6.4	143	4.5
GS-10-62-JA		1	300	4.95	10	2.02	130	1.5
" JB		1	300	15.01	35	2.33	99	2.3
" JC		1	300	5.47	60	29	143	22
" JD		1	300	7.34	64	27	180	15
GS-23-62-JA		1	400	11.0	17	1.55	122	1.27
" JB		1	400	11.3	04	0.35	128	0.27
" JC		1	400	11.4	20	1.75	127	1.38
" JD		1	400	10.5	23	2.10	144	1.46
" JE		1	400	10.1	44	4.36	226	1.93
" JF		1	400	11.8	40	3.49	197	1.77
GS-26-62-HPC								
" 5-10cm		1	400	23.19	6	0.25	64	0.4
" 50-55cm		1	400	18.43	9	0.48	nd	
" 126-130cm		1	400	30.63	12	0.39	69	0.57
GS-31-62-HPC								
" 27-36cm		1	400	33.51	12	0.35	106	0.33
" 95-102cm		1	400	36.80	6	0.16	100	0.16

Part C. Manganese

	1	2	3	4	5	6	7	8
GS-10-62-JA	1	300	4.95	6	1.21	1540	.08	
" JB	1	300	15.01	5	0.33	1530	.02	
" JC	1	300	5.47	6	1.09	2100	.05	
" JD	1	300	7.34	10	1.36	2260	.06	
GS-23-62-JA	1	400	11.0	37	3.36	1480	.23	
" JB	1	400	11.3	67	5.93	1510	.39	
" JC	1	400	11.4	80	7.02	1520	.46	
" JD	1	400	10.5	21	2.00	1740	.11	
" JE	1	400	10.1	27	2.67	3910	.07	
" JF	1	400	11.8	75	6.35	1690	.37	
GS-26-62-HPC								
" 5-10cm	1	400	23.19	19	0.81	1000	.08	
" 50-55cm	1	400	18.43	4	0.21	nd		
" 126-130cm	1	400	30.63	17	0.55	1000	.05	
GS-31-62-HPC								
" 27-36cm	1	400	33.51	7	0.20	1770	.01	
" 95-102cm	1	400	36.80	22	0.59	1020	.058	

Part D. Nickel

(N. B. The analytical limit of sensitivity for leached Ni is one microgram, therefore a zero in the following table should be interpreted as "less than or equal to one microgram.")

	1	2	3	4	5	6	7	8
GS-2-62-JA	1	250		17.5	4			
"	2	250			1.5			
"	3	250			0			
Total JA		750			5.5			
GS-2-62-JB	1	250		22.4	4.5	0.31	11	2.8
"	2	250			1.5			
"	3	250			0			
Total JB		750			6.0	0.27	13	2.1
GS-2-62-JC	1	250		20.4	3.5			
"	2	250			1.5			
"	3	250			0			
Total JC		750			5.0	0.24	14	1.7
GS-2-62-JD	1	250		12.1	8.5			
"	2	250			9			
"	3	250			3			
Total JD		750			20.5	1.7	15	11.3
GS-2-62-JE	1	250		8.0	2			
"	2	250			0			
"	3	250			1.5			
Total JE		750			3.5	0.44	16	2.8
GS-10-62-JA	1	300		4.95	0			
" JB	1	300		15.01	0			
" JC	1	300		5.47	0			
" JD	1	300		7.34	0			
GS-23-62-JA	1	400		11.0	0			
" JB	1	400		11.3	0			
" JC	1	400		11.4	2	.18	30	0.6
" JD	1	400		10.5	4	.38	32	1.2
" JE	1	400		10.1	9	.89	33	2.7
" JF	1	400		11.8	nd			
GS-26-62-HPC								
" 5-10cm	1	400		23.19	8	.35	18	2
" 50-55cm	1	400		18.43	0		nd	
" 126-130cm	1	400		30.63	6	.20	19	1
GS-31-62-HPC								
" 27-36cm	1	400		33.51	0		28	
" 95-102cm	1	400		36.80	0		26	

APPENDIX 5: TRACE ELEMENT ANALYSES OF SIZE FRACTIONS

Sample and ASTM mesh size fraction	Zr	Sr	Rb	Br	Zn	Cu	Ni	Mn	Ti				
GS-2-62-OP					(all ppm)								
+200	207	175	70	10	9	16	2	360	740				
-200+400	417	198	56	9	20	32	4	360	1590				
-400 coarse	542	267	51	10	28	34	7	640	3880				
-400 fine	146	118	99	102	185	269	28	1500	3100				
GS-28-62-OP													
+200	295	136	66	8	10	23	1	230	1200				
-200+325	821	205	69	13	18	23	3	360	2510				
-400 coarse	603	248	90	26	51	36	10	770	5940				
-400 fine	149	160	163	100	140	122	39	1670	4940				

-400 coarse = fraction remaining sedimented after repeated decanting of sediment still in suspension after one hour in a container with a four inch water column, thus, largely fine silt size particles.

-400 fine = fraction remaining after one hour in the upper two inches of water in the settling container, thus, clay size particles.

APPENDIX 6: Eh, pH, AND ALKALINITY MEASUREMENTS  
IN LAKE SUPERIOR WATERS AND SEDIMENTS

Core or Sample	pH	Eh	Sediment Type
Su-1-61 Jenkins			
Water	7.36	+391 mv	Water
1 cm depth	6.70	+344	Brown mud
7 cm	6.81	+395	"
20 cm	6.30	+139	Brown clay
S-1-61			
"69 cm"	6.60	+113	Brown clay
561 ft.	7.12	+084	gray clay
? ft.	7.68	+098	red clay, varved
? ft.	7.72	+100	" "
(Depth designations at S-1-61 may not be trusted because of sampling and coring difficulties)			
Su-4-61 H <sub>2</sub> O	7.66	+455	Water
S-2-61			
906 ft.	8.31 to 8.61	+157	gray clay, varved
888 ft.	8.22	+196	" "
921 ft.	7.95	+173	" "
	8.26	+203	red clay, varved
934 ft.	8.32	+325	"
940 ft.	8.38	+288	"
966 ft.	8.30	+185	"
992 ft.	8.00	+294	"
1012 ft.	8.10	+288	sandy red clay
Water, 450 ft.	7.58	+412	
" 300 ft.	7.63	+434	
" 100 ft.	7.60	+430	
S-3-61			
"anchor sample"	7.24	+112	gray clay
Su-6-61	8.01	+401	silt
S-5-61			
surface mud	7.10	+462	brown mud
2 inches	7.25	+125	gy brn mud
938 ft.	6.72	+051	gray clay
960 ft.	7.62	+051	gray clay
965 ft.	7.48	+118	"
993 ft.	8.01	+130	red clay
1014 ft.	8.18	+286	"
1026 ft.	8.41	+308	"
1041 ft.	8.18	+174	"
1058.5	8.20	+093	"
Water, 900 ft.	7.57	+402	
	500 ft.	+414	
	300 ft.	+426	
	100 ft.	+411	

Core or Sample	pH	Eh	Sediment Type
S-6-61			
657 ft.	7.10	- .012 mv	brown mud
676 ft.	8.54	+113	red brn clay
	8.41	+130	red clay
GS-1-62 OP	8.39	+198	"
GS-2-62	6.62 to 6.93	+351	sand
OP	6.98	+050	brown mud, silty
JA	6.82	+159	"
JC	6.87	+087	"
JE	6.87	+137	
water	7.20	+405	
Jenkins at 4 cm depth, just after opening	6.81	+443	
GS-3-62 water	7.71	+348	
OP	6.76	+165 to +231	fine silt to mud
GS-4-62 surface mud 1.8 cm	6.88	+206	Brown mud
	6.91	+084	"
GS-5-62-OP	7.00	+446 to +496	Sdy silt with clay
GS-6-62-OP	6.89	+537 erratic	sandy loam
GS-7-62 water HPC bit	7.98	+437	
	6.68	+067	gray clay
GS-23-62			
JF	6.81	+179	gray mud
JD	6.90	+005	"
JB	6.77	- .098	"
GS-26-62 HPC	6.18	+242	gray clay
GS-27-62 HPC	7.59	+043	"
S-7-62 544'	8.07	- .046	
OP	7.73	+088	
S-8-62			
water	8.36	+448	
1 ft.	6.99	+114	gray clay

## ALKALINITY

Locality	pH	Alkalinity, ppm, as CaCO <sub>3</sub>
GS-1-62	7.88	43.5
GS-3-62	7.71	42.8
GS-4-62	7.85	41.0
GS-5-62	7.85	41.5
GS-7-62	7.98	45.0
GS-8-62	7.86	42.1
GS-9-62	7.60	42.0
GS-10-62	7.53	41.9
GS-13-62	7.66	49.4
GS-14-62	7.59	42.0
GS-15-62	7.67	43.9
GS-17-62	7.64	43.1
GS-19-62	7.74	42.5
GS-23-62	7.56	41.6
GS-27-62	7.70	41.0
GS-29-62	7.55	43.3

APPENDIX 7: METHODS OF SAMPLING AND ANALYSIS

Boats

M. V. SUBMAREX: Sampling was undertaken during July 1961 and July-August 1962 on board the M. V. SUBMAREX, 176 foot vessel owned and operated by Global Marine Exploration Company. The 1961 studies were a joint project of the University of Michigan and the University of Minnesota, and the 1962 undertaking was sponsored by the University of Michigan. All Submarex operations were financed by the National Science Foundation.

R. V. INLAND SEAS: During July and August of 1962 samples were collected on board the R. V. INLAND SEAS, 117 foot research vessel of the Great Lakes Research Division of the University of Michigan Institute of Science and Technology.

Other vessels: During August of 1961 samples were taken in two brief trips on Lake Michigan: The NIAD and LADY MAGGIE, both operated by Great Lakes Research Division were used for sampling in the Charlevoix and Chicago-Milwaukee areas, respectively.

### Sampling

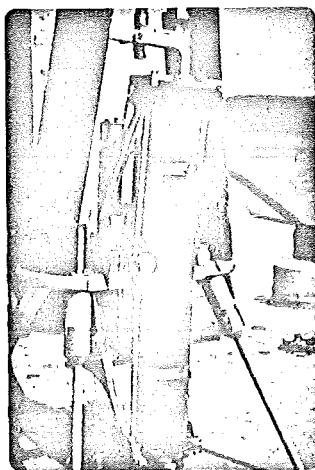
Jenkins Surface Mud Sampler: The Jenkins surface mud sampler (Figure 22) procures a relatively undisturbed sample of the surface mud and overlying water. First designed and constructed under the direction of C. H. Mortimer for his studies of sediment-water exchange in the English Lakes District (1941, 1942), the sampler has been used subsequently by several limnologists to study sediment-water interface phenomena. Our sampler was constructed in the University of Michigan Natural Sciences Shop from blueprints and castings provided by the Freshwater Biological Association, Ambleside, Westmorland, England.

The Jenkins sampler consists of a framework on which a cylindrical plastic sample tube of 2 3/4 inch I. D., and 20 inch length is mounted. Penetration of the sampling tube into the sediment and concomitant release of tension on the supporting cable trips a closing mechanism that slides lids over the top and bottom of the sampling tube. The sampler with its sample of sediment and water is then pulled to the surface. Minor modifications from the Mortimer design necessary for sampling in the Great Lakes include the addition of much heavier weights so as to double the weight of the sampler and the use of stronger springs on the sampling tube lids and on the tripping mechanism.

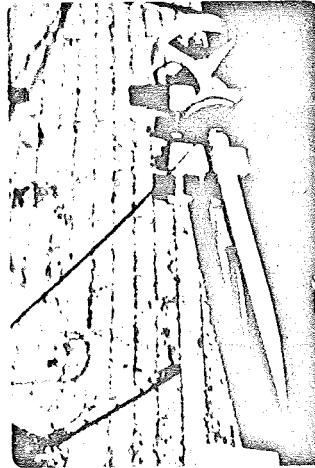
Under optimum conditions (soft mud bottom) the maximum (and optimum) penetration of ten inches, or one half of the sampling tube length is obtained. In firmer muds and in silts the penetration is considerably less, and no sample is retained in sands because of the lack of penetration and the inability of the springs to push the lids shut through such a firm substrate.

FIGURE 22

JENKINS  
SURFACE MUD  
CORER



HYDROPLASTIC  
CORER



Jenkins samples are not truly "undisturbed," as the slightest agitation of the sediment in sampling or in return of the sampler to the surface is sufficient to send the light floc at the sediment surface up into the overlying water. The advantage of the Jenkins sampler is fourfold:

- a) The sediment disturbance is far less than that found in any other samplers used or considered.
- b) The surface sediment, although disturbed to a depth of 1 to 2 cm, is entirely retained in the sampler by the automatic closing of the upper lid. Nor is there any loss incurred in retrieving and handling the sample.
- c) The plastic cylinder and lids provide a trace element-free container for handling and temporary storage.
- d) The large diameter of the sampling tube gives large sample volumes, permitting more extensive chemical and physical analyses.

Hydroplastic corer: The hydro-plastic corer (Figure 22) is fully described by the designers (Richards and Keller, 1961). It is a large diameter plastic-barreled sediment corer with a metal shroud to reduce instability during free fall and a core bit designed to give minimum resistance and maximum sediment penetration. Our corer was constructed in the University of Michigan natural science shop from plans provided by the U. S. Navy Hydrographic Office. Ten foot long, high density polyvinyl chloride core barrels were used. Recovery varied, depending on the firmness of the substrate and whether or not a free-fall device was used, with full ten foot recovery being attained only in the softest sediments.

Orange peel sampler: An orange peel sampler was used whenever the Jenkins sampler was unable to penetrate the sediment more than four centimeters. Of conventional design, the sampler has two main disadvantages: some of the sample is lost due to the erosive power of the water streaming past the incompletely protected sample as it is pulled to the surface, and one sometimes has difficulty in distinguishing between sediment from the sediment-water interface and sediment that had been 5 to 10 cm below.

Zumberge-Gast-Global Marine coring: Under the direction of Drs. J. H. Zumberge and Paul W. Gast, Global Marine Exploration Company obtained long cores of the lake bottom sediment and underlying till. The methods used are described in detail by Zumberge and Gast (1962). Cores from three of the six locations drilled were available at the University of Michigan for geochemical studies. In 1962 Global Marine obtained additional long cores, under the direction of Drs. W. R. Farrand and P. L. Cloke.

### Shipboard Analyses

pH: Measurements of pH were made within 12 hours of sampling. During the Summer of 1961 a Beckman model G pH meter was used, and a Beckman model 76 expanded scale pH meter was also available during the Summer of 1962. Beckman glass electrodes, and Beckman sleeve type saturated KCl reference electrodes were standardized against Beckman pH 6.8 buffer solution at frequent intervals, and additionally tested against a pH 4.1 buffer at least once a day. Readings are to  $\pm .02$  pH unit, and are corrected for temperature variation of the sediment and buffer solutions. They are, however, not corrected for the "suspension effect," or Donnan emf (van Olphen, 1963, p. 200). Tests on Lake Superior sediments showed the Donnan emf was nil for those flocculated near-surface sediments referred to as "muds" in this report. On the other hand, the dispersed sediments found at depth (sticky "clays") had a Donnan emf of -0.2 pH units maximum. This was determined by shaking Lake Superior sediments with Lake Superior water, allowing the suspension or floc to settle, and then observing the change in apparent pH when the calomel reference electrode was moved from the overlying supernatant into the settling suspension. The position of the glass electrode had no effect on the apparent pH.

The presence or absence of a Donnan emf is apparently as clear cut as the difference between "muds" and "clays;" no Donnan emf correction need be made to muds, while clay pH readings are about 0.2 pH unit low.

Eh: The Beckman model G and model 76 meters were also utilized for measurements of Eh. Measurements were made as soon as possible; none reported here was made more than 12 hours after sampling or 3 hours after

the sample was removed from the sample container. The platinum and sleeve type saturated KCl reference electrodes were tested daily against Zobell solution (Zobell, 1946). Although the meters may be read to  $\pm 2$  mv the accuracy of measurement is far less. Readings varied by 25 mv, or even more in some near-surface samples, if the electrodes were shifted from one part of the sample to another. Moreover, because of the low ionic strength and redox capacity of the lake and interstitial waters equilibrium was attained very slowly, especially in sediments of low Eh (less than +100 mv). The approach to equilibrium is, however, nominally exponential, and the investigator used the necessary expedient of ending the measurement when rate of drift had fallen below 4 mv per 4 minutes. The rate was below this value within a half hour in almost all cases. If drift was allowed to continue indefinitely the final reading was of dubious value, either being high because of equilibration with the atmosphere or being low because of the onset of activity of anaerobic bacteria. Neither extreme is an indication of conditions in the sediment, and it is apparent that really accurate measurement of Eh in the Great Lakes must be made with in-situ electrodes kept in-situ for several hours.

Eh measurements, like pH measurements, are subject to the "suspension effect," therefore no Donnan emf correction need be made to muds, but clay Eh readings are 12 mv low.

Carbonate saturometer: Saturometer tests were made, following the method of Weyl (1960). The change of pH of a solution on addition of solid calcite is an indicator of the degree of calcite undersaturation or supersaturation of the solution. An increase in pH indicates dissolution of calcite, hence, original undersaturation, whereas a decrease in pH is

evidence of precipitation of carbonate, hence, original supersaturation. No Donnan emf was created by the calcite used in this study.

Sample handling and storage: Jenkins samples were removed from the sampling tube by allowing segments of 3 to 5 cm of core to settle by gravity out of the bottom of the sampling tube. Each 3 to 5 cm sediment "slice" was placed in a pint-sized plastic ice-cream container. During the Summer of 1961 some of the "slicing" was done in the laboratory in Ann Arbor, but some of the 1961 and all of the 1962 samples were split in the field within 24 hours of sampling.

Orange peel samples were placed in the same pint sized plastic containers. Where clearly identifiable, surface mud was saved separately.

Hydroplastic core samples were transported to the laboratory in the plastic core barrel used in sampling, the ends being tightly sealed with plastic sheeting held by electrician's tape.

All the samples were stored in a cooler at  $5^{\circ}\text{C}$  until analyses or drying at  $110^{\circ}\text{C}$  took place. Unfortunately, one breakdown of the cooling system did occur, and for an unknown length of time, a maximum of 20 days, the sample temperature was somewhat elevated. No accelerated drying or bacterial action was observed at the end of that period, however, and the warming probably had little effect on the type of analysis made in this study.

### Laboratory Analyses

Sample preparation: Samples for chemical analyses were dried for 48 hours at 105-110°C. A portion of each was ground for 20 to 45 minutes in an automatic mortar grinder, using a porcelain mortar and pestle. To test for contamination in grinding, a sample of Brazil quartz that had previously been coarse ground, acid leached, and then thoroughly leached with de-ionized water, was ground overnight in the mortar grinder and then analyzed. None of the trace elements studied in this report were detected.

An aliquot from the mortar-ground sample was used for X-ray spectrographic determination of trace elements. The aliquot analyzed was not sieved, but sieving of representative samples showed over 95% of the sediment was finer than 200 mesh, and that the remaining 5% was largely cakes of finer grained material rather than coarse grains per se.

A second aliquot of the mortar ground sample was used for emission spectrographic analysis for trace elements. As in the case of X-ray spectrographic analysis, the aliquot was not sieved.

A third aliquot of the mortar ground sample was used for major element analyses by X-ray spectrography. This aliquot was further ground in a high frequency mixer - ball mill, using a hardened steel container and ball. The samples were not sieved, but sieving of similarly treated samples showed that 95% of the sediment grains were finer than 300 mesh, and the remaining 5% was again largely cakes of finer grained material rather than coarse grains per se. Analysis of Brazil quartz treated in the same manner showed that some iron contamination from the mixer - ball mill occurred. In quartzose sediments as much as 0.2% iron could be added

during the grinding process, but most sediments, with an appreciable clay content, probably picked up less than 0.1%. Inasmuch as even 0.2% is less than the reproducibility of the analytical technique, no correction to the data has been made.

Trace elements: X-ray spectrographic analyses: Analyses for Zr, Sr, Rb, Br, Zn, Cu, Ni, Mn, and Ti were made with a Norelco Universal Vacuum X-ray Spectrograph, using the technique of standard addition. Although standard addition is used routinely in many analytical chemistry procedures, no detailed discussion of the application of this method to X-ray spectroscopy has been published. Therefore, a critique of the method as applied to X-ray spectroscopy, and an outline of the exact procedures used is included in this report as Appendix 8.

Reproducibility: Repeated analyses of GS-26-62-HPC were made to determine analytical reproducibility. The results are shown in Table 17.

Accuracy: The Canadian Institute of Spectroscopy standards "Syenite Rock-1" and "Sulphide Ore-1" (Webber, 1961) were analyzed as a test of accuracy. The results are shown in Table 18. Taylor and Kolbe (1964), who made an extensive comparison of silicate rock standards, are in agreement with the present investigation in concluding that the averages of analyses for Sr, Cu, Ni, and Ti reported by Webber are high.

Although the analyses of the standards for manganese by the method of this investigation are within the range of values reported by other investigators, the results are high. Manganese analyses of sediment from western Lake Superior made by this study are close to the analyses of similar sediments reported by Swain and Prokopovich (1957), suggesting that the error is not large. Nevertheless, the writer has avoided basing

TABLE 17: REPRODUCIBILITY OF X-RAY SPECTROGRAPHIC  
ANALYSES OF TRACE ELEMENTS

Repeated Analyses of GS-26-62-HPB

Element	X average ppm	s	R=
			$\frac{s}{\bar{X}} \cdot 100$
Zr	170	11	6
Sr	190	5.6	3
Rb	105	5.2	5
Br	0 #		
Cu	98	4.3	4
Zn	173	12	7
Ni	28	2.3	9
Mn	1200	39	3
Ti	3780	150	4

# Tests of other samples suggest that

for Br 80 ppm.

TABLE 18: ACCURACY OF X-RAY SPECTROGRAPHIC  
ANALYSES OF TRACE ELEMENTS

Analysis of Canadian Institute of Spectroscopy

Standards. Data in PPM

CIS Sulphide Ore-1

Element	Webber, 1961 (1)			Taylor &	This
	X, ppm	s	s	Kolbe, 1964 ppm	Investigation ppm
Zr	109	22	10		103
Sr	133	29	17		93
Zn	294	143	64		240
Ni	12,280	3,720	1,406		10,900
Mn	851	282	85		1370
Ti	4580	783	248		4150

CIS Syenite Rock-1

Element

Zr	2833	736	329	2500	2850
Sr	422	197	88	205	266
Zn	200	115	66	-	165
Cu	24	10	4	22	19
Ni	46	20	8	40	38
Mn	3260	387	137	3000	4300
Ti	3100	828	293	2500	2420

(1) Data of Webber, 1961, reports on the variation between laboratories.  
Tabulated here is F, s between n laboratories.

Filby (1965) finds 0.84 ppm Bromine in the CIS Syenite Rock-1.  
This investigation found that Bromine in the CIS Syenite Rock-1 was  
less than the analytical limit of 2 ppm.

conclusions on the absolute concentration of manganese in the sediments.

Trace elements: Emission spectrochemical analyses: Emission spectrochemical analyses for B, Ga, V, Li, and Pb were performed by a commercial spectrographic laboratory on a selected suite of lake sediment samples. The samples were analyzed by an internal standard technique, using a series of synthetic samples as standards, and U. S. Geological Survey Standard W 1 as control. Samples and standards were diluted with a buffer mixture to minimize matrix effects. The spectrographic lines used were checked for line interferences. Line densities were read with a photoelectric microphotometer.

Trace Elements: Exchangeable Trace Elements: Samples of undried sediment were leached with one normal ammonium acetate to determine the degree to which trace elements present are exchangeable. The exact significance of the quantitative results of an acetate leaching is difficult to ascertain, as it is known that precision is not high, and that the result is strongly dependent on the exact technique used (Pratt and Holloway, 1954), therefore conditions are stated in full in the following paragraphs.

Leaching of trace elements: Undried sediment corresponding to 5 to 20 grams dry weight was placed in a 100 ml plastic centrifuge tube. The tube was filled with 1 normal ammonium acetate, the sediment and solution were thoroughly mixed, the tube was capped with a plastic lid, and set aside for 24 hours, with occasional stirring. After 24 hours the tube and its contents were centrifuged, and the supernatant was decanted into a plastic bottle. This process was repeated until the sediment had been leached by 300 ml of solution. For one Jenkins core the leaching was continued until

900 ml had been collected in sequential 300 ml portions.

The ammonium acetate was prepared by mixing redistilled acetic acid, de-ionized water, and redistilled ammonium hydroxide. Disposable plastic gloves, plastic or pyrex containers, and utmost care were used throughout the entire leaching experiment so as to minimize contamination.

Concentration of trace elements leached: Prior to concentration the supernatant was filtered with cellulose acetate membrane filters of 0.65 micron pore diameter.

The concentration method of Silvey (1961) was used to increase the sensitivity of the X-ray spectrograph. In this method 8-hydroxyquinolinol, tannic acid, and thionalide in a buffered solution precipitate the heavy metals. Quantitative precipitation of Co, Ni, Mo, Cu, Zn, Sn, Pb, Cr, V, Ti, Be, Ge, Mn, Al, Ag, Fe, Bi, Ga, and In occurs (in this study only Cu, Zn, Mn, and Ni were present in detectable quantities).

Silvey's procedures were followed exactly, except for the following modifications:

The solution, already 1 N in ammonium acetate, was adjusted to pH 5.2 with HCl before the precipitating agents were added.

Samples were not evaporated: Reagent volumes were increased accordingly.

The carrier used was aluminum, introduced as  $\text{AlCl}_3$ , prepared and purified by the method of Mitchell and Scott (1947). Iron, used as internal standard, was introduced as  $\text{FeCl}_3$ , and prepared by dissolving spectrographic purity iron in concentrated HCl.

Analysis: The precipitate, when vacuum filtered with a cellulose acetate filter of 0.65 micron pore diameter, formed a thin, even layer over the filter paper. The paper was removed from the vacuum filtering system,

cut to the size of an X-ray spectrographic sample holder, placed, precipitate-down in the holder over a .005 mil mylar sheet, and weighed down by a leucite cylinder. The loaded holder was immediately placed in the X-ray unit. The moist filter paper and filtrate retained uniform characteristics as long as a vacuum was not applied.

The peaks of the elements being determined and the internal standard peak were scanned at slow speed, using a large time constant ( $1/2^{\circ}$  per minute, 8 seconds). Artificial standards were prepared by diluting a quantitative mixture of salts of the elements to be analyzed to suitable concentrations with de-ionized water. A blank and a standard were analyzed each time new reagents or ammonium acetate were prepared. A series of standards of differing concentrations showed that peak height was a linear function of concentration to better than 5 percent for the four elements analyzed (Mn, Cu, Zn, Ni). In practice the height of the internal standard peak also varied by less than 5 percent, indicating that the precipitate matrix was uniform and that instrumental stability was high.

Major element analyses: For major element analyses by X-ray spectrography, samples were diluted with starch so as to reduce interelement effects. One part of sediment was mixed with nine parts of starch in a plastic container in the mixer-ball mill. The mixture was then pressed in a metallurgical press at 20,000 psi for 15 minutes. The resultant sample pellet was placed in the X-ray spectrograph and analyzed by comparing X-ray intensity of the pellet with that of a "standard sediment." Where necessary, background corrections were made.

The "standard sediment" was GS-11-62-OP that had been analyzed

without starch dilution by synthetic construction of a sample of the same composition, using reagent chemicals and Brazil quartz. Three successively more accurate approximations to its bulk composition were made by mixing reagent chemicals that had been ground and sieved with a 400 mesh sieve.

Because of particle size effects, interelement effects, and problems with instrumental stability the accuracy and reproducibility are considered to be 5 percent of the amount present for Fe and Si and 8 to 10 percent of the amount present for Ca, K, and Al.

Size fraction separations: Selected samples of undried sediment were wet-sieved using a plastic and nylon sieve set with +100, 200, 325, and 400 ASTM mesh sieves. De-ionized water was used throughout. The minus 400 fraction was further divided by repeated decanting of the sediment that was still in suspension one hour after mixing. Coarse silt is retained in the +400 sieve, and fine silt is separated from clay-sized particles by the decanting. Settling is dependent on density and shape as well as size, therefore the separation within the minus 400 fraction is in part due to shape and density. Because there is no better way to separate small particles, the effects of shape and density are traditionally ignored. Therefore the results of this study should be comparable to those of previous investigators.

Mineralogical analyses: Selected samples were examined by X-ray diffractometer. The samples, ground to -300 mesh in the mixer-ball mill, were pressed into sample holders with the metallographic press using a pressure of 18,300 psi. Peak heights and degree of preferred orientation in a given sample are reproducible to within 10 percent, but the degree

of preferred orientation in these sediments is a function of the total clay content, hence quantitative analyses of the bulk samples are unreliable. In this report the qualitative results are outlined, together with some quantitative studies that are based on the ratio of peak heights of physically similar minerals that should have similar behavior with regard to preferred orientation.

Further data on the X-ray diffractometric techniques are shown in Table 19.

TABLE 19: X-RAY DIFFRACTOMETRIC ANALYSIS OF  
LAKE SUPERIOR SEDIMENTS

Conditions:

Norelco X-ray diffractometer, with ma stabilizer, voltage regulator.  
 Cu radiation, Ni filter, kv=47, ma =18  
 Divergence and anti-scatter slits 1°  
 Receiving slit .003"  
 Proportional counter, detector voltage 1.54 kv  
 Pulse height discrimination set so as to eliminate most FeK<sub>α</sub>  
 fluorescence.

Mineral	Peak	Peak
	Å	hkl
Calcite	3.04	104
Dolomite	2.89	104
Plagioclase Feldspar	3.18	040
Potassic Feldspar	3.23	220, 002, 040
Quartz	3.33	101
Chlorite	7.0	002
Amphibole	8.4-8.6	110
Illite	10	001
Mixed Layer Clays	9.4	001?
" " "	11.0	001?
" " "	12.1	001?
Montmorillonite +Chlorite	14	001
Expanded clays	16	001

## APPENDIX 8 : APPLICATION OF STANDARD ADDITION

### TECHNIQUE TO X-RAY SPECTROCHEMICAL ANALYSIS

General: A fundamental problem of quantitative analysis by X-ray spectroscopy is the adequate compensation for changes in absorption and enhancement of the incident and excited X-ray beams due to changes in the total composition of the sample being analyzed. An improvement over direct comparison of the unknown with a sample of roughly similar composition is the use of an internal standard. Hower (1959), who has applied the technique to X-ray spectroscopy, shows, however, that the internal standard technique cannot be used if there is a major element absorption edge between the peaks of the internal standard and the element to be analyzed. Moreover, peaks that are close to major element absorption edges (eg, Ni, Mn, both close to Fe) will be subject to enhancement effects, particular to their exact wavelengths, that cannot be compensated for by an internal standard at a different wavelength.

Liebhafsky et. al. (1960, Fig. 7-5 and accompanying text) show the possible relationships between internal standard, element to be analyzed, and major element absorption edges, and the absorption and enhancement effects inherent in the possible relationships.

A second problem found in using the internal standard technique in X-ray spectroscopy is that the calibration curve is strongly dependent on the exact angle at which the peak is counted. Slight changes in alignment will shift the calibration curve significantly. Using peak area will eliminate this problem, but with attendant loss in accuracy, especially in the lower concentration ranges, because of uncertainties in peak area measurement. Thus if the usual counting techniques are used, the

calibration curve must be rerun often.

A third point, particularly critical in trace element analyses, is that any method of analysis can be no more accurate than the accuracy of the background determination.

The Internal Standard Technique: Because the X-ray unit used would not retain alignment from day to day, and because of the strong enhancement and absorption effects of Fe K the method of standard addition was used for this study. Nine parts of sediment were diluted with one part of starch. To a second nine parts of sediment a single part of "spike," consisting of small known amounts of all the elements being analyzed in a starch carrier, was added. The difference in peak intensity between the spiked and unspiked samples is the X-radiation due to the added, known spike, and constitutes an "internal standard" at the same wavelength as the unknown.

This method of standard addition is an improvement over internal standard techniques in the following respects:

1. Problems of alignment and instrumental stability are minimized because the spiked and unspiked peaks of a given element in an unknown are counted within minutes of each other.
2. The "standard," measured at the same wavelength as the unknown, and measured in the same major element matrix, is subject to identical absorption and enhancement effects.

This method of standard addition has the following disadvantages:

1. Weighing time is doubled because two rather than one mixtures must be prepared for each sediment to be analyzed.
2. Instrument time is increased, because there is a one to one

ratio between "unknowns" and "standards."

The following assumptions are made in applying the method of standard addition to trace element analysis by X-ray spectrography:

1. The added spike does not change the bulk absorption properties of the sediment. Theoretical calculation of the absorption coefficient at each of the analytical wavelengths shows this to be true to within three percent in all cases, and this is confirmed in actual practice. The background correction outlined below compensates for this slight change.
2. The small quantity of one trace element added in the spike does not enhance significantly the X-radiation of a neighboring element being analyzed. Because enhancement effects cannot be calculated directly from absorption coefficients this assumption cannot be evaluated theoretically. However, from the experimental data summarized by Liebhafsky et. al. (1960, op. cit.) the assumption appears to be valid for the small amounts of trace elements added in the spike.
3. There is a linear relationship of count rate and concentration in the range of concentrations to be analyzed. Plots of count rate versus concentration for artificial mixtures of  $\text{KNO}_3$  and varying amounts of spike showed this to be true for all of the trace elements analyzed for concentrations up to 3 to 6 times the highest concentration of each element found in any sediment analyzed. The sole exception to this statement is three sediments of high manganese content, for which linearity in manganese could be attained only by decreasing the intensity of the incident X-ray beam, and thereby decreasing the

reproducibility of the analysis.

Mixing: Grinding and mixing has been described in Appendix 7. No significant difference was found in duplicate analyses of the opposing sides of pellets, showing that mixing has been adequate.

Pelletizing: The effect of particle size on X-ray spectrographic analyses can be minimized by pelletizing (Gunn, 1961). In this study samples were compressed into a circular pellet one inch in diameter using a metallurgical press, applying 12,600 psi for 20 minutes. A few quartz rich sediments would not form coherent pellets: These were poured directly into a .005" mylar floored sample holder and gently compressed by the weight of a leucite or aluminum cylinder.

An alternate procedure for the preparation of quartzose samples is the addition of a few drops of the mineral oil of low vapor pressure used in vacuum pumps. The oiled sample will form a coherent pellet in the metallurgical press. However, the thin film of oil formed over sample grains is an absorber of X-rays that reduces the intensities of the X-rays of lighter elements (Ti, Mn) by as much as 80 percent. It is thought (but not proved) that slight differences in the amount and distribution of oil in a spiked and unspiked pair of pellets might result in analytical error in lighter element analysis, therefore the oiling of samples to obtain coherent pellets was discontinued.

Background Measurement: As stated above, an accurate determination of the background beneath an analytical line is essential for the accurate determination of trace quantities of elements no matter what analytical

procedure is used.

In order to make background corrections, the count rate was measured at specific background wavelengths on every sample. These measurements were made as near as possible to the wavelength of the analytical peak and yet not so near as to be subject to line interference, even when ten times the normal trace element concentrations were present. The background directly beneath the analytical line was routinely calculated as a function of the background at these nearby wavelengths.

The best functions found were those where the background was determined from two nearby wavelengths that bracket the wavelength of the element to be analysed. In all cases where this was feasible (Zr, Sr, Rb., Br.,) the background beneath the peak was found to be some constant fraction of the backgrounds at the bracketing wavelengths, and this fraction was relatively insensitive to changes in alignment and changes in total background intensity. Where through necessity the background was measured at a single wavelength, the ratio of background beneath the element to be analyzed was relatively sensitive to changes in alignment, and in the cases of Cu, Zn, and Ni was a function of total background intensity as well.

The best numerical constants for all background functions were derived by examination of the background of suitable reagent chemicals. Not all "reagent" chemicals are of the required purity (e. g., potassium salts have considerable rubidium contamination). On the other hand, some variation is due to statistical fluctuation in count rates. The procedure adopted was that of eliminating obviously contaminated chemicals, then calculating the constants of the background function for each element from the remaining reagents. Then, weighted average functions were

determined for each element, assuming that the remaining variation was partly statistical and partly due to the presence of micro-contaminants.

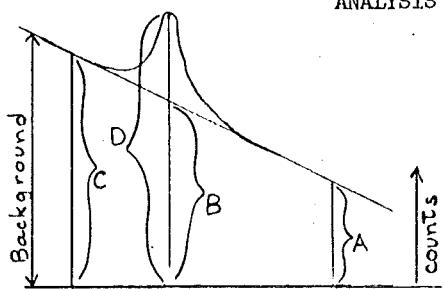
The spiked and unspiked samples often differed in total background intensity by as much as 3 percent, usually in the direction predicted by theoretical calculation of absorption coefficients. However, in the preliminary study of linearity it was found that similar variation might be expected because of slight differences in the degree of compaction of the pellets, in the orientation of the pellets in the sample holder, or in slight differences in the sample holders themselves. Adjusting peak intensities of a spiked and unspiked pair to a common background level by multiplying one by the ratio of backgrounds improved reproducibility and accuracy considerably. Therefore this procedure was used throughout the study.

Statistical Variation: The method of fixed counts was used. Peaks and backgrounds were counted for a sufficient number of counts to make the 90 percent confidence limit 2 percent or less for the trace element concentrations normally encountered. More accurate (i. e., longer) counts are not justified because of other analytical uncertainties.

Sample Calculation: A sample calculation is shown in Table 20. Actual data processing was somewhat different, primarily because the data was recorded on a fixed count rather than fixed time basis.

TABLE 20: EQUATION FOR STANDARD ADDITION

## ANALYSIS BY X-RAY SPECTROSCOPY



D = Total counts at analytical wave length

B = Background counts at the analytical wave length

A,C = Background (total) counts at nearby wave lengths.

$$f = \frac{B - A}{C - A} \quad \text{as determined from reagent chemicals.}$$

Therefore, in both the spiked and unspiked samples:

$$B = A + f(C - A)$$

Now, using the subscript u for the unspiked sample and s for the spiked sample:

$$\text{Concentration of given trace element in unknown} = \frac{\left( \frac{(D_u - B_u)}{B_u} \right)}{\left( \frac{(D_s - B_s)}{B_s} \right) - \left( \frac{(D_u - B_u)}{B_u} \right)} F$$

where F is the concentration of the trace element in the spiked sample that is due to the spike only, and where the factor  $(B_u/B_s)$  corrects for minor differences in the X-ray emission and absorption of the spiked and unspiked samples.

APPENDIX 9: DIFFUSION IN LAKE SUPERIOR SEDIMENTS

Theory of Diffusion in Exchange Media

Diffusion in Lake Superior sediments is analogous to self diffusion in ion exchange media in that there will be a dynamic partitioning of ions between exchange sites and solutions, the mobility of a given ion being different in the two positions.

Bloksma (1957) has shown how the problem may be treated mathematically. The diffusion coefficient of a cation in pure water,  $D_+$ , is given by the formula:

$$D_+ = kT\omega_+ = \frac{\omega_+ RT}{z F^2}$$

where:  $k$  = Boltzmann's constant.

$R$  = the gas constant per mole

$T$  = the absolute temperature

$F$  = the Faraday

$z$  = the valence of the ion

$\omega_+$  = ionic mobility, defined by this equation.

In a sediment-water mixture the diffusion coefficient will be reduced because of the limited geometry of the diffusion path. To take this into account, we may write:

$$D_+ = kT\omega_+ h$$

where  $h$  = the "labyrinth" factor, a measure of the "tortuosity" of the path.

$h$  can be calculated for theoretical particle shapes and packing, but it is normally determined by experiment.

A cation diffusing through a mixture of water and a substance with an exchange capacity will be slowed up not only by the tortuosity of the diffusion path but also by the forces exerted on them by the electric charges of the sorbate. One can define  $g$  as the apparent reduction

factor for the adsorbed ion while it is on an exchange site. Then if the cation is adsorbed for a fraction of time  $\frac{s}{n+s}$ , and in the pore solution for a fraction of time  $\frac{n}{n+s}$ , we can write:

$$D_+ \text{ (in exchange medium)} = kT w_+ \cdot \frac{(nh + sg)}{(n + s)}$$

$g$ ,  $h$ ,  $n$ , and  $s$  may be calculated from experimental data if a few reasonable assumptions are made (Bloksma, 1957).

#### Model for Diffusion in Lake Superior Sediments

Assume that an infinitesimally thin layer of sediment and interstitial water at the sediment-water interface is always in sorption equilibrium with the overlying water.

Assume that at the onset of "human contamination" the concentration of trace element in the lake water rose rapidly from a former low level to a new, higher level, and remained constant at the new higher level. (We know that this assumption is not the best representation of nature because the concentration of the trace element in the lake water should be buffered by the sorption processes themselves, and also that the onset of mining activity or other artificial sources should be somewhat gradual, but exact solutions of the diffusion equation for even moderately complex boundary conditions is usually impossible.)

Assume that there is no fixation or precipitation.

These conditions correspond to the following mathematical model (Crank, 1956, p. 18, Helfferich, 1959, p. 276-81):

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}$$

basic theorem  
of diffusion

$$c_i = c_{i0}, x = 0, t > 0$$

boundary conditions

$$c_i = 0, x > 0, t = 0$$

initial conditions

$$c = c_i + c_a ; c_0 = c_{i0} + c_a$$

where, in terms of Lake Superior,

$x$  = depth below the sediment-water interface.

$t$  = time

$c_a$  = initial concentration of the element in the sediment, consisting of all of the element in equilibrium with former, lower concentrations of the element in lake water, plus all of the element held in states not subject to sorption equilibria.

$c_f$  = increase in concentration of the ion being sorbed over  $c_a$  at any depth  $x$ .

$c_{i0}$  = initial increase in concentration over  $c_a$  of the ion being sorbed that is attained by the infinitesimally thin layer of sediment at the sediment-water interface at the instant when the lake water attained its new, higher concentration (or alternately stated,  $c_{i0} = c_i$  at all depths at  $t = \infty$ ).

$D_i$  = the diffusion coefficient.

By means of a Laplace transform the solution is found to be:

$$c_i(x, t) = c_{i0} \operatorname{erfc} \left( \frac{x}{2\sqrt{D_i t}} \right)$$

where:  $\operatorname{erfc} = 1 - \operatorname{erf}$ ,  $\operatorname{erf}$  = the error function, and  $c_{i0}, c_i, x, t, D_i$  are as defined above.

It will be convenient to consider the time at which  $c_1$  has reached half of the initial  $c_{10}$  at various depths. For this "half-time" we may write:

$$\operatorname{erfc} c \left( \frac{x_{y_2}}{2\sqrt{D_i t}} \right) = \frac{1}{2}$$

$$\frac{x_{y_2}}{2\sqrt{D_i t}} = 0.48$$

$$t = \frac{x_{y_2}^2}{0.92 D_i}$$

or

$$x_{y_2}(t) = \sqrt{\frac{t}{0.92 D_i}}$$

#### Quantitative Data For Lake Superior Trace Elements

If we assume that the trace element concentration of the lowest slice of a Jenkins core is  $c_a$ , and that the concentration in the highest slice (or average of the two highest slices) is  $c_{10} + c_a$ , we can determine the depth at which  $c_{\text{total}} = 1/2c_{10} + c_a$  in actual cores. For seven Jenkins cores the average and maximum depths to this "cl/2" are 8 and 10.4 cm for Cu and 9 and 9.9 cm for Zn.

Few diffusion coefficients germane to this study have been measured. For diffusion in water at infinite dilution and  $25^\circ\text{C}$ ,  $D$  for zinc is  $.56 \times 10^{-5}$  (Gray, 1957, Kolthoff and Lingane, 1952).  $D$  for copper under the same conditions is essentially the same (Kolthoff, 1946).

No measurements of  $g$  or  $h$  for Zn, Pb, or Cu are available, and Ca is apparently the only divalent ion for which these quantities have been measured. From Fletcher and Slabaugh (1960),  $g_{\text{Ca}} = 0.084$ , and  $h_{\text{Ca}} = 0.590$

for diffusion in a Ca bentonite gel (montmorillonite clay) containing 5 to 11 percent clay. The ion exchange capacity of this suspension is probably close to that of Lake Superior sediments, but Lake Superior sediments close to the sediment-water interface usually contain 15 to 25 percent solids.

We do not know n or s. If we assume that the cation is adsorbed all of the time ( $n=0$  and  $s=1$ ) D becomes equal to  $kT\omega_+$ ,  $(\frac{0.h + sg}{0 + s}) = kT\omega_+g = g.D$  pure water. Diffusion rates computed using  $n = 0$  will be maximum rates as long as h is greater than g. Thus it is not of great importance that the bentonite gel in which g was measured contained 5 to 11 rather than 15-25 percent suspended solids, as the labyrinth factor h could be reduced to one seventh of its value in the bentonite gel before it would become equal to g.

Now, combining  $D_{Zn}$ ,  $H_2O$ ,  $\epsilon_{Ca}$ , montmorillonite;  $n = 0$ ,  $g = 0.084$ , and the diffusion model, we may calculate the downward migration of  $x_{y_1}$  in time, shown by the following table:

Depth to $X_{y_1}$ , cm	Time (years) at $25^{\circ}C$
2	.27
4	1.0
8	4.3
12	9.7

Because of the approximations involved the table is no more than an "order of magnitude" estimation. Nevertheless, the data show that the rate of downward diffusion of Zn and Cu (and possibly also Pb) is sufficiently rapid to account for a significant part of the depth of surface enrichment observed. Moreover, downward diffusion would be significant even if the actual rate is more than ten times slower than the calculated rate. Most

of the discrepancy between the table and the depths of enrichment observed in Lake Superior might be the result of the assumption in the model that lake water concentrations had risen immediately to the higher level.

In this model it has been possible to consider diffusion of the trace elements without regard to existing potential ( $Eh$ ) gradients and without regard to other ions because the trace element concentrations are at most one hundredth and usually less than one thousandth of the total ionic concentration in the solutions. Thus the other ions are a "supporting electrolyte," and it has been shown that a "supporting electrolyte" concentration 50 times larger than the concentration of the diffusing ion is sufficient to nullify the effect of the existing potential gradient (Kolthoff and Lingane, 1946, p. 83).