



2453666/

LIBRARY Michigan State University

This is to certify that the

thesis entitled

Geochemical Cycling of Heavy Metals In Profundal Sediments of Lake Superior

presented by

Joseph Duane McKee 🔬

has been accepted towards fulfillment of the requirements for

____M.Sc.__degree in Geology___

Major professor

Date 21NOU89

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution

PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due.

.

DATE DUE	DATE DUE	DATE DUE
FE3 5 5 8		
1 NO21 & C 20	0	
0 MAY 1 1 2007		

MSU Is An Affirmative Action/Equal Opportunity Institution

GEOCHEMICAL CYCLING OF HEAVY METALS

IN PROFUNDAL SEDIMENTS OF LAKE SUPERIOR

BY

Joseph Duane McKee

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

ABSTRACT

GEOCHEMICAL CYCLING OF HEAVY METALS IN PROFUNDAL SEDIMENTS OF LAKE SUPERIOR

By

Joseph Duane McKee

The geochemical profiles of Fe, Mn, Cu, Pb and, Zn in sediments of Lake Superior were measured in interfacial sediments and in the sediment column, in the Caribou subbasin. The profiles were examined by studying the partitioning of the metals among solution reactive or hydromorphic phases (as operationally defined by sequential chemical extractions). Mn, Cu, and Pb were measured in pore waters from the same site. Pb, Cu, and Zn are enriched in the surface sediments. Mn and Fe are concentrated at between 5 and 10 cm. depth in the sediment. Each of the metals is uniquely partitioned among the sediment phases and the partitioning changes from the interfacial sediment to the sediment column and with depth. Pore water profiles of Mn, Cu, and Pb show evidence for post-depositional mobility. Diagenetic modeling suggests Mn pore water and sediment profiles are linked, but the profiles are not at steady state. Flux estimates for Cu and Pb show that a significant fraction of these metals could be diffusing out of the sediment column due to remobilization from the sediments.

Copyright by Joseph Duane McKee 1990

ACKNOWLEDGEMENTS

I would like to thank:

-Dr. David Long for all his help and encouragement as my advisor,

-Dr. Michael Velbel and Dr. Michael Klug, the members of my faculty commitee,

-Dr. Timothy Wilson for helping me get started and keep going,

-All the people, too numerous to mention, who instigated and participated in the National Undersea Research Program in the Great Lakes, and have made it such a rewarding experience for all involved, -and finally Becky McKee, for moral support.

TABLE OF CONTENTS

		page	
1	Introduction	.1	
	1.1 Statement of the Problem	1	
	1.2 The Study Site	5	
2	Methods	.9	
	2.1 Sampling Techniques	9	
	2.2 Sample Preparation and Analysis	12	
3	Discussion I: Metal Partitioning in the Sediments	16	
	3.1 General Results	16	
	3.1.1 Manganese	21	
	3.1.2 Iron	22	
	3.1.3 Zinc	22	
	3.1.4 Copper	23	
	3.1.5 Lead	24	
	3.2 Interpretation of Partitioning	25	
4	Discussion II: Pore Water Results and		
	Diagenetic Models	34	
	4.1 Manganese	34	
	4.1.1 Results	34	
	4.1.2 Theory of Manganese Diagenesis	36	
	4.1.3 Diagenetic Model for Manganese	38	
	4.1.4 Application of the Model	40	
	4.1.5 Discussion of the Modelling Results	48	
	4.2 Copper and Lead	51	
	4.2.1 Results	51	
	4.2.2 Flux Model for Copper and Lead	55	
5	Conclusions	61	
	5.1 Summary and Conclusions	61	
	5.2 Recommendations for Further Work	65	
Appe	endix A: Site 1388 Data	66	
Appe	Appendix B: Steady State Experiments 73		
Bib]	Bibliography 81		

LIST OF TABLES

TABLEpage1. General description of core from site 1388 taken7at 47°22.31'N 86°57.59'W at a water depth of 335 m.

2. Selective chemical attack method for a 1 gram 14 sample, modified from Gephart (1982).

3. Comparison of trace element data (dry weight of 29 sediments) from site 5 of Kemp et al. (1978a) for the Caribou sub basin and site 1388 this study.
Values are for top sediments and lower sediments where concentrations become essentially constant.
See text for locations and methods of determination.

4. Parameters used for fitting data from 1388 to 42 diagenetic model of Burdidge and Gieskes (1983).

5. Parameters used in the calculation of the fluxes 57 of Cu and Pb. A porosity of 0.93 is assumed. Concentrations are in $\mu g/g$, fluxes are in $\mu g/cm^2 * yr$.

V

6. Per cent of metal remobilized from surface sediments for various sedimentation rates at site 1388. R is in g/cm²*yr. % remobilized =(F_d/F_s)*100%.

59

A. Porosity and organic carbon concentrations at 66 site 1388.

B. Iron in sediment fractions at site 1388. 67 Concentrations in μ g/g of dry sediment.

C. Manganese in sediment fractions at site 1388. 68 Concentrations in μ g/g of dry sediment.

D. Copper in sediment fractions at site 1388. 69 Concentrations in μ g/g of dry sediment.

E. Lead in sediment fractions at site 1388. 70 Concentrations in μ g/g of dry sediment.

F. Zinc in sediment fractions at site 1388. 71 Concentrations in μ g/g of dry sediment.

G. Pore water metals at site 1388. 72

H. Steady state experiments. 74

vi

LIST OF FIGURES

FIGURE		page
1. Location of coring and dive site (site 1388	8) in	6
the Caribou Sub-Basin.		

2.a. Lower work platform of the submersible JOHNSON 10 SEA-LINK-II (JSL) showing arrangement of the sample containers, suction pump, and front compartment carrying scientists. b. Vacuum/filtration device on JSL. The vacuum nozzle is gently waved above the sediment bottom, resuspending the interfacial sediments. The sediments are vacuumed through a glass fiber filter held in a teflon filter mount.

3. pH of the sediments at site 1388. The open symbol 17 at zero depth is the overlying water.

4. C_{org} of the sediment at site 1388, (weight % of 17 dry sediment). The open symbol at zero depth is the fluff sample.

vii

5. Concentration (Log) of a. Mn and b. Fe in chemical phases of sediments at site 1388. Zero depth is the fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable). 18

- 6. Concentration (Log₁₀) of Zn in chemical phases of 19 sediments at site 1388. Zero depth is fluff sample.
 TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).
- 7. Concentration (Log_{10}) of Cu in chemical phases of 19 sediments at site 1388. Zero depth is fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).

viii

8. Concentration (Log₁₀) of Pb in chemical phases of sediments at site 1388. Zero depth is fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable). 20

9. Mn pore-water and sediment concentration profiles. 35
Values are mg/l and weight % of dry sediment
respectively. ER (easily reducible phase), MR
(moderately reducible phase), TM (sum of ER and MR
phases), and PW (pore water). The open pore water
symbol at x=0 is for Mn in the overlying water.

10 a) General zones of Mn diagenesis from model of 37
Burdidge and Gieskes (1983) and Klinkhammer (1980).
b) Hypothetical pore-water and sediment concentration profiles of Mn during steady state diagenesis.

ix

11. Results of fit of Mn pore water profile to BG model for high linear sedimentation rate (0.017 cm/yr) with L1 = 9 cm, L2 = 12 cm, and parameters from Table 3. a) Measured pore water profile and modelled profile, $k_{ox} = 4.18 \times 10^{-5}$ yr⁻¹ and $k_{red} =$ 3.18×10^{-3} yr⁻¹. b. Measured sediment profile and predicted profile from BG model.

12. Results of fit of Mn pore water profile to BG model for low linear sedimentation rate (0.0055 cm/yr) with L1 = 9 cm, L2 = 12 cm, and parameters from Table 3. a) Measured pore water profile and modelled profile, $k_{ox} = 13.2 \text{ yr}^{-1}$ and $k_{red} =$ $2.76*10^{-3} \text{ yr}^{-1}$. b) Measured sediment profile and predicted profile from BG model, dashed line is sediment profile predicted from $k_{ox} = 149 \text{ yr}^{-1}$, $k_{red} =$ $7.75*10^{-4} \text{ yr}^{-1}$, and $\underline{w} = .0015 \text{ cm/yr}$. Pore water profile resulting is the same as a).

13. Results of fit of Mn sediment profile to BG model for high linear sedimentation rate (0.017 cm/yr) with L1 = 4.5 cm, L2 = 7.5 cm, and the parameters from Table 3. a) Measured sediment profile and modelled profile, $k_{\text{OX}} = 156 \text{ yr}^{-1}$ and $k_{\text{red}} = 3.58 \pm 10^{-2}$. b) Measured pore water profile and predicted profile from BG model. 44

44

47

х

14. Results of fit of Mn sediment profile to BG model for low linear sedimentation rate (0.0055 cm/yr) with L1 = 4.5 cm, L2 = 7.5 cm, and parameters from Table 3. a) Measured sediment profile and modelled profile, $k_{ox} = 156 \text{ yr}^{-1}$ and $k_{red} = 1.16 \times 10^{-2} \text{ yr}^{-1}$. b) Measured pore water profile and predicted profile from BG model. 47

52

15. Pore-water and sediment concentration profiles of a) Cu, and b) Pb. Values are in units of $\mu g/l$ and $\mu g/g$ of dry sediment respectively. OX (oxidizable phase); MR (moderately reducible phase); TM (sum of WAS, EX, ER, MR and OX phases); and PW (pore water). The open pore water symbol at x=0 is the concentration in the bottom water.

A. Steady state experiment on exchangeable (EX) 76 fraction. Arrow is time recommended by Gephart (1982).

B. Steady state experiment on weakly acid soluble 76
(WAS) fraction. Arrow is time recommended by Gephart
(1982).

C. Steady state experiment on easily reducible (ER) 78 fraction. Arrow is time recommended by Gephart (1982).

xi

D. Steady state experiments on moderately reducible(MR) fraction. Arrow is time recommended by Gephart(1982).

CHAPTER 1

INTRODUCTION

1.1 STATEMENT OF THE PROBLEM

This thesis examines the diagenetic mobility of Mn, Fe, Zn, Cu, and Pb in sediments and waters of Lake Superior. Geochemical partitioning of the metals in the interfacial sediment and in the underlying sediments and pore water profiles of Mn, Cu, and Pb were measured. To determine if the pore water and sediment concentration profiles of Mn were in a steady state relationship, the measured Mn profiles were compared to theoretical Mn profiles predicted by the steady state diagenetic model of Burdidge and Gieskes (1983). Flux calculations similar to the those of Callender and Bowser (1980) were used to examine the net migration of Cu and Pb across the sediment-water interface. The effect of not including metal concentrations in the interfacial sediments on the flux estimates was also evaluated.

Particles settling through the water column can scavenge metals from lake waters and transport them to the bottom sediments. Biogenic-organic particles are thought to play the dominant role in scavenging metals throughout the water column, but in deeper water Mn and Fe cycling due to REDOX reactions may be important (Sigg 1985). Similar processes are thought to deplete seawater of heavy metals

(Balistrieri and Murray 1986) and enrich surface sediments in heavy metals (Klinkhammer et al. 1982).

Where high metal concentrations occur in surficial lake sediments, the concentrations typically decrease with depth to some "background" value (Leland et al. 1973). These sediment-concentration profiles have been attributed to anthropogenic inputs (Allen 1986; Kemp et al. 1978a), and used to constrain the history of the chemical loading to lakes (Edgington and Robbins 1976; Stumm and Baccini 1978).

However, all metal enrichments in surficial sediments may not be due to anthropogenic additions. The effects of diagenesis on trace metal concentrations in sediments can be misinterpreted as the results of anthropogenic inputs (Cornwell 1986). For example, Robbins and Callender (1975) demonstrated that the high Mn concentrations in surficial sediments of Lake Michigan are the result of processes associated with early diagenesis of the sediments rather than with anthropogenic inputs. They also suggested that early diagenesis might lead to the enrichment of other metals in surficial sediments. Carignan and Nriagu (1985) have shown that post-depositional migration of metals during early diagenesis important mechanism is an for the accumulation of Cu and Ni in acid-lake sediments.

Diagenesis is the chemical, biochemical, and physical changes that occur during the burial of sediments. Early diagenesis refers to these changes in the upper few cm of the sediments (Berner 1980). Metals are known to be

sequestered by different phases of lacustrine sediments such as iron and manganese oxides, organic matter, and clays (Forstner 1982; Filipek and Owen 1979). The partitioning of the metals among these phases in sediments can change during diagenesis. For example, as Fe and Mn oxides are reduced and organic matter decays, metals associated with these phases can be released to solution or resequestered on other phases of the sediment (Klinkhammer et al. 1982; Pedersen et al. 1986). Except for Mn and perhaps Fe, the effect of early diagenesis on metal behavior in the sediments of the Great Lakes is not well understood (Robbins and Callender 1975; Kemp et al. 1978a; Rea et al. 1981).

An understanding of the effect of early diagenetic processes on metal cycling at the sediment-water interface is important in predicting the fate of pollutants in and the long-term health of the Great Lakes. Modeling of diagenetic processes relies on an accurate chemical characterization of the sediment-water interface. However, sampling the interfacial sediments with gravity-driven devices is hampered by the "bow wave" created as the device approaches the bottom, dispersing the surface material before it is sampled. Thus, representative interfacial sediment may not be collected (Berner 1980; Heggie et al. 1986) resulting in incorrect diagenetic models.

Soutar and Johnson (1981), using a specially designed box corer, were able to collect interfacial sediments in a marine environment. The sediments were rich in organics

compared to underlying sediments. Murray et al. (1984), Balistrieri and Murray (1984) and Balistrieri and Murray (1986) used the manned submersible ALVIN to collect interfacial sediments at two sites in the eastern equatorial Pacific Ocean. They also found the sediments to be enriched in organics and in heavy metals compared to the sediments below. Klinkhammer et al. (1982) showed that interfacial sediments must be included in diagenetic models if accurate results are to be obtained.

Under the sponsorship of the National Underseas Research Program (NURP) of the National Oceanic and Atmospheric Administration (NOAA), The manned submersible JOHNSON-SEA-LINK-II (JSL), was used to locate and sample a 'transition zone' of interfacial sediment approximately 0.5 to 1.5 cm thick in Lake Superior (Wilson et al. 1986; McKee et al. 1986). This sediment, the benthic-sediment layer, is referred to as the "fluff" because of its in situ appearance as observed from the submersible and seems to be the true interfacial sediments in the lake.

1.2 THE STUDY SITE

The sampling site (NURP-UCAP dive site 1388) in the Caribou sub-basin was 47° 22.31' N and 86° 57.59' W, at a water depth of 335 m. The samples were collected during the 1986 dives of the JSL in the Caribou sub-basin, Lake Superior.

The Caribou sub-basin occupies approximately 13,000 km^2 in the eastern part of Lake Superior, Figure 1. The sediment is mainly clay. The post-glacial sediment is approximately 1.6 meters thick with the surface sediments comparatively rich in organic carbon (\approx 3% C_{org}) (Thomas and Dell 1978; Kemp et al. 1978b). The present-day sedimentation rate in the sub-basin, based on the Ambrosia horizon, is 0.12 mm/yr, which is not significantly different from its average postglacial sedimentation rate of 0.17 mm/yr (Kemp et al. 1978b). This is in contrast to the other sub-basins in Lake Superior which have higher present-day sedimentation rates compared to their average post-glacial rates (Kemp et al. 1978b). A possible explanation for the difference in present-day and average post-glacial sedimentation rates of the Caribou sub-basin and the other sub-basins in Lake Superior is discussed below. Table 1 gives a visual description of the core and associated interfacial sediment made during sectioning of a core from site 1388 in the Caribou sub basin of Lake Superior. In general, the basinal



Figure 1. Location of coring and dive site (site 1388) in the Caribou Sub-Basin.

Sample number	Thickness	Average Depth (cm)	Comments
F ¹	_	0	dark grey to
			chocolate brown
1	1 cm	0.5	dark grey
2	1 cm	1.5	dark grey to brown
3	l cm	2.5	brown clay
Δ		3.5	brown clay
5		4.5	brown clay
6		5.5	transition into brown
•		515	layer, sediment begins to get firmer
7	1 cm	6.5	brown layer, very firm, darker streaks
8	1 cm	7.5	brown layer, dark brown streaks, turning to reddish, grey clay
9	1 cm	9	tan-gray clay, black streaks may be sulfides,still firm
10	1 cm	10	transition to softer grey clay
11	1 cm	11	soft grev clav
12	1 cm	12	soft grey clay
13	2 Cm	13.5	soft grey clay
14	2 Cm	15.5	firm grey clay
15	3 cm	18	firm grey clay
16	3 cm	21	firm grey clay
17	3 cm	24	firm grev clav
18	3 Cm	27	firm grey clay
19	4 Cm	30.5	firm grey clay

TABLE 1. General description of core from site 1388 taken at 47° 22.31' N 86° 57.59' W at a water depth of 335 m.

1) the submersible collected interfacial sediment was assigned a depth of 0 cm on the sediment profiles

sediments of Lake Superior are similar to marine hemipelagic sediments (Johnson et al. 1982). The top 3 cm the sediments are a mix of clay and organic material and change from a chocolate brown color interfacial sediment to dark grey to brown. The clay remains brown and watery until about 6 cm where the sediments become a dark brown and firm. This coloration and consistency continues until about 10 cm where the sediments become grey and soft. Below 15 cm the sediment remains grey but then becomes firmer. The brown sediments above 6 cm appear to be oxidized while the sediments below 10 cm appear to be reduced and occasionally have a slight odor of H₂S. Within the zone of firm sediments from 6 to 10 cm, dark brown steaks, reddish streaks, and at the base, black streaks occur. This zone appears to be the transition from the reduced sediments below and the oxidized sediments above. The highest sediment concentrations of Fe and Mn occur within this zone, which will be referred to as the **REDOX** layer.

CHAPTER 2

METHODS

2.1 SAMPLING TECHNIQUES

The JOHNSON-SEA-LINK-II (JSL) is a research submersible capable of operating at depths up to 3,000 feet. The vessel is approximately 27 feet long with a forward plexiglass sphere and an aft aluminum compartment each carrying two persons. The advantages of using a manned submersible for this work, which became evident during the 1985 and 1986 cruises, are that: (1) the researcher can properly locate a observe and document the sampling area and sample collection, (2) undisturbed box cores can be taken and (3) representative interfacial sediments can be collected.

The ability of the JSL to vacuum material out of the water column and off the lake bottom was utilized to sample the fluff and was done as follows. The JSL has a lower platform which contains a hydraulically driven device for rotating 12 clear plexiglass containers (25.4 cm dia x 25.4 cm) under a suction head. The suction head is coupled to a hose connected along a mechanical arm, Figure 2. The flow rates and volumes of water through the hose are metered.



Figure 2. a. Lower work platform of the submersible JOHNSON-SEA-LINK-II (JSL) showing arrangement of the sample containers, suction pump, and front compartment carrying scientists. b. Vacuum/filtration device on JSL. The vacuum nozzle is gently waved above the sediment bottom, resuspending the interfacial sediments. The sediments are vacuumed through a glass fiber filter held in a teflon filter mount.

Each container was outfitted with a filtration system, Steve Eisenreich and Joel Baker (1989, in press). The 20.3 cm diameter filter holders are patterned after the Millipore Corporation stainless disk holders #3165. The holder is constructed from anodized aluminum, coated with teflon and holds either membrane or glass-fiber filters. Glass-fiber filters were used in this study.

After much experimentation during the 1985 and 1986 cruises, interfacial sediment samples were collected without apparent contamination from the sediments below. This was accomplished by slowly waving the suction hose over the surface of the sediment by means of the mechanical arm. By holding the nozzle pointed up, approximately 18 cm above the surface of the sediment, the interfacial sediment was gently in resuspended and captured the filter assembly. Approximately 10 minutes of pumping was required to collect a one-gram sample. At a dive site, two to three samples were collected and combined for analysis.

Gravity cores (7.6 cm dia. butyrate) were taken from the R/V Seward Johnson. In addition, box cores (30.5 cm x 30.5 cm x 30.5 cm, Al frame) and punch cores (7.6 cm dia. butyrate) were taken at the site using the mechanical arm of the JSL submersible.

Lake water was collected from approximately 1 m above the sediment surface by using the submersible's mechanical arm to extend tygon tubing into the water column, away from the submersible. The tubing was routed into the submersible,

where the sample was immediately processed and measured for pH, temperature and Eh. This sample was measured for the same components as the pore water samples and was used to estimate the composition of the bottom water of the lake.

2.2 SAMPLE PREPARATION AND ANALYSIS

The interfacial sediment samples were stored frozen. The cores were stored at 4° C (approximate <u>in situ</u> temperature) and sectioned within 2 hours of sampling under N₂ at room temperature (~15°C). The sediment/water slices were cooled to 4° C and then separated by high speed centrifuging (15,000 rpm) using a centrifuge head chilled to -25° C to keep the temperatures as close as possible to in situ conditions (Lyons et al. 1984; Robbins and Gusting 1976). Pore water and overlying lake water were filtered through 0.45 Im filters, acidified to pH's < 2 with Ultrextm HNO₃, and refrigerated until analysis. Sediments were stored frozen at -25° C until analysis.

Both the interfacial sediments and the sediment samples were dried (covered) at room temperature before analysis. The partitioning of the metals in the sediments is determined by a series of sequential-chemical extractions of the air-dried sediment samples. The procedure used in this study attempts to extract only the hydromorphic phases of the sediment; that is, the phases that can interact with aqueous solutions to either take up or release metals, this excludes metals in most silicate minerals Tessier et al. (1979). Selective chemical extractions on the sediments were performed to gain insight as to what solid phases host trace metals in the sediments. The assumption in using this technique is that the various hydromorphic phases have different resistances to chemical attack. The sediment is reacted with successively harsher chemicals. After each reaction, the leachate is separated from the sediment and analyzed for metals. The sediment remaining after the chemical attacks is the detrital fraction of the sediment. Total metal concentration of the sediment would be the sum of metals in the hydromorphic phases and the detrital fraction.

The extraction procedure used in this study, Table 2, is from Gephart (1982), and combines the methods of Tessier et al. (1979) and Gupta and Chen (1975) who calibrated the extractions against known minerals. Steady-state experiments were done to confirm that the reaction times used by Gephart (1982) for five gram samples would be appropriate for the one gram sample size used in this study, Appendix B. The reaction times used did not differ from those of Gephart (1982). Because the attacks may not be entirely selective for a phase (e.g. Fe-oxides), the results can only be interpreted in terms of operationaly defined phases. These phases are identified by the nature of the reaction between the sediment and the chemical rather than as a discrete mineral(s) (Long and Gephart 1982). For example, metals apparently associated with Fe oxides are referred to as

		-
Hypothesized sediment fraction attacked	Chemical response of sediment to extraction	Reagents Reaction used Time
loosely adsorbed such as on clays	exchangeable [EX]	1M MgCl ₂ pH 7 1 hr room temp, 8 ml
carbonates some hydroxides	weakly acid soluble [WAS]	1M NaOAc pH 5, 5 hr with HOAc room temp, 8 ml
Mn oxides	easily reducible [ER]	0.1M NH ₂ OH°HCl 0.5 hr 0.02M HNO ₃ room temp, 25 ml
Fe oxides	moderately reducible [MR]	0.04M NH ₂ OH HCl 6 hr in 25% (V/V) HOAc 96 ⁰ C, 20 ml
Organic and sulfides	oxidizable [OX]	25% H_2O_2 pH 2 5 hr with HNO ₃ , 85°C
		1M NH ₄ OAc, 5 ml 1 hr distilled H ₂ O,5 ml room temperature

TABLE 2. Selective chemical attack method for a 1 gram sample, modified from Gephart (1982)

metals associated with the moderately-reducing phase of the sediment, Table 2.

Lake water, pore water, and leachate from the chemical extractions, were analyzed for Mn, Cu, and Pb by flame or graphite furnace atomic absorption spectrophotometry (Perkin-Elmer 360 with HGA 220 graphite furnace and AS 40 auto-sampler). Standard matrices were prepared from the reagents used in the selective chemical chemical extractions. Standards and blanks for the sediment pore waters were made in double distilled H_2O . Analytical blanks were carried through all procedures. Coefficient of variation for the atomic absorption analyses of metals was estimated to be less than 10% from measurement of replicate aliquots of the extracts.

The pH profile of the sediment was measured from a second gravity core, sectioned in air, taken at site 1388. The pH of each sediment layer was measured prior to its removal from the core by inserting a Ross spear tip electrode (Orion #816300 coupled to an Orion 407A pH meter) into the layer. Total organic carbon of the sediment was measured by wet oxidation with K_2CrO_7/H_2SO_4 following the methodology of Gaudette et al. (1974).

CHAPTER 3

DISCUSSION I: METAL PARTITIONING IN THE SEDIMENTS

3.1 GENERAL RESULTS

The pH is highest in the bottom water (7.40) but rapidly decreases with depth, Figure 3. pH's vary between 5.55 and 6.00 in the oxidized zone and become a nearly constant 5.95 below the REDOX layer. Organic carbon is about 3% in the interfacial sediment and decreases to about 1.5% with depth, Figure 4, with the lowest concentrations in the REDOX layer.

Figures 5 a and b and Figures 6, 7, and 8 show the partitioning of Mn, Fe, Zn, Cu, and Pb respectively in the sediment. The concentrations are expressed as ppm sediment dry weight. The abbreviations (e.g. EX) refer to the hydromorphic phases as given in Table 1. TM refers to the sum of the metal concentrations in all of the phases. A \log_{10} concentration scale is used. The interfacial sediment sample hereafter designated I.S., is assigned the zero depth.

Zinc, copper, and lead exhibit typical anthropogenic concentration profiles in the sediment. These profiles have metal concentrations that are highest near the surface and



Figure 3. pH of the sediments at site 1388. The open symbol at zero depth is the overlying water.



Figure 4. C_{org} of the sediment at site 1388, (weight % of dry sediment). The open symbol at zero depth is the fluff sample.



Figure 5. Concentration (Log_{10}) of a. Mn and b. Fe in chemical phases of sediments at site 1388. Zero depth is the fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).



Figure 6. Concentration (Log_{10}) of Zn in chemical phases of sediments at site 1388. Zero depth is fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).



Figure 7. Concentration (Log₁₀) of Cu in chemical phases of sediments at site 1388. Zero depth is fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).



LEAD

Figure 8. Concentration (Log₁₀) of Pb in chemical phases of sediments at site 1388. Zero depth is fluff sample. TM (total hydromorphic metals), EX (exchangeable phase), WAS (weak acid soluble), ER (easily reducible), MR (moderately reducing phase), OX (oxidizable).
decrease to a constant value at depth. The changes in the relative importance of the phases in sequestering metals with depth are examined.

3.1.1 Manganese

layer (≈4 cm thick) The REDOX has the highest concentration of Mn, with the oxidized sediments above the layer containing more Mn than the reduced sediments below. This is typical of Mn profiles in many environments (Pedersen et al. 1986; Callender and Bowser 1980; Burdidge and Gieskes 1983). The concentration of Mn in the OX phase of the I.S. was not determined and was estimated to be approximately 50 ppm. Except in the REDOX layer, this is a typical Mn concentration in the OX phase of the sediments, Figure 5a. Since the OX phase is not as important as the MR and ER phases in sequestering Mn, significant enrichments of Mn in the OX phase of the I.S. would have to occur to affect the total Mn concentration in the I.S, Thus, Mn does not appear to be enriched in the I.S.

The relative partitioning of Mn among the phases changes with depth. In the I.S. Mn is partitioned in the order: easily reducible (ER) \approx moderately reducible (MR) >> oxidizable (OX) \approx weak acid soluble (WAS) >> exchangeable (EX). Below the I.S., but above the REDOX layer the order and magnitudes are, ER > MR >> OX > EX > WAS and below the REDOX layer, MR > ER > OX >> WAS > EX. The ER phase is the most important in sequestering Mn above the REDOX layer and is expected, since the ER phase is mainly Mn-oxides. Below the REDOX layer MR becomes the dominant phase.

3.1.2 Iron

The MR phase (Fe-oxides) essentially dominates the sequestering of Fe throughout the core. There is no change in the relative order (MR >> OX >> ER) and little changes in the magnitude among the phases, Figure 5b, as a function of depth. Between the I.S. and the underlying sediments, only the relationship between the EX and ER phases changes. The EX phase sequesters more Fe in the I.S. than the ER phase while below the I.S., the order is reversed.

Iron concentration is highest in the REDOX layer where it is most enriched in the lower two cm. Iron occurs in a narrower band and at a lower concentrations than Mn. This is in contrast to earlier observations (Kemp et al. 1978a) and is addressed below. Concentrations of Fe in the MR phase below the REDOX layer are only slightly lower than those above the zone. There is little change in concentration above and below the REDOX layer in the other phases.

3.1.3 Zinc

Total Zn concentrations show a typical "anthropogenic" profile, Figure 6. The MR, OX, WAS, and ER phases have similar profiles with enrichment factors for the I.S. over the lower sediments of 3.9x, 1.8x, 5.6x and 7x, respectively. Enrichment factors were calculated as the metal concentration in the I.S. divided by its concentration in the sediment at a depth where concentration becomes essentially constant. Except for the WAS phase, the relative importance of the phases sequestering Zn does not change between the I.S. and the sediments below. However, the relative magnitudes of the concentrations of Zn in the different phases do change. In addition, the partitioning of Zn among the phases is somewhat sensitive to the REDOX state of the system. In the I.S., Zn is partitioned in the order, MR >> WAS \approx OX > ER >> EX. Below the REDOX layer the relative partitioning is the same, but the magnitudes change to MR > OX >>> ER > WAS > EX. The difference in Zn concentrations of Zn between the OX and ER phases is much less above the REDOX layer than it is below.

The lesser importance of the ER phase in sequestering Zn below the REDOX layer is consistent with the lower concentrations of Mn oxides below the REDOX layer, Figure 5a. There is a slight enrichment of Zn in the REDOX layer for the phase ER and below the layer for the phases MR and OX. Since C_{org} is relatively depleted throughout the REDOX layer Figure 4, the enrichment of Zn in this phase below the layer may indicate its presence as a sulfide mineral. The procedure used to extract metals in the oxidizable phase attacks sulfides as well as organic matter, Table 1.

3.1.4 Copper

Total Cu exhibits an anthropogenic profile, but only the phases OX and MR show this type of profile, Figure 7. Although Cu in the ER, EX, and WAS phases is strongly depleted by about 3 cm into the sediment, by 5 cm, Cu in

these phases increases to values equal to those in the I.S.. Copper is highly enriched in the I.S., with enrichment factors of 7.66x and 2.8x for the OX and MR phases, respectively. In the I.S. the relative order and magnitudes of the phases sequestering Cu are OX >> MR >>> WAS >> ER > EX. In the deeper sediments partitioning changes to OX >> MR >>> ER >>> WAS >>> EX.

Copper concentrations in the MR phase in the REDOX layer are slightly higher than in the surrounding sediments. Total Cu concentrations do not show an enrichment in the REDOX layer because the Cu in the OX, ER, and WAS phases is relatively depleted in the layer. The importance of the OX phases in sequestering Cu is demonstrated in the REDOX layer, where Cu concentrations mimic C_{org} concentrations, Figure 4 and Figure 7.

3.1.5 Lead

Total Pb and the phases MR, OX, EX, and ER have anthropogenic profiles, Figure 8. The enrichments of the MR and OX phases in the I.S. over the lower sediment are 20x, and 19x, respectively. Lead was not detected in the EX and ER phases below 3cm. In the I.S., the phase order and magnitudes are, MR \approx OX >>> EX \approx WAS >>> ER. In the lower sediments the order and magnitudes are generally MR > OX to OX > MR > WAS. Pb appears to be somewhat depleted in the REDOX layer, but relatively enriched below the layer in the OX phase. Since total organic carbon does not show an enrichment at this depth, this could indicate Pb sulfide formation.

3.2 INTERPRETATION OF PARTITIONING

The changes with depth in the relative importance of the phases which sequestered metals are interpreted to indicate that Pb, Cu and Zn undergo remobilization during early diagenesis. Total hydromorphic metal concentrations as shown in Figures 5 through 8, do not reveal the effect of early diagenesis on the heavy metals as clearly as the study of the individual phases. For example, the effect of the REDOX layer on the Pb and Cu concentrations would not be apparent from just the total hydromorphic metal plots.

In most cases the concentrations of the metals in the I.S. to be continue the trends of their appear concentrations in the sediments directly below the I.S.. For some phases (the MR and OX of Pb and the OX for Cu, for example), the decrease in the log concentration of the metal with depth can be modeled as a simple exponential decline, Figures 7 and 8. This would suggest that the I.S. is not particularly unique, but only has higher metal concentrations than the sediments below the I.S.. Such a sediment concentration profile could be caused by the exponential addition of new metal at the surface or exponential removal of the metal at depth during early diagenesis. It is possible that increases in anthropogenic inputs are largely responsible for the shape of the sediment concentration profiles of the metals. However, the partitioning changes suggest that early diagenesis is also affecting the profiles. Thus, absolute shape of the profiles and elemental abundances may not be an exact record of the timing and rates of anthropogenic inputs.

The I.S. may have a unique chemistry compared to the deeper sediments. For example, Zn concentrations in the I.S. for the phases MR, OX, WAS and ER and total hydromorphic Zn cannot be modeled as an exponential extrapolation of Zn concentrations in the sediments below the I.S., Figure 6. The I.S. is more enriched in Zn than might be predicted from the sediment.

Copper in the MR phase of the I.S. appears to be deficient based on a simple extrapolation of Cu in the MR phase of the sediments below the I.S., Figure 7. We have observed this "deficiency" of Cu in the I.S. compared to the bottom sediments in other cores (Wilson et al. 1986). It may indicate the uptake of Cu by the MR phase during burial. Partitioning differences between the I.S. and the sediment for other phases sequestering Pb, Zn, and Cu also suggest that the I.S. has some unique chemical properties, Figures 6, 7 and 8. This is similar to what has been found in marine interfacial in which the sediment environments or "transition zone" was reported to have unique chemical properties (Balistrieri and Murray 1984; Pedersen et al. 1986).

The REDOX layer has not accumulated significant excesses of Cu, Zn and Pb as might be expected by the known

adsorptive properties of Fe and Mn oxides (Leckie et al. 1980; Jenne 1968). In contrast, the moderately and easily reducible phases (Fe-Mn oxides) in the oxic sediments above the REDOX layer have accumulated a large concentration of these metals, Figure 6. Iron and manganese oxides, however, are not enriched in the oxic sediments, Figure 5. The scavenging ability of the oxides is indicated in the surface sediments, but apparently not at depth.

The absence of significant enrichments Zn, Cu, and Pb in the REDOX layer may be due to a lack of a significant source of these metals to the layer. For example, the Fe and Mn oxides in the surficial sediments occur where detrital organic matter is decaying. Metals associated with the organic matter can be released to the pore waters, as has been shown for marine sediments (Pedersen et al. 1986). These metals would then be available for uptake by the oxides. The REDOX layer, on the other hand, occurs below such releases and hence is not significantly metal enriched. The slight changes in the partitioning of Pb, Cu and Zn across the REDOX layer seen in Figures 6 through 8 do suggest that the layer is slightly affecting the metal profiles and that some of the remobilized metal is interacting with the REDOX layer.

The concentration profiles for Cu, Pb, Fe, and Mn from this study are generally similar in shape to those found in an earlier study by Kemp et al. (1978a), but there are some differences. Kemp et al. (1978a) measured heavy metal

concentrations in sediments from a gravity core (their core 5) from the Caribou sub-basin. The location was 44° 32.5' N $87^{\circ}0.0'$ W (water depth of 313 m) which is sufficiently close to our study site to invite comparison. However, because of the differences in methodologies and locations between our study and theirs, caution must be used when comparing the concentrations and profiles.

Kemp et al. (1978a) used hot aqua-regia to extract metals from the sediments. Such an extraction may be more of a measure of the total metal content of the sediment because components such as clays are attacked (Malo 1977). In contrast, the chemicals used in the present study were chosen to extract only the hydromorphic phases of the sediment, as defined earlier. Since metals in lattice structures of silicates, for example, are not considered readily available to solution, the hydromorphic phases would be better indicators of the behavior of labile metals in natural systems than total metal concentrations. In addition, it is the metals in the hydromorphic phases which are most likely to interact with biota (Tessier et al. 1979).

Kemp et al. (1978a) reported higher metal concentrations than those found in this study, which suggests that either their extraction scheme was more complete or that other phases were attacked. In addition, our data show that Zn exhibits an anthropogenic profile, Figure 6a, and Table 3, which was not observed by Kemp et

al. (1978a). This suggests the sediment-concentration profile of Zn was obscured by the hot aqua-regia extraction.

Although our sediment profiles for Mn and Fe are the shape as found by Kemp et al. (1978a), the same concentrations are different. Iron concentrations are significantly greater at site 5 than site 1388 and its concentration is more enriched in the REDOX layer, as compared to the sediment above and below, at site 1388 than at site 5. The difference in Mn concentrations between sites is not as large as it is for Fe. Site 5 still has the higher concentrations, but the relative enrichments of Mn in the REDOX layer in the two sites are similar, however. Finally, Fe concentrations are generally greater than Mn at both sites. However, at site 1388, Mn in the REDOX layer is greater than Fe.

The discrepancy in Mn and Fe concentrations reported for site 1388 and site 5 may be attributed to the differences in analytical techniques already discussed. Iron is mainly in the detrital phase of the sediment (Gephart 1982) so the hot aqua-regia extraction would extract significantly more Fe than the chemicals used in the present study. The small difference in Mn concentrations between the

TABLE 3. Comparison of trace element data (dry weight of sediment) from site 5 of Kemp et al. (1978a) for the Caribou sub basin and site 1388 this study. Values are for top sediments and lower sediments where concentrations become essentially constant. See text for locations and methods of determination.

	Fo %	9	M P	In s				
Zone	<u>5</u>	1388	5	<u>1388</u>				
Тор	5.76	.66	0.15	0.072	2			
REDOX ¹	8	1.7	5	2.2				
Lower	5.56	.65	0.05	0.021				
	Pb ppm		C I	Cu opm	:	Zn ppm		
Zone	<u>5</u>	<u>1388</u>	<u>5</u>	<u>1388</u>	5	<u>1388</u>		
Тор	74.9	74.5	141	161	172	135		
Lower	20.5	4.2	84	35.2	137	40.3		
factor ³	3.7	18	1.7	6	1.3	3.4		

1. Highest concentration in REDOX layer. Values for 5 estimated from figures presented by Kemp et al. (1978a).

2. Mn in oxidizable phase estimated at 50 ppm dry weight of sediment.

3. Enrichment factor calculated as the concentration in topmost sediment sampled divided by the concentration in the lower sediment where concentrations become essentially constant. two sites may be due to this metal's presence in the hydromorphic phases (Gephart 1982) so that both analytical techniques would extract similar quantities of Mn.

The sizes and chemical stratigraphies of the REDOX layers at both sites are similar. At site 1388, the REDOX layer is approximately eight cm below the sediment surface, four cm thick, and enriched in Mn throughout and Fe in the bottom two cm. Kemp et al. (1978a) reported a REDOX layer 13 cm deep, three cm thick, with Fe in the bottom one cm. If the sampling and analytical procedures of the present study and of Kemp et al. (1978a) yield results that are representative of the natural environment, these comparisons indicate the natural chemical variability of may the environment and not temporal changes, since changes in the solid phases of the REDOX layer are thought to occur on the order of hundreds of years (Froelich et al. 1979).

Table 3 compares selected heavy metal data from Kemp et al. (1978a) to the data from this study. The chemical data compared are from the top-most sediments sampled in both studies, the lower sediments where the metal concentrations become essentially constant, and the REDOX layer.

The relative enrichments of Zn, Cu, and Pb in the surface sediments over the lower sediments are higher in the present study, in which the I.S. was known to be sampled, than in the study by Kemp et al. (1978a). For Pb, the difference is significant. The analytical techniques used in the studies are again the most probable cause of the

difference. Since the analyses of the surface sediments at both two sites have yielded similar metal concentrations, the lesser extraction of metal from the bottom sediments at site 1388 results in the apparently higher enrichments at that site.

The similarity in metal concentrations in the top sediments at both sites is curious and may indicate the unique chemistry of the I.S.. Lead concentrations are almost identical, while Cu is somewhat greater at 1388 and Zn at 5. If an analogy can be made to the bottom sediments, the top sediments at site 5 should contain significantly more metal than those at site 1388. Since this is not the case, we suggest that it is the presence of the I.S., enriched in metals, in our samples that causes the apparent similarity between top sediment values in the two studies. Due to their sampling method, Kemp et al. (1978a) may not have sampled the I.S..

According to the figures from Kemp et al. (1978a), Pb and Cu in the top sediments are enriched over the lower sediments in only the top 1 cm. In the present study the enrichment is in at least the top 3 cm. The higher enrichments and thicker surface enrichment zone in our core may further indicate that the I.S. zone was not sampled in the earlier study. Interestingly, if the top 1 to 1.5 cm of sediment was not sampled in the work of Kemp et al. (1978 a and b), their estimate of the sedimentation rate for the Caribou sub-basin could be incorrect. Adding the I.S. thickness would increase the sedimentation rate, perhaps bringing it more in line with the trend of present-day and average post-glacial sedimentation rates in the other subbasins of Lake Superior (Kemp et al. 1978b).

.

CHAPTER 4

DISCUSSION II: PORE WATER RESULTS AND DIAGENETIC MODELS

In summarizing the results of the pore water and sediment concentration profiles only the dominant hydromorphic sediment phases are shown. This allows a linear scale to used for both the concentration profiles rather than the log₁₀ scale used in chapter 3. The I.S. and the overlying lake water samples are assigned the zero depth. The total concentration profile (TM) is the sum of metal concentration in all of the hydromorphic phases and is the same as the TM profile presented in chapter 3.

4.1 MANGANESE

4.1.1 Results

Manganese is contained predominantly in the easily reducible (ER) and the moderately reducible (MR) fractions of the sediment, as operationally defined by the selective chemical extractions, Figure 9. The orange and brown sediment (REDOX layer) from the 7 to 10 cm. depth contains almost 30 times more Mn than the overlying oxic sediment layers and up to 200 times more Mn than the underlying grey sediment. Manganese concentration in the pore waters, Figure



Figure 9. Mn pore-water and sediment concentration profiles. Values are mg/l and weight of dry sediment respectively. ER (easily reducible phase), MR (moderately reducible phase), TM (sum of ER and MR phases), and PW (pore water). The open pore water symbol at x=0 is for Mn in the overlying water.

9, is generally less than 0.02 mg/l, above 10 cm, but increases to 0.58 mg/l below 10 cm. There is a small concentration peak (0.06 mg/l) at 4.5 cm. The increase in pore water Mn begins at a depth where Mn in the sediment has decreased to its lowest value. The pore water and sediment concentration profiles appear to be diagenetically linked. 4.1.2 Theory of manganese diagenesis

The Mn sediment profile does not reflect anthopogenic input, but rather the post depositional mobility of Mn (Davison 1982). Post-depositional mobility of Mn in sediments occurs when the Mn oxides formed in the shallower oxic sediments are buried and dissolve because of the lower pe's in the deeper sediments (Froelich et al. 1979). The released Mn^{2+} diffuses upward, becomes oxidized, and is redeposited as Mn oxides. The zone of Mn oxide deposition can be in the water column, at the sediment-water interface, or in the sediment column as is the case at site 1388. Iron goes through a similar REDOX cycle (Drever 1988).

The loci of Mn-oxide precipitation is determined by a balance between the downward flux of O_2 and the upward flux of Mn^{2+} . Steady state conditions will exist and Mn will build up in the sediments when the upward flux of Mn^{2+} is twice the downward flux of O_2 (Froelich et al. 1979). During this steady-state condition, the pore water and sediment concentration profiles of Mn should resemble the idealized relationship shown in Figure 10.



Figure 10. a) General zones of Mn diagenesis from model of Burdidge and Gieskes (1983) and Klinkhammer (1980). b) Hypothetical pore-water and sediment concentration profiles of Mn during steady state diagenesis.

4.1.3 Diagenetic model for manganese

Burdidge and Gieskes (1983) developed a quantitative model (BG) that constrains both sediment and pore water distributions of Mn through coupled diagenetic equations. A schematic depiction of their model is shown in Figure 10, and is similar to the model discussed by Klinkhammer (1980). From the sediment-water interface to a depth L1, the sediments are oxidized and pore water Mn is held low due to the low solubility of Mn oxides. Oxidation of upward diffusing Mn^{+2} occurs from L1 to L2 and the concentration of Mn in the sediment increases within this depth range. Dissolved Mn also increases in this range because of the removal of oxygen. Depth L2 marks the peak Mn concentration in the sediment profile and represents the boundary between the zone of oxidation above and reduction below. Solid Mn oxide dissolves in the depth range L2 to L3 because of the lower pe's. As a result the concentration of Mn in the pore water increases to its maximum value. Below depth L3, Mn concentration in the sediment profile remains at a low constant value. Manganese in the pore water below depth L3 can remains constant with its concentration determined by equilibrium with a mineral phase other than Mn oxides.

The BG model only considers the Mn oxidation and reduction zones, Figure 10. Pore water and sediment Mn concentrations in the oxidized and equilibrium zones are held constant. The model also assumes that:

1. Steady-state diagenesis is occurring;

2. Migration of dissolved Mn²⁺ occurs only by molecular diffusion following Fick's laws;

3. Porosity and diffusion coefficients are constant over the depth range considered; and

4. The sedimentation rate and the supply of reducible Mn to the sediment are constant.

The equations describing steady-state Mn diagenesis in the oxidation and the reduction zones are:

for the oxidation zone (L1 $\leq x \leq$ L2) pore waters, $D_{B} \star \delta^{2} Mn_{p} / \delta x^{2} - w \star \delta Mn_{p} / \delta x - k_{ox} \star Mn_{p} = 0;$ for the oxidation zone sediments, $-w * \delta Mn_{s} / \delta x + (\phi / 1 - \phi) * k_{ox} * Mn_{p} = 0;$ for the reduction zone (L2 $\leq x \leq$ L3) pore waters, $D_{B} \star \delta^{2} Mn_{p} / \delta x^{2} - w \star \delta Mn_{p} / \delta x + (1 - \phi / \phi) \star k_{red} \star Mn_{s} = 0;$ for the reduction zone sediments, $-w \star \delta Mn_s / \delta x - k_{red} \star Mn_s = 0;$ where $D_{\rm B}$ = bulk sediment diffusion coefficient (cm²/yr) $= D_{o} \star \phi^{2}$ (Lerman 1975) $Mn_p = Mn$ in pore water ($\mu g/cm^3$) $Mn_s = Mn$ in sediment ($\mu g/cm^3$) $Mn_s^{o} = Mn$ at sediment-water interface ($\mu g/cm^3$) w = sedimentation rate (cm/yr) k_{ox} = 1st order rate constant for oxidation (yr⁻¹) k_{red} = 1st order rate constant for reduction (yr⁻¹) ϕ = porosity x = depth

with the boundary conditions

$$(Mn_p)_{OX}(L1) = 0$$

$$(Mn_s)_{OX}(L1) = (Mn_s)^{O}$$

$$(Mn_p)_{OX}(L2) = (Mn_p)_{red}(L2)$$

$$(Mn_s)_{OX}(L2) = (Mn_s)_{red}(L2)$$

$$[\delta(Mn_p)_{OX}/\delta x](L2) = [\delta(Mn_p)_{red}/\delta x](L2)$$
as x -- ∞ , Mn_p remains finite.

The subscripts ox and <u>red</u> refer to concentrations in the oxidation and the reduction zones, respectively, Figure 10. The solution to this set of equations is:

$$(Mn_p)_{ox} = A*sinh[\alpha(x-L1)]$$
(1)

$$(Mn_p)_{red} = G - H \exp[-\beta(x-L2)]$$
(2)

$$(Mn_s)_{OX} = (Mn_s)^{O*} \cosh[\alpha(x-L1)]$$
(3)

$$(Mn_s)_{red} = E * exp[-\beta(x-L2)]$$
(4)

where

$$\alpha = \sqrt{(k_{OX}/D_B)}$$

$$\beta = k_{red}/W$$

$$Lox = L2 - L1 \quad (width of oxidation zone in cm)$$

$$A = [(Mn_s)^{O*}(1-\phi)*W]/[\alpha*\phi*D_B]$$

$$E = (Mn_s)^{O*}cosh[\alpha Lox]$$

$$G = A*(sinh[\alpha*Lox] + (\alpha/\beta)*cosh[\alpha*Lox])$$

$$H = (E*w^{2}*(1-\phi))/(k_{red}*D_B*\phi)$$

4.1.4 Application of the model

Although the measured sediment and pore water profiles of Mn appear to be diagenetically linked in Figure 9, their relationship is not exactly that expected from the steady state model, Figure 10. For example, the depths (L1) of the beginning of the concentration increase in the sediment and the pore water profiles are not equal. In addition, the shape of the measured pore water profile in the reduction and equilibrium zones does not resemble the steady state model. The sediment profile, on the other hand, exhibits a shape which is consistent with its formation under steady state conditions. The maximum concentration is a nearly symmetrical 'spike'. The Mn concentration in the sediment is low and constant above and below the maxima, with slightly higher concentrations above the maxima than below.

Pedersen et al. (1986) used the BG model to examine the non steady state nature of Mn diagenesis in hemipelagic marine sediments from the East Pacific Rise. Pedersen et al. (1986) fit their measured pore water data to the BG model to determine the rate constants k_{red} and k_{ox} . Using these rate constants and equations (3) and (4), the sediment concentration profile representing a steady state diagenetic relationship to the pore water profile was predicted . They compared the predicted sediment profile with the measured profile to make interpretations on the steady state nature of manganese diagenesis.

Table	4.	Paramete	ers	used	for	fitt	ing	data	from	1388	to
diagen	neti	c model	of	Burdi	.dge	and	Gies	skes	(1983)	•	

Parameter	Value
D _B (bulk sediment diffusion coefficient)	78.5 cm ² /yr (1)
<u>w</u> (sedimentation rate)	0.017 and 0.0055 cm/yr (2)
ø (porosity)	0.83 (3)
ρ _s (dry density of sediment)	2.65 g/cm ³ (4)
(Mn _s) ^O (sediment Mn at x=o)	$17.9 \times 10^2 \ \mu g/cm^3$ (5)

(1) D_B was calculated from the data of Li and Gregory (1974).

(2) w is the sedimentation rate from site L-42 of Kemp et al. (1978a). This location is very close (\approx 15 km. N) of site 1388 (this paper). 0.017 cm/yr is the average postglacial sedimentation rate, 0.0055 cm/yr is the recent sedimentation rate at the same site. Both values were calculated from the relation $\underline{w} = R/[(1-\phi)*\rho_S]$ Berner (1980), where R is the sediment flux rate in, mass/(area*time). (3) ϕ is the average measured porosity of the 4.5 - 11 cm interval, range 0.89 - 0.79 (McKee, unpublished data). (4) after Johnson et al. (1982). (5) (Mn_S)^o was estimated from the sediment profile of reducible Mn, (ER+MR fractions of the sediment). Measured units for Mn_S were weight %, which were converted to μ g/cm³ by multiplying by ρ_S*10^4 . To constrain the cause of the apparent non steady state conditions of Mn diagenesis at our study site, the approach of Pedersen et al. (1986) was taken. The parameters used in fitting the data to the BG model are summarized in Table 4. The best fit of the measured pore water profile to the model was determined by nonlinear regression. Two sediment flux (mass sedimentation) rates (R) are given for the study site by Kemp et al. (1978b), 25 g/m^2*yr for the recent rate and 80 g/m^2*yr for the average post glacial rate. These sediment flux rates represent sedimentation rates (W) of 0.017 cm/yr and 0.0055 cm/yr, respectively in Table 4. Both rates were used in the diagenetic modeling.

Based on the idealized pore water curve as shown in Figure 10, depths L1 and L2 were assigned 9 cm and 12 cm, respectively. Depth L1 was chosen at the beginning of the concentration increase in the pore water. Assigning depth L2 is more difficult and was chosen to approximate the inflection point of the pore water curve, similar to the methods of Pedersen et al. (1986) and Burdidge and Gieskes (1983). In the initial modeling however, the depth L2 was allowed to vary along with k_{red} and k_{ox} , producing best fit values of L2 ranging between 11 cm to 13.75 cm. Therefore, 12 cm appears to be a reasonable depth for L2 and in the solutions for the two sedimentation rates, depths L1 and L2 were held invariant for consistency.

Figures 11 and 12 show the Mn sediment profiles predicted from fitting the pore water profile to the BG



Figure 11. Results of fit of Mn pore water profile to BG model for high linear sedimentation rate (0.017 cm/yr) with L1 = 9 cm, L2 = 12 cm, and parameters from Table 3. a) Measured pore water profile and modelled profile, $k_{OX} = 4.18*10^{-5}$ yr⁻¹ and $k_{red} = 3.18*10^{-3}$ yr⁻¹. b. Measured sediment profile and predicted profile from BG model.



Figure 12. Results of fit of Mn pore water profile to BG model for low linear sedimentation rate (0.0055 cm/yr) with L1 = 9 cm, L2 = 12 cm, and parameters from Table 3. a) Measured pore water profile and modelled profile, $k_{ox} = 13.2$ yr⁻¹ and $k_{red} = 2.76 \times 10^{-3}$ yr⁻¹. b) Measured sediment profile and predicted profile from BG model, dashed line is sediment profile predicted from $k_{ox} = 149$ yr⁻¹, $k_{red} = 7.75 \times 10^{-4}$ yr⁻¹, and w = .0015 cm/yr. Pore water profile resulting is the same as a).

model for the high sedimentation (0.017 cm/yr) and low sedimentation (0.0055) cm/yr rate, respectively. In neither case does the BG model properly define the shape of the pore water curve at depth. After an initial rapid rise, there is a change in slope and the measured Mn increases linearly with depth. The BG model, predicts a curvilinear increase. The fit between the measured profile and the predicted profile is good in the oxidation zone, but degrades in the reduction zone. An identical mismatch between the measured Mn pore water profile and modelled pore water profile was also found by Pedersen et al. (1986).

The BG model is based on the hypothesis by Froelich et al. (1979) that once steady state conditions are reached, the peak concentration of Mn remains constant. The BG model, therefore, should predict the maximum and total mass concentration of the Mn in the spike. The concentration of Mn in the spike is not predicted by the use of either sedimentation rate. The high sedimentation rate does not predicts a zone of Mn build up, while the low rate predicts a fraction (<1/3) of the build up found. In addition, the predicted peak using the low sedimentation rate, Figure 12 occurs 4.5 cm below the depth of the measured peak. Pedersen et al. (1986) also found the predicted Mn concentration was higher in the predicted peak than in the measured peak.

A cause of the lack of agreement between the model predictions and measured profiles is the potential error in

assigning depths for L1 and L2 from the pore water profiles. Differing from the Mn sediment profile in the Pedersen et al. (1986) study, at site 1388 the Mn sediment profile is well defined and approximates the idealized profile shown in Figure 10. Values for L1 and L2 can easily be assigned from this profile. Therefore, we fit the sediment profile to the BG model to determine what constraints could be placed on the pore water profile, a reverse of the Pedersen et al. (1986) approach. Calculations were again made using both sedimentation rates, only in this case equations (1) and (2) were used to predict the pore water profiles. Only the sum of Mn concentrations in the MR and ER phases were used in the modeling because these phases are the phases most likely to participate in the REDOX reactions . Values for L1 and L2 were assigned 4.5 cm and 7.5 cm, respectively. Depth L1 is the depth at which the increase in sediment Mn begins, depth L2 is the center of the peak.

Figures 13 and 14 show the pore water profiles predicted by the fit of the sediment concentration profiles to the BG model for the high sedimentation and low sedimentation rates, respectively. For both rates, the BG model fits the measured sediment profiles well. In neither case, however does the predicted pore water profile match the measured profile in concentrations or shape. The predicted pore water concentrations are much higher than those measured, although they are somewhat closer to the measured concentrations when the low sedimentation rate is



Figure 13. Results of fit of Mn sediment profile to BG model for high linear sedimentation rate (0.017cm/yr) with L1 = 4.5 cm, L2 = 7.5 cm, and the parameters from Table 3. a) Measured sediment profile and modelled profile, $k_{OX} = 156$ yr⁻¹ and $k_{red} = 3.58 \pm 10^{-2}$. b) Measured pore water profile and predicted profile from BG model.



Figure 14. Results of fit of Mn sediment profile to BG model for low linear sedimentation rate (0.0055 cm/yr) with L1 = 4.5 cm, L2 = 7.5 cm, and parameters from Table 3. a) Measured sediment profile and modelled profile, k_{ox} =156 yr 1 and k_{red} = 1.16*10⁻² yr⁻¹. b) Measured pore water profile and predicted profile from BG model.

used. The model predicts that the steady state concentrations of Mn in the pore water should be reached at about 9 cm with a rapid rise to the steady state value beginning at about 5.5 cm. The measured pore water values do not appear to approach steady state until about 30 cm and with the concentration increase beginning at about 10.5 cm or 5 cm below the predicted depth.

4.1.5 Discussion of modelling results

In summary, Mn diagenesis does not match the steady state model at the study site in the Caribou sub basin of Lake Superior. The Mn pore water profile appears to be displaced downward from its thoretical steady state relationship with the Mn sediment profile. The perched REDOX layer may reflect a relict Mn depositional horizon, with Mn deposition now taking place below it. Further evidence for non steady state diagenesis is indicated by the slight increase in pore water Mn at 4.5 cm depth, Figure 9, which should not occur if the sediment above the REDOX layer is oxidized, as indicated by its visual appearance.

The concentration of Mn in the pore water at 4.5 cm could result in a downward flux of Mn to the REDOX layer causing, in part, the build up of Mn in the layer. Such a Mn flux is not considered in the BG model. If important, this flux would cause the pore water fit to the BG model to under estimate the concentrations in the sediment profile and the sediment profile fit to over estimate the pore water concentrations. Although this was found to be the case in

these calculations, the downward flux would supply less than 1/5 of the total flux of Mn to the REDOX layer. Therefore, the downward flux is the not the cause of the non steady state condition, but only an indication of it.

The timing and cause of the decoupling of the pore water profile from the sediment profile is unclear. However, the pronounced shape of the concentration peak for Mn and apparent lack of visual evidence of a new depositional zone below the REDOX layer, suggest that the shift from steady state has been recent. The shift probably represents an increase in the O_2 flux to the REDOX layer, a decrease in the Mn²⁺ flux, or both. This can be demonstrated by varying the sedimentation rate on the model predictions.

The present sedimentation rate in the Caribou sub basin is not well constrained. The sedimentation rate cited by Kemp et al. (1978b) may have been underestimated if the true surface sediments were not sampled. Additionally, their rate is based on the depth in the sediment of the last occurrence of Ambrosia pollen. Since Ambrosia was only detected in the first one cm section taken, the actual depth of the Ambrosia within this cm section is unknown and thus the sedimentation rate could be over estimated.

The formation of the Mn sediment concentration profile under a sedimentation rate lower than reported is consistent with the observation that decreasing the sedimentation rate, increases the Mn concentration in the REDOX layer predicted by the BG model, Figures 11 and 12. Therefore, the BG model

was used to calculate the sedimentation rate needed to produce the peak concentration of Mn in the study core, assuming present day O_2 and Mn^{2+} fluxes. The result of this calculation is a sedimentation rate of 0.0015 cm/yr, Figure 12. Even though the highest concentration of Mn is matched using this sedimentation rate, the total mass of Mn in the REDOX layer is over estimated, as evidenced by the greater width of the predicted REDOX layer than the measured layer. To be able to correctly model the peak at this low sedimentation rate, the oxidation and reduction rates would have to be increased from their present values.

Thus, these calculations demonstrate that changes in sedimentation rate alone cannot account for the apparent non steady state Mn diagenesis. Also the present oxidation and reduction rates of Mn can not account for the Mn concentration at this site if the REDOX layer was produced under steady state conditions. The O_2 and Mn^{2+} fluxes must have changed in a direction which has slowed the oxidation rate in recent times. Since a sedimentation rate of 0.0015 cm/yr is rather low compared to rates in other depositional areas of Lake Superior (Johnson et al. 1982), a higher sedimentation rate, such as reported by Kemp et al. (1978b), might be expected for the Caribou sub basin. This implies that the oxidation and reduction rates during the formation the concentration profile of Mn might have been of significantly higher than at present.

Pedersen et al. (1986) interpreted the downward displacement of the Mn pore water profile with respect to its steady state relationship with the sediment profile to increased penetration of 0_2 into the sediment. They attributed the increased O_2 supply to be due to decreased productivity in the water column causing less Cora sedimentation and therefore less oxygen consumption at the sediment water interface. Lower concentrations of organic carbon in surface sediments compared to deeper sediment was interpreted to be evidence for the decreases productivity. My profile and other profiles for organic carbon in Lake Superior do not support recent decreases in productivity (Johnson et al 1982). Other factors causing changes in the O_2 and Mn^{2+} fluxes must be considered. However, with the data available, the cause of the apparent increase of O_2 in pore water below the REDOX layer at site 1388, or the permanency of the increase, can not be determined.

4.2 COPPER AND LEAD

4.2.1 Results

The sediment profiles of Cu and Pb exhibit apparent anthropogenic signatures in which their total hydromorphic concentrations (TM) are greatest near the surface and decrease with depth to a relatively constant value, Figure 15. Both metals are significantly enriched in the I.S. layer over their concentrations in deeper sediments. The moderately reducible (MR) and oxidizable phases account for



Figure 15. Pore-water and sediment concentration profiles of a) Cu, and b) Pb. Values are in units of μ g/l and μ g/g of dry sediment respectively. OX (oxidizable phase); MR (moderately reducible phase); TM (sum of WAS, EX, ER, MR and OX phases); and PW (pore water). The open pore water symbol at x=0 is the concentration in the bottom water.

most of the Cu and Pb in the hydromorphic fraction, although the relative importance of these two phases in sequestering the metals changes with sediment depth. In the I.S., the OX phase sequesters the most Cu, while both the OX and MR are of equal importance in sequestering Pb.

In the sediments below the I.S., the MR phase becomes relatively more important in sequestering Cu, while MR and OX phases remain nearly equal for Pb. A similar change in Cu partitioning between the I.S. and the sediments below the I.S. has been found in other areas of Lake Superior (Wilson et al. 1986). Concentrations of Cu and Pb in the REDOX layer are slightly higher than in the sediment above and below this layer.

The pore water concentrations of Cu and Pb near the sediment-water interface are higher than in the lake water, Figure 15. This indicates the release of these metals from the sediment to the pore water as a result of their postdepositional remobilization. Both metal profiles are similar to the Mn pore water profile, (Figure 9). Pore water concentrations increase between 2.5 and 4 cm, decrease from 4 to 10 cm, increase between 10 and 14 cm, and increase or remain constant below 15 cm. However, concentration maxima are not always at the same depths. For example, the pore water maxima for Pb near the top of the core occurs at 2.5 cm, while the maxima for Cu is between 3.5 and 4.5cm and for Mn at 4.5 cm. This indicates that different mechanisms affect the release of the metals from the sediment.

The similarity of the pore water profiles of Cu, Pb, and Mn in sections of the core and the slight enrichments of Cu and Pb in the MR phase (metals associated with Fe oxides) in the REDOX layer, indicate that the geochemical behavior of Cu and Pb is in part related to the Mn and Fe REDOX cycles. These results are similar to observations on trace metal behavior in marine hemipelagic sediments (Graybeal and Heath 1984). However, the lack of a direct correlation between the Pb and Mn maxima in the first 5 cm and broad nature of the Cu maxima in the same zone, indicate that processes other than REDOX reactions are affecting the geochemical behavior of Pb and Cu. We suggest that these metals are released during the decomposition of organic matter. Such a process has been shown to be important in marine sediments (Gobeil et al. 1987; Ridgeway and Price; 1987; Westerlund et al. 1986; Fischer et al. 1986; Klinkhammer 1980; Sawlan and Murray 1983)).

At this site, organic carbon in the sediment decreases from approximately 3% by weight in the I.S. to 1.5% between 3 and 4.5 cm., Figure 4. Decreasing concentrations of organic carbon in sediment of Lake Superior with burial has been interpreted to be due to carbon loss from decomposition (Johnson et al 1982). The most rapid decrease of organic carbon occurs between the I.S. and 2 cm into the sediment, which is also the interval for the most rapid decrease of Cu and Pb in the sediment. The increase in the pore water concentration of Cu and Pb, overlaps with their decrease in the sediment. Copper appears to be lost from the OX phase during burial while lead is lost from both the MR and OX phases. These observations are consistent with a model for metal release to the pore waters during the decomposition of organic matter.

4.2.2 Flux model for copper and lead

The pore water concentration gradients of Cu and Pb near the sediment-water interface suggest that these metals could be diffusing out of the sediments to the overlying lake water. The potential importance of this diffusive flux (Fd) on the cycling of Cu and Pb at the sediment-water interface was estimated from their pore water gradients. These fluxes were then compared to an estimated particle bound metal flux (Fs) or the rate of hydromorphic metal addition to the sediment-water interface from the water column.

The diffusive flux (F_d) was estimated using Fick's law; $F_d = -\phi * D_B * d[Me]_p / dx$,

where

 ϕ = average porosity of the sediment over Δx ,

 D_B = bulk sediment diffusion coefficient (cm²/yr), and d[Me]_p/dx = measured pore water concentration gradient (μ g/cm³)/cm.

This use of Fick's law assumes that D_B is constant over the depth range of interest and neglects burial of pore water and compaction. The concentration gradients $(d[Me]_p/dx)$ are considered linear from the sediment-water

interface to the maxima in the upper portion of the pore water profiles, Figure 15. Diffusion coefficients (D_0^*) for 4⁰C are calculated from the data of Li and Gregory (1974) assuming a linear change of the diffusion coefficients at infinite dilution (D_0) between 0° and $18^{\circ}C$. The solute metals are assumed to be free ions. The bulk sediment diffusion coefficient is calculated as $D_B = \phi^2 * D_o^*$ (Lerman 1975). Because (1) no visible evidence of bioturbation was detected in the core and (2) the effect of bioturbation on metal migration in Lake Superior is considered negligible (Johnson and Eisenreich 1979, Eisenreich personnel communication 1988), bioturbation is not considered in these calculations.

The particle bound metal flux (F_s) is estimated as the mass sedimentation rate (R) times the total hydromorphic metal concentration in the incoming sediment particles $[Me]_o$. The mass sedimentation rates used are taken from Kemp et al (1978b) and also from the results of the Mn modeling in this study. The ratio of the diffusive and particle bound metal fluxes $[(F_d/F_s)*100\%]$ indicates the fraction of hydromorphic sediment bound Cu and Pb that is remobilized within the upper sediments (Callender and Bowser 1980).

Because interfacial sediment (I.S.) is frequently not collected, errors may result in the calculation of diagenetic fluxes (Berner 1980). We evaluated the potential error in flux estimations by calculating two values for the bound metal flux, F_s . One flux, F_s , includes the metal
Table 5. Parameters used in the calculation of the fluxes of Cu and Pb. A porosity of 0.93 is assumed (see appendix, Table A). Concentrations are in $\mu g/g$, fluxes are in $\mu g/cm^2 * yr$.

Element	R (g/cm ² *yr)	[Me] ₀ (I.S.)	[Me] ₀ (0-1cm)	F _s (I.S.)	F _s (0-1)
	8*10 ⁻³	161	136	1 30	1 10
Cu	2 5+10-3	161	136	0 40	0 34
Cu	0.68×10^{-3}	161	136	0.11	0.09
 Dh	8*10 ⁻³	74.5	42.2	0.60	0.34
Ph	2.5 ± 10^{-3}	74.5	42.2	0.19	0.11
Pb	0.68*10 ⁻³	74.5	42.2	0.057	0.029
Element	d[Me]/dx (µg/cm ⁴)	dx (cm)	D _B (cm²/yr)	F _d (µg/cm ² *	yr)
Cu	1.5*10-3	3.5	109	0.15	
Pb	1.7*10-3	2.5	146	0.23	
R [Me]	sediment flu concentratio	x rate n in I.S. d	or 0-1 cm in	nterval as	s noted

[Me] concentration in I.S. or 0-1 cm interval as noted F_s, F_s' sediment bound metal flux calculated using I.S. and 0-1 cm interval respectively.

d[Me]_p/dx concentration gradient of pore water metal over interval dx in top sediments

D_B diffusion coefficient of pore water metal adjusted for tortuosity

F_d estimated diffusive flux of pore water metals up to sediment-water interface

concentration in the I.S. as $[Me]_0$ while the other, $F_{s'}$, uses the concentration in the 0-1 cm. interval of the sediment core as $[Me]_0$. The latter value would be typical of calculations made not including the I.S..

Table 5 lists the parameters used in the calculations, the estimated bound metal fluxes (F_s and F_s'), and the diffusive fluxes of Cu and Pb. Estimated diffusive fluxes for Cu and Pb of are 0.15 and 0.23 μ g/cm²*yr, respectively. The flux for Cu is comparable to fluxes of Cu in marine hemipelagic sediments. For example, Sawlan and Murray (1983) estimated from pore water profiles at 6 hemipelagic sites in the equatorial Pacific, that diffusive fluxes (Fd) of Cu from sediments ranged between 0.17 to 0.46 μ g/cm²*yr.

The data presented in table 5 illustrates that the calculation of the metal sedimentation rates (F_s) are significantly affected by the value of the sedimentation rate. Furthermore, by not considering metal concentrations in the I.S., F_s is under estimated by 20% and 50% for Cu and Pb, respectively. The results in Table 6 show that significantly more Pb is remobilized than Cu and that when mass sedimentation rates are less than $25*10-3g/cm^2*yr$ the amount of Pb remobilized becomes significantly greater than 100%. If 25*10-3 g/cm^2*yr is representative of the mass sedimentation rate in the Caribou sub basin, then the amount of remobilized Cu and Pb remobilized in the hemipelagic

sediments for various sedimentation rates at site 1388. R is in g/cm ² *yr. % remobilized = (F _d /F _s)*100%				
Sediment flux rate (R)	8*10 ⁻³	2.5*10 ⁻³	0.68*10 ⁻³	
Element				
Cu	12%	388	136%	
Pb	38%	121%	404%	

Table 6. Per cent of metal remobilized from surface

 F_d = estimated diffusive flux from Table 4 F_s = estimated sediment bound metal flux, I.S. only, for various possible sediment flux rates discussed in text

sediments of Lake Superior is similar to amounts remobilized in hemipelagic sediments in the ocean. For example, Fischer et al (1986) estimated that 45% and 100% of the Cu and Pb, respectively, are recycled in hemipelagic sediments at site H of the MANOP program. Allowing for uncertainties in the mass sedimentation rate, remobilization of Cu and Pb appears to be significant at site 1388 in the Caribou sub basin of Lake Superior .

The fate of the remobilized metals is unclear. They could be adsorbed by the I.S. sediments before escaping to the water column, adsorbed by the sediments settling to the sediment surface, or taken up by biota. Regardless of their fate, the amount of metal remobilization suggests that sediment concentration profiles of Cu and Pb at this site may not indicate either the timing or amounts of the anthopogenic input of metal to Lake Superior.

CHAPTER 5

CONCLUSIONS

5.1 SUMMARY AND CONCLUSIONS

Studies of sediments and pore waters at a site in the Caribou sub-basin, Lake Superior, were made to evaluate the effects of early diagenesis on trace metal behavior. Selective chemical extractions on the sediments were made to discern what hydromorphic phases are controlling metal behavior. Diagenetic modeling and calculation of fluxes across the sediment-water interface were used to quantify the extent of metal remobilization between the sediments and the pore waters and the overlying lake waters. Pb, Zn, Cu, Fe, and Mn concentrations were measured in the hydromorphic phases of sediments collected by gravity core and compared to their concentrations in surface sediments (I.S.) collected by manned submersible. The submersible allowed a representative sampling of the sediment-water interface. Mn, Cu, and Pb were measured in pore waters at the same site. The following conclusions can be made:

1. A transition zone of interfacial sediment 0.5 to 1.5 cm thick exists between the particles settling through the water column and the sediment column. This interfacial

material is referred to as the 'fluff' because of its in situ appearance. It resembles the transition zone or interfacial sediments found in marine environments in having elevated concentrations of organic carbon and trace metals such as Cu and Pb.

2. The dominant phases sequestering the metals are the moderately reducible (metals associated with Fe and Mn oxides) and the oxidizable (organics and sulfides), but their importance is different for each metal. The moderately reducible phase sequesters the most Zn, the oxidizable phase the most Cu, and the oxidizable and the moderately reducible phases both sequester most of the Pb in subequal proportions.

3. The I.S. is highly enriched in Pb, Cu, and Zn compared to the lower sediments, but is not enriched in Fe and Mn. The relative importance of phases sequestering the metals changes from the I.S. to the sediments below the I.S.. This suggests that the metals are undergoing remobilization during early diagenesis. Diagenetic remobilization of the metals is only evident when the individual hydromorphic phases are studied. Study of total metals or total hydromorphic metals in the sediments obscures such interpretations of metal behavior.

4. In most cases the concentrations of Pb and Cu in the various phases of the I.S. are an exponential extrapolation of their concentrations in the sediment below the I.S.. However, there are chemical differences, such as the Zn

concentrations in the I.S. and the sediment below, that suggest the I.S. may have some unique properties.

5. The general sediment concentration profiles of Pb, Cu, and Zn are similar to typical "anthropogenic" profiles in lakes. The Zn "anthropogenic" profile was not found in earlier studies. A comparison of the Pb and Cu profiles to an earlier study suggests that in the earlier study the I.S. was not sampled.

6. The concentration profiles of Fe and Mn reflect early diagenetic processes. Mn and Fe oxides in the REDOX layer have not accumulated significant excesses of Cu, Zn and Pb, even through such accumulations occurs in the surface sediments. This was interpreted to indicate that the decay of organic matter in the surface sediments supplies metal to the oxides near the sediment-water interface , but not to those at depth.

7. Manganese pore water and sediment concentration profiles indicate its diagenetic remobilization. The profiles are decoupled from their theoretical diagenetic steady-state relationship. Although recent changes in sedimentation rates could account for some of the decoupling, changes in the fluxes of O_2 and Mn^{2+} must also have occurred. These changes must be in a direction to cause a deeper penetration of O_2 into the sediments and a reduced rate of Mn^{2+} oxidation.

8. The concentrations of Cu and Pb in the sediment decreases with depth. Their pore water profiles indicate a

potential diffusive flux of these metals from the upper sediments to the overlying lake water. These upward fluxes may be nearly as large as the downward flux of sediment bound Cu and Pb and suggest substantial remobilization of Cu and Pb is occurring in the sediment column. Metal released during decay of organic matter may be the principle source for these metals to the pore water. The amount of Cu and Pb remobilization during early diagenesis is large at this site and may prevent interpretation of their sediment concentration profiles as historical records of metal inputs to the lake.

9. The cycling of Mn, Cu and possibly Pb within the hemipelagic sediments of the Caribou sub basin in Lake Superior is analogous to that observed in hemipelagic marine sediments. The cycling is similar in terms of benthic fluxes, sediment and pore water profiles, amounts of metal remobilizations during early diagenesis, and source of the released metals.

5.2 RECOMMENDATIONS FOR FURTHER WORK

Some very important questions about trace metal behavior in Large Lakes are left unanswered by this study. The spatial variability should be examined at a greater number of sites in the Great Lakes, and possibly some similar marine settings. Pore water and solid phase data should be examined together in a similar fashion to this study. The general behavior of the trace metals could be atypical at this one site.

More attention should be given to determining the flow of metals within the lake as a whole. This should involve capturing suspended and/or settling particles from the water column and examining them by methods similar to those used on the bottom sediments. This would allow better mass balance models to be developed than the simple ones used in this study. The diffusive fluxes of copper and lead out of the sediments appear to be important factors in the budget of these metals in the bottom sediments. In the whole lake budgets they might not be; but these facts are yet to be determined.

These recommendations, and others that are not directly related to the topic of this thesis, are among the goals of the continuing N.O.A.A./N.U.R.P. Great Lakes of the World research ongoing here at M.S.U. I am fortunate to have the chance to address these unanswered questions as part of this ongoing program.

APPENDICES

sample	depth (cm)	porosity	organic carbon (wt%)
I.S.	0.0	N.M. ¹	2.84
6-1	0.5	0.96	2.43
6-2	1.5	0.91	2.18
6-3	2.5	0.92	1.53
6-4	3.5	0.91	1.50
6-5	4.5	0.89	1.40
6-6	5.5	N.M.	1.08
6-7	6.5	0.85	0.80
6-8	7.5	N.M.	0.96
6-9	9.0	0.83	1.13
6-10	10.0	0.79	1.48
6-11	11.0	0.79	1.41
6-12	12.0	0.82	1.63
6-13	13.5	0.78	1.40
6-14	15.5	0.84	1.51
6-15	18.0	0.80	1.54
6-16	21.0	0.83	1.67
6-17	24.0	0.73	1.30
6-18	27.0	0.77	1.43
6-19	30.5	0.75	1.31

Table A. Porosity and organic carbon concentration at site 1388.

(1) N.M.=not measured.

APPENDIX A. SEDIMENT AND PORE WATER DATA

sample	depth (cm)	EX	WAS	ER	MR	ох
I.S.	0.0	257.0	5.6	47	5660	1580
6-1	0.5	43.0	5.4	96	6240	1120
6-2	1.5	38.2	7.2	89	6460	1180
6-3	2.5	18.6	6.2	84	6210	1480
6-4	3.5	31.2	3.8	89	7600	1560
6-5	4.5	12.3	5.0	110	6010	1580
6-6	5.5	143.0	3.4	142	5820	1450
6-7	6.5	103.0	3.8	129	5890	1170
6-8	7.5	218.0	84.2	291	14900	2400
6-9	9.0	60.0	10.0	198	7950	2260
6-10	10.0	N.M.	^L 4.2	58	5450	1880
6-11	11.0	5.9	1.4	78	4060	955
6-12	12.0	8.8	3.4	115	5030	997
6-13	13.5	2.5	6.0	92	4860	1230
6-14	15.5	N.M.	7.2	94	5460	1330
6-15	18.0	2.7	5.6	67	5100	987
6-16	21.0	25.0	11.0	189	5410	1670
6-17	24.0	25.7	2.6	55	4990	1250
6-18	27.0	4.4	1.6	96	4960	1530
6-19	30.5	5.8	0.0	82	4970	1520

Table B. Iron in sediment fractions site 1388. Concentrations in μ g/g of dry sediment.

sample	depth (cm)	EX	WAS	ER	MR	ох
I.S.	0.0	5.76	45.1	354	320	N.M. ¹
6-1	0.5	46.8	24.0	380	295	N.M.
6-2	1.5	37.4	20.0	442	295	N.M.
6-3	2.5	29.2	22.0	475	295	54.0
6-4	3.5	29.8	21.0	527	405	64.4
6-5	4.5	25.8	24.0	579	345	78.5
6-6	5.5	5.60	7.3	1980	875	164
6-7	6.5	2.52	5.9	2380	1080	155
6-8	7.5	4.96	N.M.	13600	7520	649
6-9	9.0	4.08	6.7	1260	503	114
6-10	10.0	1.04	4.3	28	70	39.4
6-11	11.0	0.24	3.6	42	45	22.9
6-12	12.0	3.00	6.1	46	50	26.0
6-13	13.5	0.52	3.5	48	50	23.7
6-14	15.5	10.5	14.0	31	90	30.8
6-15	18.0	0.24	3.9	46	85	23.7
6-16	21.0	5.52	N.M.	62	85	33.4
6-17	24.0	0.52	3.3	44	110	32.2
6-18	27.0	0.60	6.7	68	95	33.1
6-19	30.5	1.12	6.1	65	105	37.9

Table C. Manganese in sediment fractions site 1388. Concentrations in μ g/g of dry sediment.

sample	depth (cm)	EX	WAS	ER	MR	ох
I.S.	0.0	1.4	4.8	2.3	37.9	115.0
6-1	0.5	0.8	4.6	6.6	45.9	77.7
6-2	1.5	0.5	0.4	1.8	20.5	37.6
6-3	2.5	<0.1	0.6	0.6	10.8	17.2
6-4	3.5	<0.1	0.8	1.0	11.5	17.6
6-5	4.5	N.M. ¹	1.2	1.9	14.6	16.6
6-6	5.5	<0.1	2.4	2.9	17.0	15.5
6-7	6.5	1.7	3.6	2.6	16.9	13.0
6-8	7.5	0.2	1.4	2.7	20.2	8.6
6-9	9.0	1.0	3.0	1.0	14.7	13.4
6-10	10.0	N.M.	4.2	1.4	14.1	21.0
6-11	11.0	<0.1	1.4	2.3	14.5	15.8
6-12	12.0	0.2	<0.1	2.3	14.8	18.3
6-13	13.5	0.3	<0.1	2.3	15.0	15.8
6-14	15.5	N.M.	1.4	2.9	15.3	20.6
6-15	18.0	0.3	2.4	3.4	13.3	14.9
6-16	21.0	N.M.	4.4	3.3	14.1	22.7
6-17	24.0	0.3	1.0	2.2	12.9	18.5
6-18	27.0	0.5	1.6	4.3	12.1	21.4
6-19	30.5	0.2	0.8	3.0	11.8	23.7

Table D. Copper in sediment fractions site 1388. Concentrations in μ g/g of dry sediment.

sample	depth (cm)	EX	WAS	ER	MR	οχ
I.S.	0.0	6.4	7.0	1.3	31.1	28.7
6-1	0.5	4.0	3.0	0.8	18.9	15.5
6-2	1.5	<0.5	1.0	<0.3	8.2	7.4
6-3	2.5	0.8	<0.4	<0.3	3.5	3.0
6-4	3.5	<0.5	<0.4	<0.3	2.1	1.9
6-5	4.5	N.M. ¹	<0.4	<0.3	1.9	2.3
6-6	5.5	<0.5	<0.4	<0.3	2.3	2.3
6-7	6.5	<0.5	<0.4	<0.3	2.7	1.9
6-8	7.5	<0.5	<0.4	<0.3	<0.2	<0.2
6-9	9.0	<0.5	<0.4	<0.3	1.9	1.5
6-10	10.0	N.M.	<0.4	<0.3	1.8	2.7
6-11	11.0	<0.5	<0.4	<0.3	2.6	1.5
6-12	12.0	<0.5	<0.4	<0.3	2.7	1.5
6-13	13.5	<0.5	1.0	<0.3	2.1	2.1
6-14	15.5	N.M.	<0.4	<0.3	2.6	1.9
6-15	18.0	<0.5	<0.4	<0.3	2.4	3.0
6-16	21.0	N.M.	<0.4	<0.3	2.1	2.7
6-17	24.0	<0.5	2.0	<0.3	1.4	2.1
6-18	27.0	<0.5	1.0	<0.3	1.4	2.3
6-19	30.5	<0.5	<0.4	<0.3	1.5	2.3

Table E. Lead in sediment fractions site 1388. Concentrations in μ g/g of dry sediment.

Table F. Zinc in sediment fractions site 1388. Concentrations in μ g/g of dry sediment.

sample	depth (cm)	EX	WAS	ER	MR	ох
I.S.	0.0	1.9	28.0	14.7	77.3	22.0
6-1	0.5	6.1	5.7	9.6	52.0	12.1
6-2	1.5	3.0	2.6	5.9	38.7	8.6
6-3	2.5	1.3	1.0	3.0	25.0	6.9
6-4	3.5	1.3	1.0	2.8	23.3	11.2
6-5	4.5	N.M. ¹	1.0	2.9	21.7	10.8
6-6	5.5	0.5	0.7	5.0	21.5	10.6
6-7	6.5	0.6	0.6	4.2	19.8	9.2
6-8	7.5	0.9	N.M.	8.4	22.7	8.8
6-9	9.0	1.2	0.3	1.3	28.5	21.4
6-10	10.0	N.M.	0.3	0.9	24.1	17.1
6-11	11.0	0.3	0.5	2.0	22.7	12.1
6-12	12.0	0.5	0.3	1.6	23.1	11.9
6-13	13.5	0.6	0.4	1.4	22.9	12.7
6-14	15.5	N.M	0.5	0.9	23.1	14.5
6-15	18.0	0.8	0.8	1.0	21.1	11.5
6-16	21.0	N.M.	N.M.	1.8	24.2	15.1
6-17	24.0	0.3	0.5	0.5	19.7	13.3
6-18	27.0	0.2	1.1	1.3	19.1	14.4
6-19	30.5	0.5	0.6	1.1	19.7	15.3

Table G. Pore water metals site 1388.

sample	depth (cm)	Mn mg/l	Cu µg/l	Pb µg/l
B.W. ¹		0.002	2.8	0.81
6-1	0.5	0.010	3.3	0.87
6-2	1.5	0.007	4.5	1.32
6-3	2.5	0.018	4.6	5.40
6-4	3.5	0.023	8.7	1.62
6-5	4.5	0.059	8.0	N.M. ²
6-6	5.5	N.M.	N.M.	N.M.
6-7	6.5	0.016	4.0	0.97
6-8	7.5	0.008	3.6	0.89
6-9	9.0	0.005	6.6	1.50
6-10	10.0	0.017	17.6	1.39
6-11	11.0	0.101	19.9	1.61
6-12	12.0	0.153	10.7	1.50
6-13	13.5	0.107	18.8	2.86
6-14	15.5	0.171	8.2	0.74
6-15	18.0	0.293	15.1	1.57
6-16	21.0	0.229	9.6	1.44
6-17	24.0	0.314	18.3	1.44
6-18	27.0	0.526	12.3	N.M.
6-19	30.5	0.582	14.3	2.50

(1) B.W.=bottom water.(2) N.M.=not measured.

APPENDIX B. STEADY STATE EXPERIMENTS.

To determine if the selective chemical attack scheme of Gephart (1982) was suitable for the sediments examined in this study, "steady state experiments" were performed. The purpose of these experiments was not to make a detailed investigation of selective chemical extractions, but only to confirm that the experimental conditions were optimal.

This was done by subjecting 1 gram samples of sediments from Lake Superior to the extractions. The sediments used in the experiments were from core 2, taken in 1986 on the same cruise as site 1388 and treated in exactly the same manner. The sediments were all similar to those found at site 1388 in being largely clay.

The concentration of selected elements was monitored as a function of time during the course of the leaching experiments. Small aliquots of leachate were removed during the experimental run and analyzed for selected metals by A.A.S. The leaching runs were done sequentially in the same order and under the same conditions as given in Table 2. Only a limited number of analyses were possible on each aliquot because of the limited volume available. Very small

Table H. Steady	state	experiments.
-----------------	-------	--------------

TIME hr.	Fe BBL3 µg/g	Mn 2-5 µg∕g
0	0	0
0.6	22	21
1.1	12	20
1.5	15	25
2.0	29	17
3.1	-	27
4.1	31	32

EXCHANGABLE FRACTION

WEAKLY ACID SOLUBLE FRACTION

TIME hr.	Mn BBL3 µg∕g
0	0
0.6	88
1.6	85
4.1	99
6.6	102
7.9	108
9.2	128

EASILY REDUCIBLE FRACTION

TIME hr.	Fe BBL3 µg/g	Fe 2-5 µg/g	Mn 2-5 µg/g	
0	0	0	0	
0.27	42	95	212	
0.55	94	105	303	
0.85	146	104	329	
1.17	-	187	395	
1.43	217	176	407	
1.87	304	267	490	

TABLE H. (cont.)

MODERATELY REDUCIBLE FRACTION

TIME hr.	Fe BBL3 µg/g	Fe 2-15 µg/g	Fe 2-5 µg/g	Mn 2−5 µg/g	Zn 2-5 µg/g
0	0	0	0	0	0
0.5	4990	3140	2530	176	6.3
1.6	9330	5380	5830	272	17.4
4.1	14740	7340	7710	298	21.4
6.1	14710	8340	9090	330	32.7
7.4	15970	8370	9000	323	-
8.4	-	-	-	376	30.0

aliquots,(0.1 ml.), were removed, so as not to change the solid to solution ratio significantly. The first four extractions only were monitored. The results are summarized in Table H.

The criterion used to judge how well the extractions were tuned was to look for a distinct plateau or leveling off in metal released during the progress of the extraction. If one was found that corresponded to one found by Gephart (1982) the conditions and the reaction time was judged to be suitable.

The steady state experiments indicated that the times recommended by Gephart (1982) were also suitable for sediments from Lake Superior. The exchangeable (EX) fraction was monitored for Fe in one sample and for Mn in another. Metal release for the two samples was mostly complete after 1 hour, the recommended time, Figure A. The results were rather 'noisy'from these runs, limited readsorption or reequilibration of the sediments with the near neutral pH solution is possibly the cause of this scatter.

In the weakly acid soluble fraction, (WAS), Figure B., such low metal concentrations were released that only Mn in one sample could be monitored. Most of the manganese was released within one hour of leaching. The recommended time was 5 hours for this extraction. Although the recommended time was longer than necessary, no reason to alter the sequence was seen. The concentration of released manganese remained stable after the first hour.



Figure A. Steady state experiment on exchangeable (EX) fraction. Arrow is time recommended by Gephart (1982).



Figure B. Steady state experiment on weakly acid soluble (WAS) fraction. Arrow is time recommended by Gephart (1982).

Figure C. shows the results for the easily reducible (ER) fraction for Mn in one sample and for Fe in two samples. There is much more rapid release of Mn in the first half hour than afterward but a satisfactory steady state is not reached. After the initial burst of Mn and Fe release Fe and Mn are evolved at a nearly constant rate for the duration, (1.87 hrs.), of the experiment. It appears that more than one mineral is attacked by this reagent. This accords well with Gephart (1982) findings.

The reaction time recommended by Gephart (1982) was retained in this study. It would seem to be the best possible compromise between leaching out the interpreted first, most easily reducible, mineral or group of minerals completely and minimally affecting the more slowly reduced mineral(s). It is interpreted that the most easily reduced mineral(s) are the hydrous Mn-oxides this extraction is targeted for, and that the more slowly reduced mineral(s) are Fe-oxides.

Figure D. shows the results for the moderately reducible fraction of sediment (MR). The recommended reaction time for this extraction was 6 hours. A good 'plateau' in leachate concentrations was found at this time for Fe, Mn, and Zn in selected samples. No reason to alter the recommended reaction time was inferred from these results.



Figure C. Steady state experiment on easily reducible (ER) fraction. Arrow is time recommended by Gephart (1982).



Figure D. Steady state experiments on moderately reducible (MR) fraction. Arrow is time recommended by Gephart (1982).

BIBLIOGRAPHY

BIBLIOGRAPHY

- Allen, R.S. 1986. <u>The Role of Particulate Matter in the Fate</u> <u>of Contaminants in Aquatic Ecosystems</u>. Scientific Series #142, Environment Canada, Inland Waters Directorate National Water Research Institute Canada Centre for Inland Waters, Burlington, Ontario.
- Balistrieri, L.S. and Murray, J.W. 1984. Marine scavenging: trace metal adsorption by interfacial sediment from MANOP Site H. Geochimica et Cosmochimica Acta. 48:921-929.
- Balistrieri, L.S. and Murray, J.W. 1986. The surface chemistry of sediments from the Panama Basin: The influence of Mn oxides on metal adsorption. Geochimica et Cosmochimica Acta. 50:2235-2243.
- Berner, R.A. 1980. <u>Early Diagenesis</u>. Princeton University Press.
- Burdidge, D.J. and Gieskes, J.M. 1983. A pore water/solid phase diagenetic model for manganese in marine sediments. American Journal of Science. 283:29-47.
- Callender, E., and Bowser, C.J. 1980. Manganese and copper geochemistry of interstitial fluids from manganese nodule-rich pelagic sediments of the northeastern equatorial Pacific Ocean. American Journal of Science. 280:1063-1096.
- Carignan, R. and Nriagu, J.O. 1985. Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario. Geochimica et Cosmochimica Acta. 49:1753-1764.
- Cornwell, J.C. 1986. Diagenetic trace-metal profiles in Artic lake sediments. Environmental Science and Technology. 20: 290-302.
- Davison, W. 1982. Transport of iron and manganese in relation to the shape of their concentration-depth profiles. Hydrobiologica. 92: 463-471.
- Drever, J.I. 1988. <u>The Geochemistry of Natural Waters</u>. New Jersey: Prentice-Hall.
- Edgington, D.N. and Robbins, J.A. 1976. Records of lead deposition in Lake Michigan sediments since 1800. Environmental Science and Technology. 10:266-274.

- Filipek, L.H. and Owen, R.M. 1979. Geochemical associations and grain size partitioning of heavy metals in lacustrine sediments. Chemical Geology. 26:105-117.
- Fischer, K., Dymond, J., and Lyle, M. and Soutar, A., and Rau, S. 1986 The benthic cycle of copper: Evidence from sediment trap experiments in the eastern tropical North Pacific Ocean. Geochimica et Cosmochimica Acta. 50: 1535-1543.
- Forstner, U. 1982. Accumulative phases for heavy metals in limnic sediments. in <u>Developments in Hydrobiology 9:</u> <u>Sediment/Freshwater Interaction</u>, ed. P.G. Sly, pp. 269-284. The Hague: Junk Publishers.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica et Coshmochimica Acta. 43:1075-1090.
- Gaudette, H.E., Flight, W.R., Toner, W.R., and Folger, D.W. 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. Journal of Sedimentary Petrology. 44:249-253.
- Gephart, C.J. 1982. <u>Relative Importance of Iron-Oxide</u>, <u>Manganese-Oxide and Organic Material on the Adsorption</u> <u>of Chromium in Natural Water Sediment Systems</u>. M.S. Thesis, Michigan State University.
- Gobeil, C., Silverberg, N., Sundby, B., and Cossa, D. 1987. Cadmium diagenesis in Laurentian Trough sediments. Geochimica et Cosmochimica Acta. 51: 589-596.
- Graybeal, A.L., and Heath, G.R. 1984. Remobilization of transition metals in surficial pelagic sediments from the eastern Pacific. Geochimica et Cosmochimica Acta. 48: 965-975.
- Gupta, S.K. and Chen, K.Y. 1975. Partitioning of trace metals in selective chemical fractions on near shore sediments. Environmental Letters. 10:129-158.
- Heggie, D., Kahn, D., and Fischer, K. 1986. Trace metals in metalliferous sediments, MANOP Site M: interfacial pore water profiles. Earth and Planetary Science Letters. 80:106-116.

- Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant roles of hydrous Mn and Fe oxides. American Chemical Society Advances in chemistry Series. 73:337-383.
- Johnson, T.C., and Eisenreich, S.J. 1979. Silica in Lake Superior: mass balance considerations and a model for dynamic response to eutrophication. Geochimica et Cosmochimica Acta. 43: 77-91.
- Johnson, T.C., Evans, J.E., and Eisenreich, S.J. 1982. Total organic carbon in Lake Superior sediments: Comparisons with hemipelagic and pelagic marine environments. Limnology and Oceanography. 27:481-491.
- Kemp, A.I.W., Williams, J.D.H., Thomas, R.I., and Gregory, M.I. 1978a. Impact of man's activities on the chemical composition of the sediments of Lakes Superior and Huron. Water, Air, and Soil Pollution. 10: 381-401.
- Kemp, A.L.W., Dell, C.I., and Harper, N.S. 1978b. Sedimentation rates and a sediment budget for Lake Superior. Journal of Great Lakes Research. 4:276-287.
- Klinkhammer, G.P 1980. Early diagenesis in sediment from the eastern equatorial Pacific, II. pore water metal results. Earth and Planetary Science Letters. 49:81-101.
- Klinkhammer, G., Heggie, D.T., and Graham, D.W. 1982. Metal diagenesis in oxic marine sediments. Earth and Planetary Science Letters. 61:211-219.
- Leckie, J.O., Benjamin, M.M., Hayes, K., Kaufman, G., and Altman S. 1980. Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide. Electric Power Research Institute Research Project 910-1.
- LeLand, H.V.S., Shukla, S., and Shimp, N.L. 1973. Factors affecting distribution of lead and other trace elements in sediments of southern Lake Michigan. in <u>Trace Metals</u> <u>and Metal-Organic Interactions in Natural Waters</u>. ed. P. Singer, pp 89-138. Ann Arbor Science, Ann Arbor, MI.
- Lerman, A. 1975. Migrational processes and chemical reactions in interstitial waters. in <u>The Sea</u>, vol. 6, pp. 695-738. E.D. Goldberg, I.N McCave, J.J O'Brien, and J.H. Steele eds. New York: Wiley.
- Li, Y.H. and Gregory, S. 1974. Diffusion of ions in seawater and in deep-sea sediments. Geochimica et Cosmochimica Acta. 38:703-714.

- Long, D.T. and Gephart, C.A. 1982. Competition analysis of Cr adsorption on Fe-oxides, Mn-oxides and organic matter in natural systems. Fall annual meeting, Geological Society of America Abst. with Programs. 14:549.
- Lyons, W.B., Hines, M.E., Gaudette, H.E. 1984. Major and minor element pore-water geochemistry of modern marine sabkhas. in <u>Microbial Mats: Stromatalites</u> ed. P. Liss, pp. 411-423. New York.
- Malo, B. 1977. Partial extraction of metals from aquatic sediments. Environmental Science and Technology. 11:227-282.
- McKee, J.D., Wilson, T.P., Long, D.T., and Owen, R.M. 1986. Geochemical processes at the sediment/water interface in profundal lakes: experiments with a manned submersible. Fall annual meeting, Geological Society of America, Abst. with programs. 18:469.
- Murray, J.W., Balistrieri, L.S., and Paul, B. 1984. The oxidation state of manganese in Marine sediments and ferromanganese nodules. Geochimica et Cosmochimica Acta. 48:1237-1247.
- Pedersen, T.F., Vogel, J.S., and Southon, J.R. 1986. Copper and manganese in hemipelagic sediments at 21^ON, East Pacific Rise: diagenetic contrasts. Geochimica et Cosmochimica Acta. 50:2019-2031.
- Olivarez, A.M., Owen, R.M., and Long, D.T. 1988. Geochemistry of rare earth elements in benthic layer particulates and sediments of Lake Superior. Journal of Great Lakes Research (in press).
- Rea, D.K., Owen, R.M., and Meyer, P.A. 1981. Sedimentary processes in the Great Lakes. Reviews of Geophysics and Space Physics. 19: 635-648

- Ridgeway, I.M., and Price, N.B. 1987. Geochemical associations and post-depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. Marine Chemistry. 21: 229-248
- Robbins, J.A. and Callender, E. 1975. Diagenesis of manganese in Lake Michigan sediments. American Journal of Science. 275:512-533.
- Robbins, J.A. and Gusting, J. 1976. A squeezer for efficient extraction of pore water from small volumes of anoxic sediment. Limnology and Oceanography. 21:905-909.
- Sawlan, J.J. and Murray, J.W. 1983. Trace metal remobilization in the interstitial waters of red clay and hemipelagic marine sediments. Earth and Planetary Science Letters. 64:213-230.
- Sigg, L. 1985. Metal transfer mechanisms in lakes:a the role of settling particles. in <u>Chemical Processes in Lakes</u> ed. W. Stumm, pp. 282-310. John Wiley, New York.
- Soutar, A. and Johnson, S. 1981. Sampling the sediment-water interface--evidence for an organic-rich surface layer (Abst.). EOS. 62:905.
- Stumm, W. and Baccini, P. 1978. Man-made chemical perturbations of lakes. in <u>Lakes: Chemistry, Geology,</u> <u>Physics</u>. ed. A. Lerman, pp. 91-126. Springer-Verlag, New York.
- Tessier, A., Campbell, P.G.C., and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry. 51:844-851.
- Thomas, R.L., and Dell, C.I. 1978. Sediments of Lake Superior. Journal of Great Lakes Research. 4:264-275.
- Westerlund, S.F.G., Anderson, L.G., Hall, P.O.J., Iverfeldt, A., van der Loeff, M.M.R., and Sundby, B. 1986. Benthic fluxes of cadmium, copper, nickel, zinc and lead in the coastal environment. Geochimica et Cosmochimica Acta. 50: 1289-1296.
- Wilson, T.P., Long, D.T., and Owen, R.M. 1986. The water/sediment interface via manned submersible. (Abst.). International Association of Great Lakes Research. 29th Conference: 52.

