

FORMS OF IRON, PHOSPHORUS AND TRACE-METAL IONS IN A LAYERED SEDIMENT CORE FROM LAKE ONTARIO

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ABSTRACT

Mössbauer spectroscopy and chemical fractionation have been used to study Fe, Mn, P and trace-metal ions found in a core of silty clay sediment from beneath 100 m of oxic water in the Niagara Basin of Lake Ontario. The top 10 cm of the core has several unusual features: (a) clay (Al), chlorite (Fe^{2+}) and Fe concentrations are erratic, (b) ~0.1 cm thick Fe-rich red and Mn-rich black layers occur 5 to 6 cm below the sediment-water interface, and (c) phosphorus concentrations are extremely high, e.g., 0.88% P at 0 to 1 cm, 1.08% in the red layer. Trace-metal, Mn (except for these Fe- or Mn-rich layers), and Ca concentrations agree well with those measured in more uniformly deposited cores from other parts of Lake Ontario. Trace-metal ions are enriched at the sediment-water interface, most of the enrichment being associated with the iron and manganese oxides fraction; these ions are mainly nonbioavailable. Brown amorphous $\text{Fe}(\text{OH})_3$, refractory ferric compounds and detrital hematite have been identified and measured in the oxidized surface layer. The principal Fe compound in the red layer is an X-ray-amorphous superparamagnetic oxide, with grain size $< 100 \text{ \AA}$. Ferrous ions, found only in chlorite in all sections, are useful conservative indicators. The phosphorus in the core is present mainly as non-apatite inorganic phosphate (NAIP) bonded to iron compounds. Most of the surficial P is nonbioavailable.

Keywords: sediment, Great Lakes, phosphorus, iron, trace metals.

SOMMAIRE

On a étudié par spectroscopie Mössbauer et fractionnement chimique, des ions de Fe, de Mn, de P et de métaux en traces, présents dans un échantillon d'argile silteuse prélevé sous 100 m d'eau dans le bassin de Niagara du lac Ontario. Les 10 cm supérieurs de la carotte présentent des caractères peu banals: a) les concentrations d'argile (Al), de chlorite (Fe^{2+}) et de Fe sont erratiques; b) des couches de 0.1 cm d'épaisseur, les unes rouges et riches en Fe, d'autres, riches en Mn et noires, se trouvent à 5 ou 6 cm sous l'interface

sédiments-eau; c) les concentrations de phosphore sont extrêmement élevées, notamment 0.88% entre 0 et 1 cm, et 1.08% dans la couche rouge. Les concentrations de métaux en traces, de Mn (sauf dans les couches riches en Fe ou en Mn) et de Ca correspondent à celles qu'on a mesurées dans des dépôts plus uniformes provenant d'autres parties du lac Ontario. Les ions des métaux en traces sont enrichis à l'interface sédiments-eau, et surtout dans la fraction d'oxydes de fer et de manganèse; la plupart de ces ions ne sont pas biodisponibles. Du $\text{Fe}(\text{OH})_3$ amorphe brun, des composés ferriques réfractaires et de l'hématite détritique, relevés dans la couche superficielle oxydée, ont été titrés. Le principal composé de Fe dans la couche rouge est un oxyde surparamagnétique, amorphe aux rayons X, en grains de moins de 100 Å de diamètre. Des ions ferreux, qui se trouvent uniquement dans la chlorite, quoique dans toutes les sections, sont néanmoins des indicateurs utiles. Dans la carotte, le phosphore se trouve surtout sous forme de phosphate inorganique, non-apatitique, lié à des composés de fer. Rare est le P de surface qui soit biodisponible.

Mots-clés: sédiment, Grands Lacs, phosphore, fer, métaux en traces.

INTRODUCTION

Releases of phosphorus and trace-metal ions from lake sediments are of concern because of eutrophication and the introduction of toxic cations into the food chain. Iron hydroxides in rivers and lakes are intimately associated with the binding, transport and sedimentation of phosphorus and trace metals (Bortleson & Lee 1974, Burns & Ross 1972, Gibbs 1973, Mackereth 1966, Manning *et al.* 1981, Mortimer 1941, Syers *et al.* 1973, Williams *et al.* 1976a, b). A scheme has been proposed for the estimation of refractory ferric compounds (RFCs) and brown amorphous Eh-sensitive $\text{Fe}(\text{OH})_3$ in the oxidized surface layer (OSL) of Great Lakes sediment (Manning *et al.* 1981, Manning & Jones 1982). Calculated concentrations of $\text{Fe}(\text{OH})_3$ -adsorbed P agree well with chemically

derived concentrations of non-apatite inorganic phosphorus (NAIP), indicating that the adsorption hypothesis is valid. The RFCs may be amorphous aluminosilicates formed at the sediment-water interface from $\text{Fe}(\text{OH})_3$ and hydrated alumina and silica. The term *refractory* refers to the persistence of these compounds in reduced sediments (Manning *et al.* 1980, Manning & Ash 1978).

Large areas of Lake Ontario are characterized by ferromanganese-coated sands, by ferromanganese nodules and by Fe-Mn layered cores (Sly & Thomas 1974). The origin of the ferromanganese-coated sands has been attributed to the release of Fe and Mn from deep-water low-redox surficial sediments and to subsequent precipitation in shallower zones of high redox potential (Sly & Thomas 1974); the layers, on the other hand, are often observed in high-redox depositional sediments. We retrieved a silty clay core, with the following sectional color properties, from beneath 100 m of oxic water in the Niagara Basin of Lake Ontario at 43°21'03"N, 79°20'10"W on 23 July, 1981:

0 to 1 cm:	uniform brown, similar to the OSL of nearby Niagara Basin cores (Manning <i>et al.</i> 1981, Manning & Jones 1982),
1 to 2 cm:	mainly grey,
2 to 3 cm:	grey,
3 to 5 cm:	light grey,
5½ cm:	crusty 1-mm-thick black layer,
5½ to 6 cm:	crusty 1- to 2-mm-thick red layer,
8 to 10 cm:	uniform light grey,
15 to 21 cm:	mottled light to dark grey,
105 to 107 cm:	mottled light to dark grey.

Similar layered cores were retrieved from ~15 km southeast of this location, confirming that these muds are widespread.

Importantly, the brown OSL and the red layer contain 0.88% P (wt. % dry sediment) and 1.08%, respectively, values considerably in excess of the concentrations of P in Great Lakes muds, generally 0.1 to 0.16% P (Manning & Jones 1982, Manning *et al.* 1981, Williams *et al.* 1976a, b). Two cores retrieved previously from a nearby location (14 km NW, 43°24'06"N, 79°26'40"W) display prominent brown OSLs (~1.7% Fe^{3+} in RFCs, ~0.5% in $\text{Fe}(\text{OH})_3$, 0.16% total P; Manning *et al.* 1981, Manning & Jones 1982), but no red layer. Trace-metal concentrations are similar in cores from both locations. The current core is also unusual in that the chlorite (Fe^{2+}) and clay (Al) contents

vary with depth. In order to compensate for any dilution on changes in deposition, Fe^{3+} concentrations must be normalized against Fe^{2+} in chlorite before diagenetic effects can be observed (Manning & Jones 1982).

In this article, we describe a collation of Mössbauer spectral and chemical extraction studies of Fe, P and trace-metal forms in the layered core. Major aims of the work are the definition of the major iron compounds and their role in the binding of trace metals and, in particular, the abundant phosphate ions.

EXPERIMENTAL DETAILS

The 1-m-long × 8-cm-diameter (Benthos) gravity core was extruded and sectioned at 1 cm intervals over the top 15 cm under nitrogen within nine hours of retrieval; the sections were frozen immediately, freeze-dried and then stored under N_2 at -20°C. Oxidation during processing is considered minimal, but it is conceivable that the chemical extraction properties of the muds may be modified on freeze-drying.

Mössbauer spectra were recorded at room temperature and at 4 K and over different velocity ranges using equipment at McMaster University. Spectra were computed using the programs of Stone (1967). Lorentzian line shapes were assumed; area ratios and half-widths of peaks in a quadrupole doublet were constrained to be equal. Chi-squared values and visual examination were used as criteria for goodness of fit.

Approximately 0.5 g of freeze-dried sediment was chemically fractionated following the sequential procedure of Tessier *et al.* (1979). The fractions are: A. exchangeable metal, extracted by 1 M MgCl_2 at pH 7 in 10 minutes; B. carbonate- and surface-oxide-bound metals, leached with acetate buffer at pH 5; C. metals bound to Fe-Mn oxides, leached with 0.02 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc; D. organically and sulfide-bound metals, leached with H_2O_2 and then with $\text{NH}_4\text{OAc}/\text{HNO}_3$; E. lattice-bound residue. This was digested in 5 mL of freshly prepared *aqua regia* and 3 mL of 30% H_2O_2 to near dryness at moderate heat. Five mL of HF and 2 mL of a solution of 30% H_2O_2 were added and the mixture heated to dryness. Finally, 3 mL of HCl and 10 mL of distilled water were added, the solution was heated for 30 minutes and the extract diluted to 25 mL. All extractions were carried out in polysulfone (Du Pont) centrifuge tubes.

Elemental determinations were carried out by D.C. Argon Plasma Atomic Emission Spectro-

metry (DCPAES) using a Spectraspan III three-electrode system equipped with a DBC-33 background compensator module. Al, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were done simultaneously using a multi-element cassette; the remaining elements were measured sequentially. Samples and standards for emission analysis were subjected to three replicate 5-s integrations during a single period of nebulization. Calibration stability was monitored every sixth sample (matrix change).

No *Ambrosia* pollen was observed in the red layered material, although pine pollen is abundant; the layers are consequently at a sediment depth corresponding to precolonial deposition, say before 1840 (N. Harper, priv. comm.). Lead-210 dating of the layers in a similar core retrieved ~6 km south of our location yielded a date of ~1820 (H. Wong, priv. comm.).

RESULTS AND DISCUSSION

Spectral resolution and assignments

The room-temperature Mössbauer spectra of the 1-to-2-cm freeze-dried sediment (Figs. 1 and 2) are representative qualitatively of all sections, showing in the +4 to -4 mm s⁻¹ range (Fig. 1) the quadrupole doublets marking Fe²⁺ in chlorite (outer doublet) and Fe³⁺ in mainly amorphous compounds (broadened inner doublet) (Manning & Ash 1978, Manning *et al.* 1981). Over a wide energy-range (Fig. 2), additional peaks appear characteristic of magnetically ordered iron oxides; the two weak innermost peaks of the six-line pattern are obscured by the Fe²⁺ and Fe³⁺ doublets. Computed Mössbauer parameters and iron concentrations for the three moieties are listed in Tables 1 and 2; the chlorite assignment is consistent with the Fe content of fraction E. The magnetically ordered oxide is probably well-crystallized hematite (Greenwood & Gibb 1971), which likely plays an insignificant role in P binding.

The 4 K spectrum of the 0-to-1-cm sample is identical with that measured at room temperature; hence, either no ultrafine (<100 Å across) superparamagnetic ferric oxides are present (Coe & Readman 1973) or, alternatively, all oxide particles are < 40 Å across. Normalizing the measured Fe³⁺ concentrations to 2.43% Fe²⁺ (*i.e.*, from Table 2, 3.32% Fe³⁺ at 0 to 1 cm, $(2.43/1.59) \times 1.82 = 2.78\%$ Fe³⁺ at 1 to 2 cm, 2.70% at 2 to 3 cm, and 1.65% at 9 to 10 cm) yields the significant surficial enrichment of ~0.5% Fe³⁺ also observed in two nearby Niagara Basin cores (Manning *et al.* 1981, Manning & Jones 1982). This excess Fe³⁺

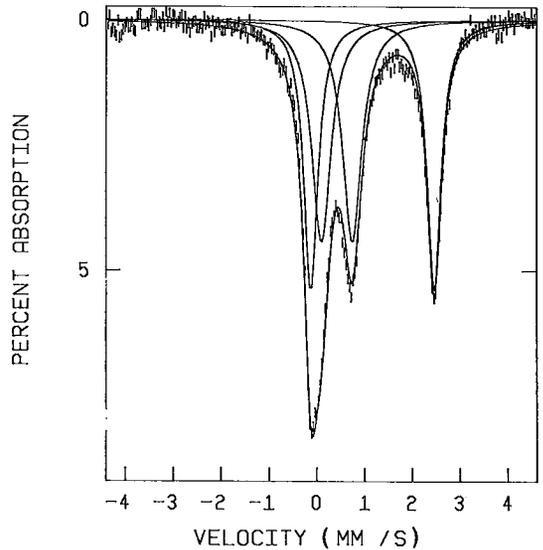


FIG. 1. Room-temperature Mössbauer spectrum of the 1-to-2-cm section of Niagara Basin sediment core. Solid lines depict individual absorption bands and computed fit, based on two doublets.

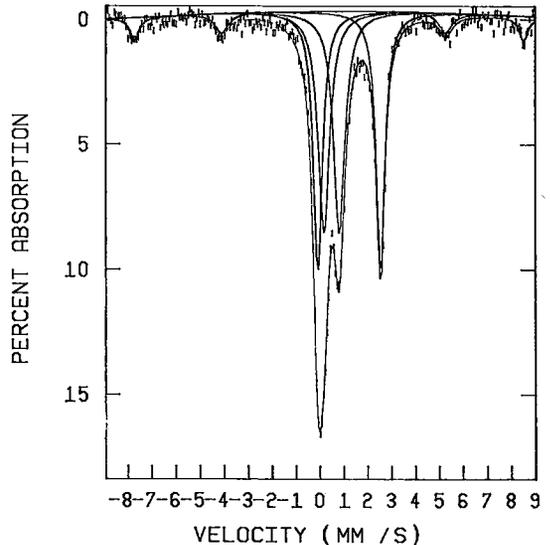


FIG. 2. Room-temperature Mössbauer spectrum of 1-to-2-cm section of Niagara Basin core over an expanded energy range. Solid lines depict individual absorptions and computed fit. Outlying peaks are assigned to hematite, Fe₂O₃.

is attributed to the Eh-sensitive brown Fe(OH)₃ responsible for the characteristic color of the oxidized surface layer. No magnetic splitting was observed by us in the 4 K spectrum of

TABLE 1. MOSSBAUER PARAMETERS, CONCENTRATIONS, AND ASSIGNMENTS OF MAIN IRON COMPOUNDS IN SEDIMENT CORE

Section cm	IS mm s ⁻¹	QS mm s ⁻¹	HM mm s ⁻¹	HK0e	% of Fe _T	Assignment
0 to 1	0.35	0.66	0.50	-	50.2	RFC + Fe(OH) ₃
	1.11	2.64	0.34	-	36.6	Fe ²⁺ in chlorite
	0.33	-0.11	0.63	493	13.2	hematite
1 to 2	0.35	0.64	0.48	-	47.3	RFC
	1.10	2.64	0.36	-	41.2	Fe ²⁺
	0.39	-0.10	0.68	507	11.5	Fe ₂ O ₃
2 to 3	0.36	0.63	0.50	-	46.2	RFC
	1.10	2.59	0.36	-	41.6	Fe ²⁺
	0.37	-0.11	0.59	508	12.1	Fe ₂ O ₃
5.5, Black	0.35	0.68	0.53	-	56.6	RFC + red oxide
	1.10	2.66	0.38	-	37.2	Fe ²⁺
	0.33	-0.12	0.52	514	6.2	Fe ₂ O ₃
5.8, Red	0.35	0.79	0.50	-	80.9	RFC + red oxide
	1.08	2.64	0.31	-	14.5	Fe ²⁺
	0.34	-0.11	0.58	493	14.6	Fe ₂ O ₃
9 to 10	0.38	0.60	0.56	-	36.4	RFC
	1.11	2.59	0.36	-	53.5	Fe ²⁺
	0.36	-0.16	0.52	509	10.1	Fe ₂ O ₃
5.8, Red 4K	0.37	-	1.18	458	90.4	RFC + Fe ₂ O ₃
	1.32	2.70	0.66	-	9.6	Fe ²⁺

IS = isomer shift relative to Fe Fo1, QS = quadrupole splitting and HM = half-width; all values are good to ±0.02 mm s⁻¹.

surficial and reduced sections of Lake Erie Central Basin cores, in which most of the Fe³⁺ is in RFCs. Therefore, most of the ferric iron in the top 3 cm of the core is present, as in the more uniformly deposited cores (Manning *et al.* 1981, Manning & Jones 1982), in "background" RFCs and in surficial Fe(OH)₃. Minor amounts of Fe³⁺ are located in the structure of clays (Manning & Ash 1978).

The 4 K spectrum of the crusty red sediment is dominated by a six-line magnetic pattern, with Mössbauer parameters (Table 1) similar to those reported for amorphous small (~40 Å across) particles of a ferric gel (Coe & Readman 1973) formed on the oxidation of ferrous-ion-rich surface spring-waters. X-ray-diffraction measurements of the red sediment did not yield an iron hydroxide or oxide pattern; hence, the major moiety of iron is an amorphous superparamag-

netic ultrafine (<100 Å) hydrated ferric oxide, which causes the redness and the high quadrupole splitting (Table 1). Small amounts of this red oxide probably are present in the Mn-rich black layer (Tables 1 and 2), but the redness is masked by the black of MnO₂. Color, QS values and the 4 K spectrum for the 0-to-1 cm fraction suggest that insignificant amounts of the red oxide are present in the top 3 cm of core. Significantly, the QS value (0.79 mm s⁻¹) for the red oxide is similar to the value reported for ferrihydrite (Murad & Schwertmann 1980), 5Fe₂O₃·9H₂O, which is formed, as particles ~100 Å across, by microbial oxidation of groundwater containing ferrous iron. X-ray-diffraction patterns of our red material did not show the broad lines of ferrihydrite, possibly because of the poor crystallinity and low concentration of the red oxide. Conceivably, a continuous range of particle sizes may exist between Fe(OH)₃ and the red oxide, the two compounds being of similar composition and structure. Increased aggregation or crystallization of surficial Fe(OH)₃ is probably hindered by adsorption of organic matter and foreign ions. The influence of adsorbed ions and particle size on QS values is not known. The different colors of the red oxide and Fe(OH)₃ suggest different magnetic interactions and, possibly, different structures. The main iron compounds are listed in Table 1.

The Mössbauer-derived Fe²⁺ concentrations and total Al concentrations (Table 2, Manning & Jones 1982) depict a nonuniform rate of sedimentation; ~90% of Al is nonextractable, consistent with its presence in clay minerals. The reasonably constant values of the ratio of hematite to Fe²⁺ concentration indicate that hematite behaves conservatively, and its presence at sediment depths beneath the Ambrosia horizon shows it to be of natural origin and, hence,

TABLE 2. ELEMENTAL CONCENTRATIONS IN LAYERED NIAGARA BASIN SEDIMENT CORE (WT % DRY SEDIMENT)

Depth cm	Fe _T	Fe ₂ O ₃	Fe ³⁺	Fe ²⁺	Fe Frac.E	Al _T	Mn _T	Mn A+B	Mn C	P _T	P Frac.E	Ca _T	Ca A+B+C	Ca E
0 - 1	6.62	0.87	3.32	2.43	2.57	6.95	0.63	0.014	0.56	0.88	0.78	7.63	6.46	0.71
1 - 2	3.85	0.44	1.82	1.59	3.42	4.55	0.32	0.05	0.21	0.62	0.53	6.48	5.55	0.38
2 - 3	2.41	0.29	1.11	1.00	1.87	3.20	0.24	0.09	0.09	0.43	0.34	3.62	2.70	0.46
Black L.	4.04	0.25	2.29	1.50	3.20	7.83	8.0	0.34	6.64	0.20	0.06	1.30	1.01	0.20
Red L.	10.54	0.48	8.53	1.53	6.03	6.48	0.80	0.35	0.30	1.08*	0.77	2.57	1.08	0.23
9 - 10	1.92	0.19	0.70	1.03	1.66	1.58	0.08	0.04	0.02	0.28	0.23	0.61	0.34	0.20

Fractions refer to the Tessier *et al.* (1979) extraction scheme.

Al, 90% non-extractable (E).

Fe²⁺:Al_T = 0.42 ± 0.02 for cores from the nearby location.

*P in A + B = 0.002%, P in C = 0.12% and P in D = 0.18%; in other sections P_{A+B} = 0.002%, P_C = 0.05%, P_D = 0.08%.

In uniformly deposited cores, Ca in apatite (Fraction E) = 0.08%

Iron concentrations derived from Fe_T and Mossbauer data. Fe³⁺ concentrations do not include Fe in α-Fe₂O₃. Most extractable Fe is in C.

not derived from the steel mills at Hamilton, 40 km west of the core location (Manning *et al.* 1980). Calcium concentrations, as expected (Kemp & Thomas 1976), decrease with sediment depth (Table 2); therefore, the diluting background element is a major component such as Si, possibly biogenic. Significantly, total Si is 20.2% at 0 to 1 cm and 24.2% at 2 to 3 cm; the loss of Si in clays is more than counterbalanced by increased deposition of other Si compounds.

The concentration of Fe^{2+} in the 0-to-1-cm section (Table 2) agrees with the concentration of nonextractable iron, suggesting that almost all the Fe^{3+} and hematite is extractable (mostly in fraction C). The extraction of some hematite (or Fe^{2+}) further indicates that the extraction scheme may not be specific. Beneath the top cm, the Fe^{3+} is poorly extracted, which is consistent with the persistence of RFCs in the reduced zones of sediments (Manning & Ash 1978, Manning *et al.* 1980, 1981). Increased crystallization of RFCs may occur on burial. $\text{Fe}(\text{OH})_3$ is undoubtedly wholly extractable.

Phosphorus interactions

Total P concentrations in the current core (Table 2) are remarkably high relative to the values measured (P_T 0.1 to 0.16%, NAIP 0.03–0.08%, apatite P \sim 0.04%, organic P \sim 0.03%) for cores retrieved from the nearby locations in the Niagara Basin (Manning *et al.* 1981, Manning & Jones 1982) and from several other locations in lakes Ontario and Erie (Kemp *et al.* 1974, Williams *et al.* 1976a, b, Williams *et al.* 1980b). The 10% of P_T extracted in fraction D (Table 2) is probably an overestimation of organic P; low rates of sedimentation and oxic waters suggest that organic P should not exceed the background value of 0.03%. Chemical extraction procedures are not perfectly selective and should be regarded as operationally defined separations (Tessier *et al.* 1979, Rendell *et al.* 1980). The elevated levels of P are unlikely to be due to apatite for several reasons: (i) there is insufficient Ca in fraction E to bind the P, (ii) Ca levels are typical of Lake Ontario muds (Kemp & Thomas 1976), (iii) a 20-to-30-times increase in apatite deposition from land erosion would be matched by a parallel increase in chlorite deposition: no such increase is observed, and (iv) the marked separation of the Mn-rich and Fe-rich layers and the presence of a brown oxidized surface layer with elevated Mn concentrations strongly suggest that redox processes are important; hence, adsorption or precipitation of ferric phosphate moieties can be expected under oxic conditions. More-

over, some Ca is present in plagioclase (Thomas 1969). The concentration of P in the Fe-rich red layer and the similar trends in Fe^{3+} and P concentrations (Table 2) suggest that P is associated with Fe^{3+} , but only weakly so with Mn and Al (see Berner 1973). Hence, most of the P in this core is NAIP.

Apart from nonuniform depositional patterns, the chemistry of most of the Fe in the top 3 cm of the current core seems similar to that described for more uniform Niagara Basin cores (Manning *et al.* 1981, Manning & Jones 1982). Assuming that the concentration of brown $\text{Fe}(\text{OH})_3$ in the top cm is \sim 0.95% $\text{Fe}(\text{OH})_3$ (*i.e.*, \sim 0.5% Fe^{3+} ; see above, Manning *et al.* 1981, Manning & Jones 1982) and that $\text{Fe}(\text{OH})_3$ adsorbs 5% of its weight of P (as PO_4) (Stamm & Kohlschutter 1965, Lijklema 1980, Berner 1973, Sholkovitz & Copland 1982), then $\text{Fe}(\text{OH})_3$ -P equals 0.05% P, clearly in total disagreement with measured P_T (largely NAIP). If all the Fe^{3+} in the top cm is $\text{Fe}(\text{OH})_3$, the adsorbed P equals 0.32%, significantly below P_T . It is, however, unrealistic to place all Fe^{3+} in $\text{Fe}(\text{OH})_3$, firstly because most of the Fe^{3+} is probably in RFCs of low P-binding capacity (Manning *et al.* 1981, Manning & Jones 1982), and secondly, because the loss of the brown color in the 1-to-2-cm and 2-to-3-cm sections, indicative of reducing conditions, is not accompanied by a large decrease in Fe^{3+} concentrations (after normalizing against Fe^{2+}) on dissolution. Therefore, adsorption on $\text{Fe}(\text{OH})_3$ seems inadequate in explaining the high surficial NAIP levels; consequently, precipitation of a ferric phosphate, either as \sim 1:1 crystalline or an amorphous compound, must be considered. If nonextractable, such a compound would explain the different extractabilities of Fe^{3+} and P in the 0-to-1-cm section (Table 2). However, re-adsorption of P on the geological matrix of the sediment may be a problem (Williams *et al.* 1980a). The Mössbauer parameters for the ferric phosphate would be too similar to those of the various iron oxides for simple identification. Potentially available P is, therefore, limited to anoxic release from $\text{Fe}(\text{OH})_3$ -P (*i.e.*, \sim 0.05% P) but, because the bottom waters are permanently oxic, almost all P is nonbioavailable. Treatment with citrate-dithionite-bicarbonate reagent led to the extraction of 0.08% P from the 0-to-1-cm fraction.

Concentration trends (Table 2) suggest that the red layer contains \sim 8% Fe^{3+} in the superparamagnetic oxide and \sim 0.8% P. This Fe^{3+} :P ratio agrees well with that for surficial $\text{Fe}(\text{OH})_3$ -P in cores from the nearby location (Manning

et al. 1981, Manning & Jones 1982), suggesting that the P is mainly NAIP adsorbed on the red oxide.

Forms of carbon

Concentrations of organic C (4.7% at 0 to 1 cm, 2.1% at 9 to 10 cm) and of inorganic C (1.8% and 0.01%, respectively) agree well with values for the nearby location (Kemp & Thomas 1976). In the red layer, organic C is ~0.6%, reflecting strongly oxidizing conditions, and inorganic C is ~0.08%. The surficial inorganic C occurs mainly as calcite (Kemp & Thomas 1976), and mass-balance calculations suggest that little Ca is left over in the core to bind the high surficial NAIP.

Forms of manganese

Most of the Mn is extractable in fractions A, B and C, and in some sections the A + B fraction is relatively important (Table 2). The pattern of Mn extractability is not consistent with that for P, and P is relatively impoverished in the Mn-rich black layer (Table 2). The color of the layer is probably due to MnO₂. Mn concentrations are also elevated in the surficial muds (Table 2), consistent with high redox conditions and brown surficial Fe(OH)₃ (Kemp & Thomas 1976). The trend in decreasing Mn

concentrations over the top 3 cm follows that measured by us in cores from the nearby location in the Niagara Basin (0.65% Mn at 0 to 1 cm, 0.20% at 2 to 3 cm, 0.17% at 13 to 14 cm) and by Kemp & Thomas (1976). Mn is insufficiently abundant to account for the high P_r.

Forms of trace metals

Trace-metal concentrations agree well with those measured in cores from the nearby location (Table 3, Kemp & Thomas 1976), surficially and at depths corresponding to precolonial settlement. These comparisons confirm the early colonial or precolonial time of deposition of the red and black layers. The increase in surficial Pb and Zn concentrations is particularly dramatic (Table 3), most of the increase being extracted in fraction C. Cu is the only cation ostensibly bound to organic matter (fraction D). In general, trace metal concentrations over the top 3 cm do not follow the trend in Fe³⁺, clay and P_r, nor are trace metals elevated in the red or black layers (Tables 2 and 3). However, if concentrations of brown surficial Fe(OH)₃ are similar in the present core and at the nearby location cores and if Fe(OH)₃ adsorbs significant amounts of trace metals, similar profiles would be expected.

The surficial (depositional) sediments of the Niagara Basin remain oxic year-round, suggesting that the bioavailable trace metals are bound in fractions A and B (Table 3). In general, minor amounts of the metals are bioavailable. The dumping of metal-contaminated dredged harbor-sediments in these deep oxic waters may cause release of heavy metals to the lake from interstitial waters, but it is probable that the metals will be re-adsorbed rapidly on sediment ferric oxides.

GENERAL DISCUSSION

It would be unwise to consider the origin of the black and red layers in detail on the basis of one core. However, the layers are either a relict depositional feature reflecting unusual surficial conditions promoted by early land clearing and possibly exacerbated by the cold summers (low productivity) of the early 1800s (Stommel & Stommel 1979) or, alternately, they are subsurface diagenetic products. The data presented here do not permit an unequivocal decision. The Fe, Mn, Al and P enrichments of the black and the red layers are clearly derived from the precipitation of upwardly mobile pore-water ions; these ions are impoverished relative to chlorite in mud beneath the

TABLE 3. DISTRIBUTION OF TRACE METALS BETWEEN DIFFERENT FRACTIONS

Depth cm	Fraction*	Cd	Co	Cr _{org} g ⁻¹	Cu	Mn	Pb	Zn
0 - 1	A	0.5	nd	0.05	0.5	0.06	nd	0.7
	B	0.1	0.5	0.05	0.3	1.5	7	10
	C	1.3	4.4	28	13	37	130	187
	D	nd	1.2	14	38	10	34	38
	E	2.6	13.8	66	31	28	21	120
	Total	4.5(4.9)	20(28)	108(116)	83(92)	77(57)	192(167)	355(424)
1 - 2	A	nd	0.07	0.04	0.3	0.6	nd	1.3
	B	0.3	0.5	0.04	0.2	2.4	9	11
	C	1.7	3.3	27	7	27	134	163
	D	nd	1.4	18	47	12	39	56
	E	3.5	16	68	33	31	24	154
	Total	5.5	21	113	88	73	206	385
2 - 3	A	nd	0.1	0.02	0.2	0.9	nd	0.8
	B	nd	0.4	0.07	0.07	2.8	9	6.2
	C	1.6	4.5	24	4.1	23	107	142
	D	0.3	2.0	20	56	17	52	81
	E	4.3	18	59	29	30	22	147
	Total	6.2	25	103	89	74	190	377
Black layer	A	nd	nd	0.4	0.1	nd	nd	nd
	B	nd	2.1	nd	nd	3	11	nd
	C	nd	8.9	2.5	17	26	22	22
	D	nd	nd	2.3	5	5	8	8
	E	3.1	16	62	18	25	12	74
	Total	3.1	27	67	40	59	53	104
Red layer	A	nd	nd	0.1	0.7	nd	nd	nd
	B	nd	1.3	0.1	0.9	0.7	10	nd
	C	3	13	4	15	6	6	19
	D	nd	1.2	2	12	3	3	8
	E	6.3	27	59	18	24	14	80
	Total	9.3	43	65	45	34	35	107
9 - 10	A	nd	0.08	0.03	0.1	nd	nd	nd
	B	nd	0.14	nd	0.1	0.09	1.8	nd
	C	0.1	1.6	1.0	4.3	4.1	5	8
	D	nd	1.6	2.2	19	7	6	14
	E	2.2	13	83	20	31	5	61
	Total	2.3(3.7)	16.3(48)	86(63)	43(50)	42(48)	18(19)	83(163)

* Tessier et al. (1979).

nd = not detected

Bracketed are our corresponding data for core from nearby Niagara Basin location.

layers (data for the 9-to-10-cm fraction in Table 2). The separation of the layers indicates a steep redox gradient, which could be generated at the sediment-water interface or at horizons of Mn-oxidizing and Fe-oxidizing bacteria living a few cm below the sediment surface. In the latter case, the layers may be continuously dissolving and re-precipitating, thus keeping the layers at constant depth below the interface. If the layers are a relict surface feature, short-term conditions at the sediment-water interface may have promoted the crystallization of the red oxide which, in some way, is protected from rapid reduction on burial.

The similarity in Ca, Mn, and trace-metal concentrations over the top 3 cm between this core and that from the nearby location (Table 3) suggests that their deposition is unrelated to that of Fe^{3+} and clays. This is not inconsistent with trace metal adsorption on brown surficial $\text{Fe}(\text{OH})_3$; most of the surficial trace metals are extracted in fraction C (Table 3). The cause of the erratic deposition of clay is not known, but clay minerals may be cemented together, possibly by ferric hydroxide coatings, to yield silt-sized particles. The clay-silt distribution in this core is 35% clay at 0 to 1 cm, 55% at 1 to 2 cm and 70% in other sections.

The current core may be representative of muds over ~10% of the Niagara Basin. Sedimentation rates are probably 3 to 5 times greater at the nearby location than at this location (Kemp *et al.* 1974; see above), indicating that comparable amounts of P are sedimented annually. The form of most of the NAIP in the current surficial muds has not been identified, but Fe^{3+} is probably implicated; small amounts of NAIP are adsorbed on $\text{Fe}(\text{OH})_3$. Note that in the top cm of sediment, NAIP is mainly in nonbioavailable RFCs in muds of the Lake Erie Central Basin, adsorbed on Eh-sensitive $\text{Fe}(\text{OH})_3$ over most of the Niagara Basin (Manning *et al.* 1981, Manning & Jones 1982), and in an unknown form in and around the current location.

Hematite is identified unambiguously. Based on $\text{Fe}^{2+}:\text{Fe}^{3+}$ (RFC) and $\text{Fe}^{2+}:\text{Al}$ ratios for the top 3 cm of core, the loss of Fe^{3+} and Al ions in mud beneath the red layer suggests that RFCs contain major amounts of Fe^{3+} and Al ions and, probably, Si ions. The structural and compositional relationship between $\text{Fe}(\text{OH})_3$ and the red oxide cannot be answered from these data. Identification of these and the ferric phosphate compounds requires additional investigations using electron microscopy (and EDAX) and pore-water studies.

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