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IRON–PHOSPHATE LAYERS IN SEDIMENTS OF LAKE ONTARIO

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ABSTRACT

Mössbauer spectral and chemical fractionation studies of four sediment cores retrieved from the Niagara Basin of Lake Ontario reveal layers enriched in Fe^{3+} ion and in non-apatite inorganic phosphorus (NAIP). At least two layers occur in the top 20 cm of core. These (secondary) layers are not as visually or compositionally prominent as the (primary) red layer present in cores from an adjacent ~200 km^2 area. The red layer and the secondary layers are of similar origin. The red layer does not mark a unique event but rather one particularly intense episode of precipitation. Most of the precipitated phosphorus is retained within the layers over more than 150 years. A core from the Central Basin of Lake Erie shows no evidence of layering; however, the phosphorus-binding capacity of the surficial sediments has increased in the last few years.

Keywords: sediments, phosphorus, iron, layers, Lake Ontario.

SOMMAIRE

Les études du fractionnement chimique et des spectres de Mössbauer portant sur quatre carottes de sédiments prélevées dans le bassin Niagara du lac Ontario ont mis en évidence la présence de couches enrichies en ion Fe^{3+} et en phosphore inorganique d'origine autre que l'apatite. On a trouvé au moins deux couches dans les 20 premiers centimètres de l'échantillon. Ces couches (secondaires) ne sont pas, visuellement ou par leur composition, aussi évidentes que la couche rougeâtre (primaire) des échantillons provenant d'un domaine avoisinant d'environ 200 km^2. La couche rougeâtre et les couches secondaires sont de même origine. La couche rougeâtre ne représente pas un seul événement, mais plutôt un épisode particulièrement intense de précipitation. La plus grande partie du phosphore précipité est retenue dans les couches pendant une période de plus de 150 ans. On n'a relevé aucune trace de stratification dans une carotte provenant du bassin central du lac Érié; toutefois, la capacité de lier le phosphore des sédiments superficiels a augmenté au cours des dernières années.

Mots-clés: sédiments, phosphore, fer, couches, lac Ontario.

INTRODUCTION

A visually prominent iron- and phosphorus-rich reddish brown layer occurs five to ten cm beneath the sediment–water interface over an area of approximately 200 km^2 in the Niagara Basin of Lake Ontario (Fig. 1) (Manning *et al.* 1985, Sly & Thomas 1974). The layer contains more than 20000 tonnes of non-apatite inorganic phosphorus (NAIP), an amount exceeding the recommended annual phosphorus input to Lake Ontario (7000 tonnes; Great Lakes Water Quality Board, 1983). NAIP is the principal source of bioavailable phosphorus (Williams *et al.* 1980). Concentrations of NAIP and of iron are well correlated in Great Lakes sediments (Williams *et al.* 1976, Manning *et al.* 1984). Consequently, the stability of the reddish brown layer in the anoxic zone of sediments is important to nutrient loading in Lake Ontario. Only one such obvious layer has been observed in a core, although thin dark grey or black layers are relatively frequent within a light grey background in Lake Ontario sediments (Kemp 1969).

Here, we report on the results of ^{57}Fe Mössbauer spectral and phosphorus fractionation studies of four sediment cores retrieved from the northern and northeastern flanks of the ~200 km^2 area covered by the red layer (Fig. 1). Iron and phosphorus data for two previously studied cores are re-examined in order to better determine the areal extent of the layering. The aims of the work are to determine (a) the extent of, and the amount of phosphorus contained in, subsurface layers in the Niagara Basin and (b) the long-term persistence of phosphorus in the layers.

EXPERIMENTAL

Sixty-cm-long gravity cores were retrieved from four locations in the Niagara Basin (Table 1, Fig. 1). One core was retrieved from the Central Basin of Lake Erie for comparative purposes (Table 1). The cores were extruded and sectioned under nitrogen at 1-cm intervals down to ~20 cm, and at ~5 cm intervals thereafter. Sections were frozen within ten minutes of extrusion, except for some black sections, which were frozen immediately to preserve the black FeS component from oxidation. Freeze-dried residuals were bottled and stored at 4°C. All cores displayed a prominent 1- to 2-cm-thick brown oxidized surface-layer overlying mottled or striated light grey to dark grey to black muds. Subsurface red or brown layers were not immediately obvious in any core. Central portions of the cores were selected to eliminate shearing along core-liner walls. The Munsell color of the dry reddish brown layer is 5 YR 4/4.

Mössbauer spectra were recorded at the National Water Research Institute using a microprocessor-

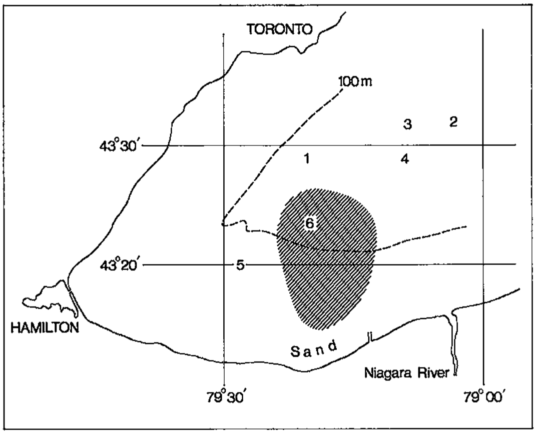

FIG. 1. Locations of cores in the Niagara Basin. Hatched area represents the ~200 km^2 primary area of the red layer, the boundaries of which have been determined by extensive coring.

TABLE 1. DATA FOR LAKES ONTARIO (NIAGARA) AND ERIE (CENTRAL) CORES

Core	Date	Basin	Depth	Latitude	Longitude
1	25 Oct 82	Niagara	112	43'29'00"	79'20'00"
2	6 Nov 84	Niagara	129	43'32'03"	79'05'02"
3	29 Mar 85	Niagara	126	43'32'00"	79'09'00"
4	16 Oct 84	Niagara	130	43'29'00"	79'09'00"
5	28 Sep 83	Niagara	91	43'20'00"	79'28'00"
6	26 Oct 82	Niagara	106	43'24'00"	79'20'00"
7	19 Aug 83	Central	23	41'59'00"	81'55'00"

based spectrometer (Cryophysics Ltd., MS103). Computation of spectra was based on the assumed equality of peak half-widths and of peak areas within a quadrupole doublet. Values of chi-squared and the visual examination of computed fits were used as criteria of goodness of fit. The spectrometer was calibrated against iron foil. Spectra were recorded at room temperature.

Concentrations of NAIP were measured according to Williams *et al.* (1976). Concentrations of total Fe and of total manganese were measured by bomb or acid digestion and atomic absorption spectrometry (Agemian & Chau 1975, Desjardins 1978). Concentrations of organic and inorganic carbon were measured using a Leco induction furnace. All concentrations are expressed in weight percent of dried sediment.

RESULTS AND DISCUSSION

Mössbauer spectral assignments

All Mössbauer spectra can be adequately fitted assuming two doublets (Fig. 2). The outer doublet is characterized by the following measured parameters (Table 2): isomer shift (IS) 1.14±0.02 mm s^{-1}, quadrupole splitting (QS) 2.62±0.02 mm s^{-1}, and half-width (HW) 0.43±0.02 mm s^{-1}; it reflects mainly ferrous ions in octahedral positions in chlorite (Coey *et al.* 1974, Manning *et al.* 1984, Readman *et al.* 1976). Chlorite was detected by X-ray-diffraction methods. Illite and chlorite are the principal constituents of the clay minerals in Great Lakes sediments (Kemp & Thomas 1976). Illite contains relatively low concentrations of ferrous ions (Deer *et al.* 1962). The broadened inner doublet marks ferric ions in a range of octahedral positions in hydrated oxides, in clay structures and in amorphous aluminosilicates formed surficially (Coey *et al.* 1974, Manning *et al.* 1984, Nriagu 1978). The Mössbauer parameters for ferric iron are: IS 0.40±0.02 mm s^{-1}, QS 0.57 to 0.71 mm s^{-1}, and HW 0.54 to 0.64 mm s^{-1} (Table 2). Half widths increase with increasing depth of burial, whereas QS values are significantly elevated at the oxidized surface-layer and particularly at the secondary layers (Table 2). The ferric iron absorption-envelope cannot meaningfully be resolved into component doublets because of absorption overlaps. Tables 3 and 4 list measured concentrations of ferrous and ferric ions and normalized concentrations of ferric ions, using ferrous ions in chlorite as a conservative element (Manning *et al.* 1984). Normalization corrects for loss of calcium and magnesium carbonates and organic matter on burial (Tables 3, 4). Clay minerals are unlikely to be affected by diagenesis, and they provide an acceptable basis for purposes of normalization (Kemp & Thomas 1976, Kemp *et al.* 1976). Significantly, normalization factors are considerably smaller for Niagara Basin cores than for Lake Erie cores (Tables 3, 4, 7), consistent with the marked surficial enhancement in calcite concentrations in Lake Ontario muds (Kemp & Thomas 1976).

The ferric iron profiles (Fig. 3) for cores 1 and 2, over the top 7 cm, follow those for earlier cores (Manning *et al.* 1984, 1985), displaying elevated ferric concentrations over the top 1 or 2 cm, *i.e.*, over the brown oxidized surface-layer. The ferric iron profiles for cores 1 and 2 display, in addition, two concentration maxima, *e.g.*, at 8 to 9 cm and 13 to 14 cm for core 2, which correspond to two maxima in the NAIP profiles (Fig. 3). The ferric iron and NAIP trends for core 3 suggest three or four maxima of differing intensity (Table 4). Core 4 profiles show one significant Fe^{3+}–P coincidence at 8 to 9 cm and an NAIP peak at 13 to 14 cm (Table 4); the paucity of material prevents a more complete analysis of deeper sections.

The surficial enhancement in ferric iron concentrations can be assigned to Eh-sensitive ferric ions ($EhFe^{3+}$), the oxides of which are precipitated on diffusion of porewater ferrous ions into the surface layer (Manning *et al.* 1984). Concentrations of manganese are also enhanced surficially (Tables 3, 4 and

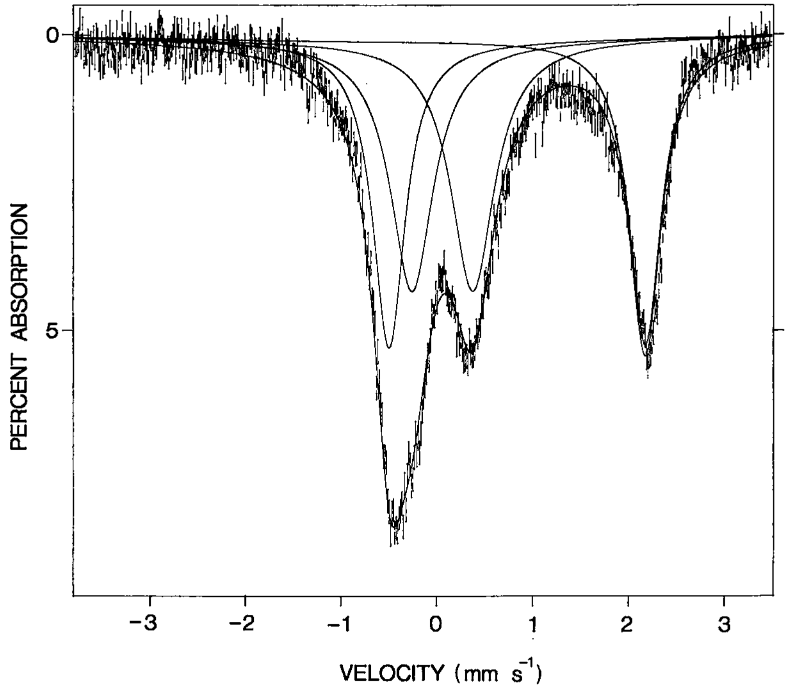

FIG. 2. Representative room-temperature spectrum of Niagara Basin sediment, in this case the 1- to 2-cm section of core 2. Chi-squared = 550 for 495 degrees of freedom. Velocities relative to Fe foil.

5), confirming the existence of strongly oxidizing surface conditions (Kemp & Thomas 1976). Concentrations of EhFe^{3+} in the top cm may be calculated by averaging ferric concentrations over the range 2 to 3 cm and 6 to 7 cm or 7 to 8 cm and subtracting this value from the total ferric concentration in the top cm. Ferric ions that persist in the anoxic zone of a core are termed refractory ferric compounds, RFCs (Manning *et al.* 1984); they include Fe^{3+} ions in clay structures, in aluminosilicates and in refractory oxides. Measured values of EhFe^{3+}, RFCs and Fe^{2+} in the top cm (Table 5) are in good agreement with those for other cores from Lake Ontario (Manning *et al.* 1984, Manning 1986), including red-layer cores.

Re-analysis of earlier results

The secondary Fe^{3+}–P peaks of cores 1 to 4 have, on re-analysis, counterparts in the ferric iron and NAIP profiles of earlier cores (Manning 1987). Core 5, retrieved from ~5 km west of the ~200 km^2 area (Fig. 1), displays secondary Fe^{3+}–P maxima at 7 to 8 cm and 22 to 23 cm beneath the sediment-water interface (Table 6). Core 5, and two others from the immediate vicinity, were earlier described as having normal profiles over the top 7 cm, beneath which the Fe^{3+} iron and NAIP profiles were erratic (Manning 1987). Core 6, a primary red layer core from within the ~200 km^2 area, displays the visually and compositionally prominent red layer

TABLE 2. ISOMER SHIFTS (IS), QUADRUPOLE SPLITTINGS (QS) AND HALF-WIDTHS (HW) FOR SECTIONS OF CORES 1, 2 AND 3

Section cm	IS mm s^{-1}	QS mm s^{-1}	HW mm s^{-1}	IS mm s^{-1}	QS mm s^{-1}	HW mm s^{-1}
For Core 1						
0-1	0.39	0.66	0.54	1.14	2.63	0.39
1-2	0.39	0.64	0.54	1.15	2.62	0.42
2-3	0.39	0.62	0.56	1.15	2.60	0.44
3-4	0.39	0.60	0.54	1.15	2.61	0.42
4-5	0.40	0.62	0.55	1.15	2.61	0.44
5-6	0.39	0.65	0.56	1.14	2.61	0.44
7-8	0.41	0.60	0.56	1.14	2.60	0.44
8-9 dk	0.39	0.63	0.56	1.14	2.61	0.42
8-9 lt	0.41	0.60	0.57	1.14	2.61	0.42
10-11 dk*	0.38	0.69	0.61	1.14	2.62	0.47
10-11 br*	0.41	0.71	0.63	1.14	2.63	0.44
12-13	0.41	0.57	0.60	1.14	2.61	0.42
15-16	0.41	0.58	0.57	1.14	2.61	0.43
16-17	0.41	0.58	0.60	1.14	2.60	0.41
16-17 dk*	0.38	0.69	0.60	1.14	2.59	0.43
17-18 dk*	0.39	0.68	0.59	1.14	2.62	0.43
19-20	0.41	0.58	0.59	1.14	2.60	0.42
For Core 2						
8-9*	0.40	0.70	0.59	1.12	2.59	0.44
11-12	0.41	0.60	0.61	1.15	2.62	0.42
13-14*	0.40	0.71	0.62	1.13	2.61	0.44
For Core 3						
7-8*	0.37	0.71	0.62	1.13	2.63	0.40
14-15	0.41	0.60	0.64	1.13	2.62	0.42

dk=dark grey or black; lt=light grey; br=brown. Asterisks represent secondary layers. Note the relatively high quadrupole splittings (~0.70 mm s^{-1} versus ~0.60 mm s^{-1}) of Fe^{3+} ions in secondary layers.

TABLE 3. CONCENTRATIONS OF FORMS OF Fe, Mn, NAIP and CARBON IN SECTIONS OF CORES 1 (UPPER) AND 2

Section cm	Color	Fe_T wt.%	Fe^{2+} %	Fe^{2+} wt.%	N.F.	Fe^{3+} wt.%	Fe^{3+}_{norm} wt.%	Mn_T wt.%	NAIP wt.%	C_{org} wt.%	C_{inor} wt.%
0-1	brown	4.11	38.7	1.590	1.000	2.52	2.52	0.98	0.044	4.00	2.47
1-2	brown/grey	4.40	44.1	1.940	0.820	2.46	2.02	0.49	0.067	4.20	1.69
2-3	grey	4.79	49.55	2.373	0.670	2.42	1.62	0.24	0.077	n.d.	n.d.
3-4	grey	4.94	51.8	2.556	0.622	2.38	1.48	n.d.	0.062	n.d.	n.d.
4-5	dk grey	5.31	50.65	2.690	0.591	2.62	1.55	0.22	0.070	n.d.	n.d.
5-6	dk grey	5.66	49.85	2.821	0.564	2.84	1.60	n.d.	0.059	n.d.	n.d.
6-7	grey	4.83	52.1	2.516	0.632	2.31	1.46	n.d.	0.043	n.d.	n.d.
8-9	dk grey	4.89	51.3	2.509	0.634	2.38	1.51	n.d.	0.036	n.d.	n.d.
8-9	lt grey	4.89	52.8	2.582	0.616	2.31	1.42	n.d.	0.035	n.d.	n.d.
9-10	dk grey	5.57	48.3	2.690	0.591	2.88	1.70	n.d.	0.076	n.d.	n.d.
10-11*	dk grey	5.06	45.25	2.290	0.694	2.77	1.92	n.d.	n.d.	n.d.	n.d.
10-11*	lt brown	6.35	43.9	2.785	0.571	3.56	2.03	n.d.	0.460	n.d.	n.d.
12-13	lt grey	5.14	55.8	2.869	0.554	2.27	1.26	0.10	0.024	n.d.	n.d.
15-16	lt grey	4.44	60.65	2.691	0.591	1.75	1.03	0.09	0.016	1.79	0.04
16-17	lt grey	4.62	59.2	2.735	0.581	1.88	1.10	n.d.	0.018	1.50	0.36
16-17*	black	5.59	42.1	2.353	0.676	3.24	2.19	n.d.	0.198	1.57	0.16
17-18*	black	5.59	44.95	2.513	0.633	3.08	1.95	n.d.	n.d.	1.59	0.14
19-20	lt grey	4.39	59.8	2.625	0.606	1.76	1.07	0.08	0.017	n.d.	n.d.
0-1	brown	2.89	41.3	1.194	1.000	1.70	1.70	0.67	0.047	4.48	2.11
1-2	brown/olive	2.90	43.7	1.267	0.942	1.63	1.54	0.28	0.088	4.11	2.31
2-3	olive	3.89	50.4	1.961	0.609	1.93	1.18	0.19	0.059	2.64	1.43
3-4	grey	3.89	50.05	1.947	0.613	1.94	1.19	n.d.	0.072	2.60	0.91
4-5	dk grey	3.63	49.1	1.782	0.670	1.85	1.24	0.13	0.055	2.50	0.61
5-6	dk grey	3.63	50.6	1.837	0.650	1.79	1.17	n.d.	0.052	2.25	0.40
6-7	dk grey	3.63	50.4	1.830	0.652	1.80	1.17	n.d.	0.048	2.13	0.15
7-8	dk grey	3.63	51.9	1.884	0.634	1.75	1.11	n.d.	0.118	1.76	0.07
8-9*	lt brown	4.00	40.2	1.608	0.743	2.39	1.78	n.d.	0.386	1.69	0.04
9-10	lt grey	3.71	50.2	1.862	0.641	1.85	1.18	0.08	0.044	1.32	0.08
10-11	lt grey	3.71	56.5	2.096	0.570	1.61	0.92	n.d.	0.023	1.10	0.04
10-11	grey	3.71	57.9	2.148	0.556	1.56	0.87	n.d.	0.024	1.06	0.04
12-13	grey	3.71	54.85	2.035	0.587	1.68	0.98	n.d.	0.129	1.10	0.05
13-14*	dk grey	4.00	46.6	1.864	0.641	2.14	1.37	n.d.	0.527	1.17	0.05
14-15	dk grey	4.29	51.0	2.188	0.546	2.10	1.15	0.09	0.094	1.05	0.06
18-19	lt grey	3.71	54.0	2.003	0.596	1.71	1.02	n.d.	0.018	n.d.	n.d.
21-22	lt grey	3.71	59.2	2.196	0.544	1.51	0.82	0.04	0.016	n.d.	n.d.

Normalization factor (NF) for core 1=1.590/(Fe^{2+} concentration in a section). Asterisks denote high Fe^{3+}, high NAIP layers. dk=dark, lt=light, n.d.=not determined.
Total S values in core 1 are: 10-11 cm (dk grey) 0.40%, 12-13 cm (lt grey) 0.12%, 15-16 cm 0.15%, 16-17 cm (lt grey) 0.13% and 17-18 cm (black) 1.10%.

(Table 6) and also a secondary Fe^{3+}–P peak at 12 to 13 cm.

Manganese trends

All cores demonstrate the surficial enrichment in manganese consistent with strongly oxidizing surface layers (Tables 3, 4) (Kemp & Thomas 1976). As a result of burial to 10 to 15 cm, manganese concentrations attain background levels of less than 0.1% (Tables 3, 4). Note, however, that manganese concentrations are significantly enhanced in secondary layers of core 3 (7 to 8 cm, Table 4) and of core 6 (12 to 13 cm, Table 6). This suggests that the secondary layer formed under strongly oxidizing conditions.

General discussion

The strong association of Fe^{3+}, Mn and NAIP in the secondary and in the primary layers suggests that the layers are of similar origin and differ only in the concentrations of the ions. The secondary layers can be colored dark grey, black or a light brown, and they are not easily recognized on sectioning. The following observations support the similarity in origin: (a) the relatively large quadrupole splittings measured for ferric iron in the secondary layers compared to ferric ions in other sections of core (Table 2). The QS values for ferric iron in primary red layers (~0.77 mm s^{-1}, Manning *et al.* 1985) are similar to those reported for ferrihydrite (~0.80 mm s^{-1}, Murad & Schwertmann 1980). The "intermediate" QS values measured here for ferric ions in the secondary layers reflect the similar concentrations of "background" RFCs and of the ferrihydrite-like oxide (Table 2). (b) The primary and secondary layers occur in the same basin, in muds in similar depths of water (50 to 70 m) and at similar depths beneath the sediment–water interface (5 to 10 cm) (Manning *et al.* 1984). The infrequent occurrence of the two layers suggests that they may have formed contemporaneously and in response to the same environmental stimulus. (c) The ferric iron concentrations are significantly lower beneath the primary and the secondary layers compared to concentrations above the layers (Fig. 3, Table 4) (Manning *et al.* 1985). Changes in redox potentials with time have clearly been compatible in the two types of layered core.

Muds containing the secondary layers occur on the

TABLE 4. FORMS AND CONCENTRATIONS OF IRON AND PHOSPHORUS IN CORES 3 (UPPER) AND 4

Section cm	Color	Fe^{2+} %	Fe^{2+} wt.%	N.F.	Fe^{3+} wt.%	Fe^{3+}_{norm} wt.%	NAIP wt.%	$NAIP_{norm}$ wt.%	Mn_T wt.%
0-1	brown	38.2	1.528	1.000	2.47	2.47	0.051	0.051	0.82
1-2	brown								
2-3	olive	46.9	1.876	0.814	2.12	1.73	0.078	0.063	
3-4	dk grey	44.2	1.768	0.864	2.23	1.93	0.057	0.049	
4-5	dk grey	45.5	1.820	0.840	2.18	1.83	0.049	0.041	
5-6	dk grey	45.2	1.808	0.845	2.19	1.85	0.044	0.037	0.16
6-7	dk grey	45.3	1.812	0.843	2.19	1.85	0.186	0.157	
7-8*	dk grey	41.6	1.664	0.918	2.34	2.14	0.241	0.221	0.37
8-9	lt grey	49.4	1.976	0.773	2.02	1.56	0.042	0.032	0.09
9-10	lt grey	48.5	1.940	0.788	2.06	1.62	0.037	0.029	
10-11	grey	50.4	2.016	0.758	1.98	1.50	0.031	0.023	
11-12	grey	48.8	1.952	0.783	2.05	1.60	0.031	0.024	
12-13*	dk grey	44.4	1.776	0.860	2.22	1.91	0.058	0.050	0.10
13-14	lt grey	48.8	1.952	0.783	2.05	1.60	0.072	0.056	0.10
14-15	lt grey	55.7	2.228	0.686	1.77	1.22	0.024	0.016	0.07
15-16*	dk grey	46.9	1.876	0.814	2.12	1.73	0.105	0.085	0.10
16-17	grey	55.1	2.204	0.693	1.80	1.24	0.058	0.040	0.07
17-18	grey	52.2	2.088	0.732	1.91	1.40	0.036		
18-19	grey	53.8	2.152	0.710	1.85	1.31	0.050		
19-20	grey	51.9	2.076	0.736	1.92	1.42	0.201		0.12
20-21	grey	53.6	2.144	0.713	1.86	1.32			
21-22	grey	56.7	2.268	0.674	1.73	1.17			
0-1	brown	40.3	1.209	1.000	1.79	1.79	0.067	0.067	0.56
1-2	olive	45.8	1.374	0.880	1.63	1.43	0.077	0.068	0.24
2-3	olive/grey	50.5	1.514	0.779	1.49	1.19	0.084	0.067	0.24
3-4	grey	50.1	1.503	0.804	1.50	1.20	0.084	0.068	
4-5	dk grey	50.2	1.506	0.803	1.49	1.20	0.103	0.083	
5-6	dk grey	51.5	1.544	0.783	1.46	1.40	0.074	0.058	
6-7	grey	51.0	1.530	0.790	1.47	1.16	0.051	0.040	0.11
7-8	grey	50.4	1.511	0.800	1.49	1.19	0.084	0.067	
8-9*	grey	43.8	1.314	0.920	1.69	1.55	0.126	0.116	
9-10	grey	51.3	1.538	0.786	1.46	1.15	0.049	0.039	0.07
12-13	grey	53.3	1.599	0.756	1.40	0.06	0.035	0.026	
13-14	grey	54.0	1.620	0.746	1.38	1.03	0.106	0.079	
14-15	grey	53.5	1.605	0.753	1.40	1.05			0.06
16-17	grey	58.2	0.746	0.692	1.25	1.25			

N.F.=normalization factor. *denotes secondary Fe^{3+}-P layer. dk=dark, lt=light.
For core 4: % C_{org}=4.18 at 0-1 cm, 4.06 at 1-2 cm, 4.04 at 2-3 cm, 3.05 at 8-9 cm and 2.22 at 13-14 cm; % C_{inorg}=2.62 at 0-1 cm, 2.44 at 1-2 cm, 0.22 at 8-9 cm and 0.18 at 13-14 cm.

northern and western flanks of the ~200 km^2 area (Fig. 1); the southern flank merges into shallow sands. One core retrieved from the eastern side of the ~200 km^2 area, in a region of high rates of sedimentation (Durham & Oliver 1983), displayed a low surficial enhancement in EhFe^{3+}, reflecting a lower redox potential (Manning *et al.* 1984). The presence of two secondary Fe^{3+}-P layers in cores 1, 2, 3 and 5 and of a primary red and a secondary layer in core 6 demonstrates that the conditions causing the precipitation of Fe, Mn and P as a red layer were not unique. Rather, the conditions locally within the ~200 km^2 area led to one particularly intense precipitation producing a red layer, whereas peripherally, milder conditions induced formation of secondary layers. The similar profiles of ferric iron above the primary red and secondary layers (Fig. 3) (Manning *et al.* 1985), including the elevated values at the oxidized surface-layer, suggest that the secondary layers were formed as such and are not root remnants of primary layers.

The strongly oxidizing conditions required for the formation of ferrihydrite or other poorly crystallized ferric oxide, in the primary or secondary layers, are consistent with oligotrophic conditions in the Niagara Basin (Sly & Thomas 1974). Red layers have not been observed visually in cores from the Central Basin of Lake Erie (Sly & Thomas 1974), nor have primary or secondary layers been detected by Mössbauer or chemical methods (Manning *et al.* 1984). The surficial sediments of the Central Basin are less well oxidized than those of the Niagara Basin because of oxygen depletion in the hypolimnion during summer stratification (Burns & Ross 1972). Surficial Mn-enrichment is absent (Kemp & Thomas 1976). Cores retrieved in 1979 to 1980 showed minor or zero EhFe^{3+} values and minor enhancement of NAIP. The Fe^{3+} and P data for the Central Basin core 7 show no evidence of well-defined primary or secondary layers, but show a strong enhancement in surficial redox-sensitive Fe^{3+} (0.63% EhFe^{3+}, Tables 5, 7) and in adsorbed NAIP (Table 7). Both values are consistent with data for several Lake Erie and Lake Ontario cores (Manning *et al.* 1984). They also indicate, in conjunction with Fe^{3+} and NAIP values for one core retrieved from the Central Basin in September 1981 (Manning *et al.* 1984), a significant increase in EhFe^{3+} concentrations and in the phosphorus-

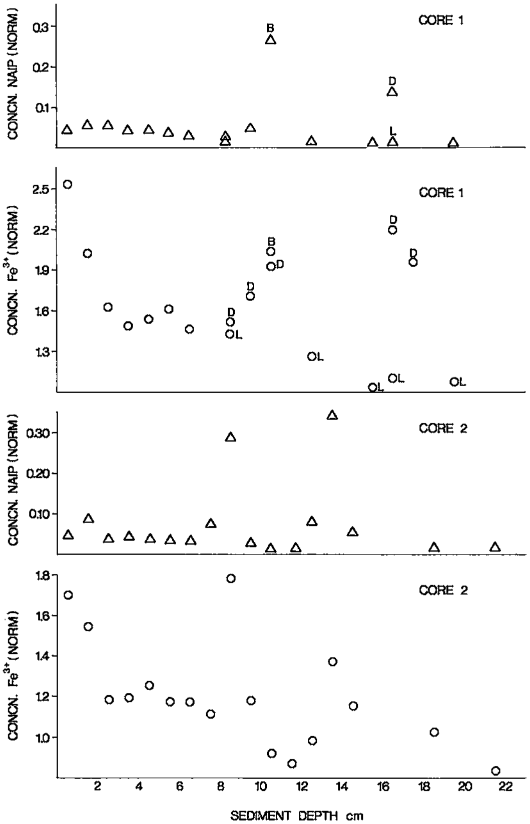

FIG. 3. Plots of normalized concentrations of Fe^{3+} and NAIP *versus* depth beneath the sediment–water interface for cores 1 and 2. Symbols: B black, D dark grey, L light grey.

TABLE 5. IRON AND MANGANESE VALUES IN TOP CM OF SEVEN CORES

Core	Fe^{3+}_T wt.%	RFC wt.%	$EhFe^{3+}$ wt.%	Mn_T wt.%
1	2.52	1.54	0.98	0.98
2	1.70	1.18	0.52	0.67
3	2.47	1.84	0.63	0.82
4	1.79	1.22	0.57	0.56
5	1.90	1.38	0.52	0.77
6	2.00	~ 1.50	~ 0.50	0.61
7	2.46	1.83	0.63	0.08

TABLE 6. NORMALIZED CONCENTRATIONS OF FERRIC IRON, TOTAL MANGANESE AND NAIP FOR CORES 5 AND 6

Core Section	Core 5			Core 6		
cm	Fe^{3+} wt.%	NAIP wt.%	Mn wt.%	Fe^{3+} wt.%	NAIP wt.%	Mn wt.%
0-1	1.90	0.090	0.77	2.00	0.051	0.61
1-2	1.64	0.086	0.34	1.69	0.053	0.39
2-3	1.39	0.068	0.19	1.52	0.040	0.14
3-4	1.39	0.047		1.48	0.031	
4-5	1.35	0.056	0.14	10.6*	1.83	1.73
5-6	1.40	0.040	0.20		0.013	
6-7	1.36	0.045		1.19	0.012	
7-8	1.57*	0.109		1.22	0.012	0.08
8-9	1.19	0.025			~0.012	
9-10	1.27	0.071	0.15	1.29		
10-11	1.42	0.040			~0.012	
11-12	1.42	0.027		1.15	0.021	0.09
12-13	1.26	0.019		1.55*	0.224	0.22
13-14	1.03	0.019			~0.06	
18-19				1.06	0.013	0.05
21-22	0.92					
22-23	1.38*	0.267				
25-26				1.32	0.016	

*denotes primary red or secondary Fe^{3+}-P layers. Includes data from Manning (1986).

TABLE 7. CONCENTRATIONS OF IRON, MANGANESE AND PHOSPHORUS IN A CORE FROM LAKE ERIE

Section cm	Fe^{2+} wt.%	Fe^{3+} wt.%	Fe^{3+}_{norm} wt.%	NAIP wt.%	$NAIP_{norm}$ wt.%	Mn_T wt.%
0-1	2.007	2.46	2.46	0.092	0.092	0.08
1-2	1.984	1.88	1.90	0.044	0.045	0.05
2-3	2.050	1.84	1.80	0.052	0.051	0.05
3-4	2.118	1.88	1.78	0.052	0.049	
4-5	2.148	1.85	1.73	0.045	0.042	
5-6	2.172	1.83	1.69	0.044	0.041	
6-7	2.260	1.88	1.67	0.063	0.056	0.07
7-8	2.215	1.93	1.74			
8-9	2.202	1.94	1.77			
9-10	2.140	2.00	1.88	0.045	0.042	
10-11	2.132	2.01	1.89			
11-12	2.132	2.01	1.89			
12-13	2.169	1.93	1.79	0.033	0.031	0.05
13-14	2.148	1.95	1.82			
14-15	2.243	1.86	1.66			
15-16	2.286	1.81	1.59			
16-17	2.247	1.85	1.65			
17-18	2.255	1.85	1.64	0.013	0.012	

binding capacity of the surficial sediments since 1980. This probably reflects improved oxic conditions in, and lower input of organic matter to, the sediments as a consequence of reductions in phosphorus loading (Great Lakes Water Quality Board, 1983). However, redox potentials have not increased sufficiently to precipitate Mn ions (Table 7).

The 16 to 17 cm and 17 to 18 cm sections of core 1 were earmarked, on sectioning, for study because of their intense blackness; these sections are clearly sites of secondary Fe^{3+}–P precipitation (Table 3, Fig. 3). Therefore, black layers do not correspond to periods of heavy deposition of organic matter and consequent strongly reducing conditions (Berner 1971). Black coatings of FeS on suspended ferric oxide particles have been observed by Davison & Dickson (1984), who suggested that the FeS prevented further reduction of the oxide.

The formation of the layers may be related to current flow patterns in Lake Ontario (Fig. 4) (Pickett 1977, Pickett & Bermick 1977). The ~200 km² area lies on the western edge of the main gyres. The suspended load of the Niagara River flows mainly eastward and is deposited in the eastern basins (Kemp & Harper 1976). The presence of ferromanganese nodules and coated sands along the north shore of Lake Ontario (Cronan & Thomas 1972, Sly & Thomas 1974) suggests that regeneration of iron and phosphorus occurs in the eastern basins, reflecting the relatively high rates of sedimentation and lower surficial redox potentials. The regenerated iron, car-

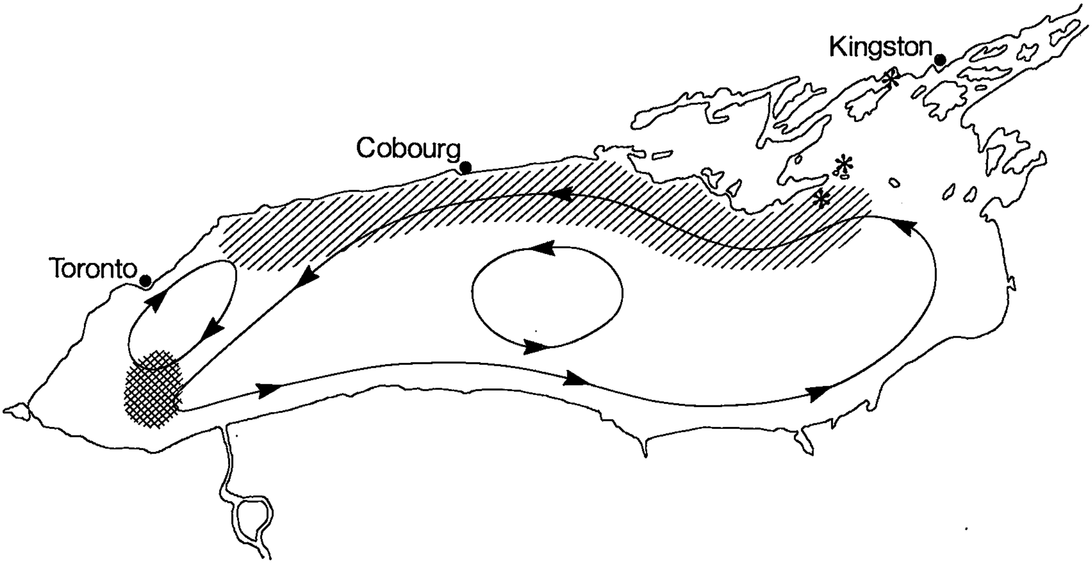

FIG. 4. Diagram depicting main pattern of water flow in Lake Ontario (after Pickett 1977, Pickett & Bermick 1977). Hatched area represents extensive beds of ferromanganese-coated sands. Asterisks mark occurrences of ferromanganese nodules (Cronan & Thomas 1972). Thatched circle shows the ~200-km^2 area of the primary red layer.

ried by currents along the main gyre, flows westward along the north shore, and some is precipitated in the Niagara Basin. Moreover, the area encompassed by the sediment layers lies at the western extremity of the main gyre (Fig. 4); consequently, rates of sedimentation may be variable. Crystallization of surficial ferric hydroxides to ferrihydrite would be promoted by a period of low rates of sedimentation, during which the input of organic matter and of other adsorbing ions would be reduced.

The primary red layers are overlain by ~70 years (or ~8 cm) of continuous deposition (Manning *et al.* 1985). The similar Fe^{3+} and NAIP values for both the upper and lower secondary layers (Tables 3, 4, Fig. 3) indicate that most of the phosphorus is retained within the layers for at least 15 to 20 cm burial, *i.e.*, for more than 150 years (Kemp & Harper 1976, Manning *et al.* 1985). The 5- to 8-cm separations of the secondary layers suggest that, if layer formation is periodic, another layer will form at or near the sediment–water interface in the next few decades. Presumably, the primary red layer will be equally persistent in the anoxic zone. A black layer of FeS has not yet formed as it has with, for example, the 16 to 17 cm and 17 to 18 cm sections of core 1 and the 13 to 14 cm section of core 2 (Table 3); hence sulfide production and reducing conditions are not well developed. Moreover, the thin black laminations observed (Kemp 1969) at greater depths, 30 to 50 cm, may be remnants of layers formed several hundred years ago. Hence, primary and secondary layers have half-lives of hundreds of years.

If the muds containing the secondary layers occur as a band 5 km wide (indicated by core sampling) surrounding the ~200 km^2 area and extending over an arc of 180°, then the area of the band is ~160 km^2 and that of the total layered area is ~360 km^2. A secondary layer containing 0.25% NAIP (Tables 3, 4) over 360 km^2 binds ~5000 tonnes P, whereas the primary red layer in the ~200 km^2 area binds >20000 tonnes P. The total amount of phosphorus contained within the two upper layers, primary and secondary, exceeds 30000 tonnes, which compares with annual binding-capacities of phosphorus for the Niagara Basin and for Lake Ontario of 600 tonnes and 3500 tonnes, respectively (Manning 1987). The rate of accumulation of phosphorus by a secondary layer, assuming a ~100-year periodicity, is clearly small (8000 tonnes per 100 years). An input of 80 tonnes P annually would sustain ~0.5 $\mu g\ L^{-1}$ P over the whole lake, compared to current values of ~10 $\mu g\ L^{-1}$ (Great Lakes Water Quality Board, 1983).

Nevertheless, the layers are important indicators of the health of a basin, because oxic conditions at the sediment–water interface are sufficiently intense and prolonged in time to permit crystallization of an oxide such as ferrihydrite. Ferrihydrite is precipitated in surface springwater when percolating groundwaters meet an oxidizing horizon (Coey & Readman 1973, Schwertmann & Fischer 1973). On the other hand, higher organic sedimentation and anoxic conditions could lead to rapid dissolution of the upper layers, causing massive release of phosphorus.

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REFERENCES

AGEMIAN, H. & CHAU, A.S.Y. (1975): An atomic absorption method for the determination of twenty elements in lake sediments after acid digestion. *Anal. Chim. Acta* **80**, 61-66.

BERNER, R.A. (1971): *Principles of Chemical Sedimentology.* McGraw-Hill, New York, N.Y.

BURNS, N.M. & ROSS, C. (1972): Project Hypo: an intensive study of the Lake Erie Central Basin hypolimnion and related surface water phenomena. *Can. Centre Inland Waters, Pap.* **6**, *U.S. Environ. Prot. Agency Tech. Rep.* **TS-05-71-208-24.**

COEY, J.M.D. & READMAN, P.W. (1973): Characterization and magnetic properties of natural ferric gel. *Earth Planet. Sci. Lett.* **21**, 45-51.

______, SCHINDLER, D.W. & WEBER, F. (1974): Iron compounds in lake sediments. *Can. J. Earth Sci.* **11**, 1489-1493.

CRONAN, D.S. & THOMAS, R.L. (1972): Geochemistry of ferromanganese oxide concretions and associated deposits in Lake Ontario. *Geol. Soc. Amer. Bull.* **83**, 1493-1502.

DAVISON, W. & DICKSON, D.P.E. (1984): Mössbauer spectroscopic and chemical studies of particulate iron material from a seasonally anoxic lake. *Chem. Geol.* **42**, 177-187.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals. 3. Sheet Silicates.* Longman, London.

DESJARDINS, J.G. (1978): Acid dissolution. *In* Manual on Soil Sampling and Methods of Analysis (J.A. McKeague, ed.). Can. Soc. Soil Sci., Ottawa, Ontario.

DURHAM, R.W. & OLIVER, B.G. (1983): History of Lake Ontario contamination from the Niagara River by sediment-radiodating and chlorinated hydrocarbon analysis. *J. Great Lakes Res.* **9**, 160-168.

GREAT LAKES WATER QUALITY BOARD (1983): Report on Great Lakes Water Quality. Appendix: Great Lakes Surveillance. Int. Joint Commission, Windsor, Ontario.

KEMP, A.L.W. (1969): Organic matter in the sediments of Lakes Ontario and Erie. *Proc. Conf. Great Lakes Res.* **12**, 237-249.

______ & HARPER, N.S. (1976): Sedimentation rates and a sediment budget for Lake Ontario. *J. Great Lakes Res.* **2**, 324-340.

______ & THOMAS, R.L. (1976): Impact of man's activities on the chemical composition in the sediments of Lakes Ontario, Erie and Huron. *Water, Air, Soil Poll.* **5**, 469-490.

______, ______, DELL, C.I. & JAQUET, J.M. (1976): Cultural impact on the geochemistry of sediments in Lake Erie. *J. Fish. Res. Board Can.* **33**, 440-462.

MANNING, P.G. (1987): Phosphate ion interactions at the sediment–water interface in Lake Ontario: relationship to sediment adsorption capacities. *J. Fish. Aquat. Sci.* (in press).

______, BIRCHALL, T. & JONES, W. (1984): The partitioning of non-apatite inorganic phosphorus in sediments from Lakes Erie and Ontario. *Can. Mineral.* **22**, 357-365.

______, LUM, K.R., WONG, H.K.T. & BIRCHALL, T. (1985): Origin and age of ferrihydrite layers in Lake Ontario sediments. *Can. Mineral.* **23**, 103-110.

MURAD, E. & SCHWERTMANN, U. (1980): The Mössbauer spectrum of ferrihydrite and its relations to those of other iron oxides. *Amer. Mineral.* **65**, 1044-1049.

NRIAGU, J.O. (1978): Dissolved silica in pore waters of Lakes Ontario, Erie, and Superior sediments. *Limnol. Oceanogr.* **23**, 53-67.

PICKETT, R.L. (1977): The observed winter circulation of Lake Ontario. *J. Phys. Oceanogr.* **7**, 152-156.

______ & BERMICK, S. (1977): Observed resultant circulation of Lake Ontario. *Limnol. Oceanogr.* **22**, 1071-1075.

READMAN, P.W., COEY, J.M.D., MOSER, C. & WEBER, F. (1976): Analysis of some lake sediments from Greece. *J. Phys. (Paris)* **37** (Colloq. 6), 845-848.

SCHWERTMANN, U. & FISCHER, W.R. (1973): Natural "amorphous" ferric hydroxide. *Geoderma* **10**, 237-247.

SLY, P.G. & THOMAS, R.L. (1974): Review of geological research as it relates to an understanding of Great Lakes limnology. *J. Fish. Res. Board Can.* **31**, 795-825.

WILLIAMS, J.D.H., JAQUET, J.-M. & THOMAS, R.L. (1976): Forms of phosphorus in the surficial sediments of Lake Erie. *J. Fish. Res. Board Can.* **33**, 413-429.

______, SHEAR, H. & THOMAS, R.L. (1980): Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materials from the Great Lakes. *Limnol. Oceanogr.* **25**, 1-11.

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