

## ORIGIN AND AGE OF THE FERRIHYDRITE LAYER IN LAKE ONTARIO SEDIMENTS

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### ABSTRACT

Lead-210 dating, chemical extraction and Mössbauer spectral methods have been used to study the age and origin of an iron- and phosphorus-rich crusty red layer in sediment cores retrieved from the Niagara Basin of Lake Ontario. Immediately overlying the ~0.5-cm-thick red layer is a thin Mn-rich black layer. The results suggest that the layer formed ~65 years ago at the sediment-water interface during a brief period (a few years) of very low sedimentation, permitting crystallization of brown surficial ferric hydroxides to red ferrihydrite. There is no loss of adsorbed P on crystallization. The red layer invariably overlies 3 to 4 cm of very light grey  $\text{Fe}^{3+}$ - and P-deficient muds. The cores depict three Eh regimes upon deposition: (i) the last ~65 years of continuous deposition of well-oxidized muds, (ii) a few years of very low sedimentation corresponding to high surficial Eh and formation of the red layer, and (iii) the pre-red-layer period of more strongly reduced muds featuring significant reduction of ferric ions bonded to clays and in amorphous ferric aluminosilicates. Production of organic matter has presumably decreased since pre-red-layer times, suggesting an improved trophic status in the Niagara Basin.

*Keywords:* sediments, Lake Ontario, red layer, ferrihydrite, dating.

### SOMMAIRE

Trois méthodes, datation au plomb-210, extraction chimique et analyse par spectroscopie Mössbauer, ont été utilisées pour déterminer l'âge et l'origine de la couche rouge riche en fer et en phosphore, qui se présente sous forme de croûte dans des carottes de sédiments prélevées dans le bassin de Niagara du lac Ontario. La couche rouge, épaisse d'environ 0.5 cm, est recouverte d'une mince couche noire riche en manganèse. Les analyses font penser que la couche s'est formée il y a environ 65 ans à l'interface sédiments-eau pendant une brève période (quelques années) de très faible sédimentation, ce qui a permis la cristallisation d'hydroxydes ferriques bruns de surface pour former de la latérite ferrugineuse. Il n'y a pas eu de perte de P adsorbé lors de la cristallisation. La couche rouge recouvre invariablement des boues, pauvres en P et en  $\text{Fe}^{3+}$ , de couleur gris très clair. Les carottes révèlent trois régimes Eh lors du dépôt: (i) période correspondant aux 65 dernières années environ, au cours de laquelle il y a eu dépôt de boues bien oxydées; (ii) quelques années de sédimentation très faible correspondant à un haut potentiel réduction-oxydation (Eh) de surface et à la formation d'une couche rouge; et (iii)

période précédant la formation de la couche rouge, caractérisée par une forte réduction des ions ferriques liés à des argiles et à des aluminosilicates ferriques amorphes. La production de matières organiques a probablement diminué depuis la période antérieure à la formation de la couche rouge, ce qui indiquerait un état trophique amélioré dans le bassin de Niagara.

*Mot-clés:* sédiments, lac Ontario, couche rouge, latérite ferrugineuse, datation.

### INTRODUCTION

Stones and rocks in streams and lakes commonly are coated with a ferromanganese crust (Ljunggren 1953, Landergren 1948, Gorham & Swaine 1965). Gorham & Swaine (1965) attributed crust formation to a low rate of sedimentation and a continuous supply of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions to an unchanging high-Eh sediment-water interface, e.g., where modern sediments are thin or absent above basal glacial deposits. On this basis, Nussman (1965) attributed the Mn-rich yellow-brown crust in Lake Superior sediments to a period of low sedimentation; he observed no iron enrichment. Nevertheless, Fe- and Mn-rich layer does occur extensively in Lake Superior muds (Sly & Thomas 1974).

A 0.2- to 1-cm-thick red Fe- and P-rich layer is present in silty clay sediments covering ~100 km<sup>2</sup> of the bottom of the Niagara Basin of Lake Ontario (Manning *et al.* 1983, Sly & Thomas 1974). The red layer lies beneath a much thinner black Mn-rich layer; it also overlies, invariably from our sectioning of over a dozen red-layer cores, 3 to 4 cm of very light grey mud. The origins of the black, red and very light grey layers are clearly interrelated. The red oxide in an earlier core has Mössbauer parameters (Manning *et al.* 1983) and a particle-size distribution indicative of ferrihydrite  $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ , which is precipitated when percolating groundwaters meet an oxygen-rich horizon, e.g., in drainage ditches, freshwater springs and podzol B soil horizons (Coe & Readman 1973, Murad & Schwertmann 1980). A single red layer is present in each Niagara Basin core, hence its origin is related to a single event since the recession of the glaciers ~10000 years B.P.

In this article, we describe data on Mössbauer

TABLE 1. CONCENTRATIONS (WT%) OF IRON, PHOSPHORUS MANGANESE AND Mn IN SEDIMENT CORE RETRIEVED 27 JULY 82

Section cm	Color	Fe total	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>3+</sup> norm	Mn total	Mn norm	P total	P norm	NAIP total	Mg norm	Al norm	Si norm
0-1	brown	3.81	1.48	2.06	2.06	0.63	0.63	0.16	0.16	0.07			
1-2	brown	3.89	1.65	1.96	1.76	0.25	0.23	0.17	0.15		2.13	5.79	15.3
2-3	olive/grey	3.78	1.84	1.68	1.35	0.17	0.14	0.16	0.13				
3-4	dark grey	4.08	1.91	1.89	1.46	0.15	0.12	0.14	0.11	0.04			
6-7	dark grey	4.15	1.99	1.87	1.39	0.10	0.08	0.11	0.08		1.72	5.39	17.0
8-9	light grey	4.48	2.11	2.06	1.44	0.10	0.07	0.10	0.07				
10-17	sandy brown	-	-	-	-	-	-	-	0.04				
17-17.2	red crust	8.81	1.70	6.49	5.66	0.72	0.63	0.61	0.53	0.52	1.46	5.02	17.9
17-18	red cake	7.90	1.56	5.79	5.50	0.33	0.47	0.49	0.31	0.47			
20-21	very light grey	3.59	1.90	1.44	1.12	0.05	0.04	0.09	0.07		1.76	6.04	17.6
41-42	light grey	3.92	1.23	1.42	0.94	0.09	0.06	0.08	0.05	0.01	2.10	4.93	13.2

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> contains % of total Fe. A thin black Mn-rich layer overlies the red crust but it could not be isolated. The 17-to-17.2 cm red crust is texturally harder than the red cake. Very light grey sediment lies immediately beneath the red cake. Normalized concentrations are represented by norm.

TABLE 2. TOTAL ELEMENTAL CONCENTRATIONS IN SEDIMENT CORE RETRIEVED 7 JULY 1982

Section cm	Color	Fe wt. %	Al wt. %	Mn wt. %	P wt. %	Pb $\mu\text{g q}^{-1}$	Ca wt. %	P extract* wt. %
0-1	brown	4.90	8.68	1.08	0.14	175	13.7	0.02
1-2	brown	4.90	8.17	0.80	0.15	164	12.9	0.02
2-3	grey	4.54	9.02	0.64	0.14	178	9.2	0.02
3-4	grey	5.43	8.67	0.49	0.09	164	4.3	0.02
4-5	brown/grey	5.05	8.52	0.31	0.13	137	2.0	0.03
5-6	mixture red +	5.96	9.72	0.86		54	1.5	0.08
6-7	black, gritty	4.88	8.31	2.94	0.11	35	1.1	0.04
7-8	red layer	11.50	3.67	1.33	1.48	14	2.0	0.15
8-9	very light grey	2.89	4.58	0.11	0.09	23	0.9	0.04
9-10	very light grey	4.62	10.04	0.10	0.08	28	0.8	0.03
10-11	very light grey	4.22	8.75	0.10	0.08	25	0.9	0.02
11-12	dark	5.07	9.79	0.21		31	0.8	0.03
12-13	mottled dark	5.21	8.59	0.20	0.08	67	0.9	0.01
13-14	and light	6.10	9.35	0.09	0.08	22	0.7	0.02

\* Phosphorus extractable by a modified method of Tessier *et al.* (1977).

TABLE 3. TOTAL ELEMENTAL CONCENTRATIONS IN CORE RETRIEVED 26 OCTOBER 1982

Section cm	Color	Fe wt. %	Mn wt. %	P wt. %
0-1	brown	3.80	0.61	0.14
1-2	brown/grey	3.70	0.42	0.15
2-3	grey	3.88	0.17	0.13
4.0-4.5	red layer	13.9	1.95	1.88*
4.5-5.0	red	nd	nd	1.83
5-8	very light grey	3.77	0.10	0.08
11-12	light grey	3.89	0.12	0.13
12-13	dark grey	5.49	0.36	0.64
14-15	light grey	3.58	0.07	0.14
14-15	dark grey	4.57	0.10	0.08
18-19	light grey	3.82	0.07	0.09

n.d. = not determined.

\* Contains 1.83% non-apatite inorganic phosphorus.

spectra, <sup>210</sup>Pb dating and chemical composition for a sediment core retrieved from the Niagara Basin on 27 July 1982 (from 43°18.10'N, 79°20.00'W; beneath 85 m water, and overlying ~ 3 m of post-glacial sediment). Supportive data are presented for three other cores retrieved on 7 July 1982 and 7 August 1983 (both from 43°22.50'N 79°20.00'W; 99 m, ~ 4 m) and on 26 October 1982 (from 43°24.00'N 79°20.00'W; 106 m, 5 m). The three locations are approximately 11 km apart. Comparative Mössbauer and analytical data are available for an earlier core (Manning *et al.* 1983); clay concen-

trations in this core are very erratic, making interpretation difficult. Sectional color properties of the cores are listed in Tables 1 to 3.

The aims of this work are to better define (a) the age and conditions of crust formation and (b) ferric iron - phosphate ionic interactions in sediments. The highly oxidized layer represents an important barrier to the release of phosphorus into the overlying waters. Thus it influences the bioavailability of phosphorus.

## EXPERIMENTAL DETAILS

Methods of retrieval, sectioning and processing of sediment cores have been described earlier (Manning *et al.* 1981, 1983). Mössbauer spectra of freeze-dried sections of the 27 July 1982 core have been recorded and computer-fitted following earlier methods (Manning *et al.* 1981, 1983). Area ratios and half widths within a quadrupole doublet were constrained to be equal. Chi-squared values and visual examination of whole spectra were used as criteria of goodness of fit.

The cores were dated using the <sup>210</sup>Pb method (Robbins & Edgington 1975, Matsumoto 1975, Nriagu *et al.* 1979). Approximately 2 g of dry sediment and 10 mL of aqua regia were heated for two hours at 95 ± 5°C. The mixture was cooled, and 5 mL of perchloric acid added. The mixture was heated, cooled, filtered and evaporated to near dryness. Ten mL of concentrated HCl were added, and the solution evaporated to near-dryness; this step was repeated three times to eliminate the nitrate ion. The residues were dissolved in dilute HCl, and calculated amounts of ascorbic acid were added to bind the ferric iron. The solution was adjusted to pH 1.4 and then transferred to polythene bottles for plating on a silver disk. Alpha activity was monitored using a NMC-2 proportional counter. Dates were estimated

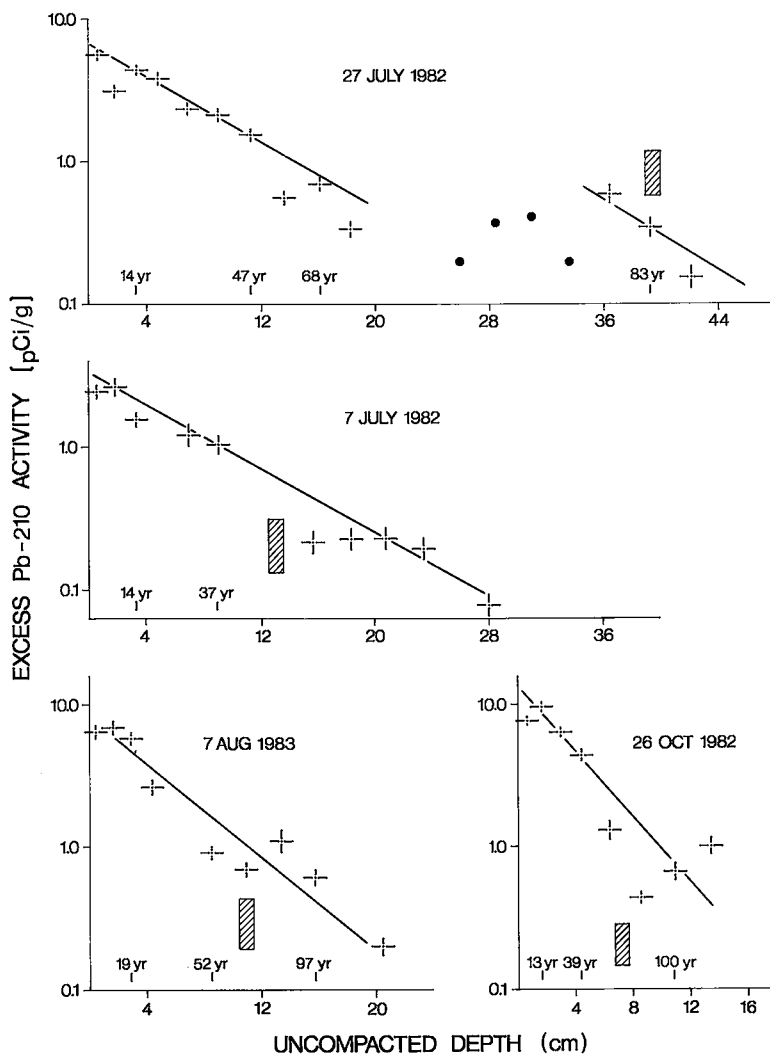


FIG. 1. Plots of excess Pb-210 activity versus uncompact sediment depth for four layered Niagara Basin cores. Hatched area represents depth of red layer. Filled circles are in the zone of foreign materials.

assuming that the concentration of unsupported  $^{210}\text{Pb}$  in the depositing material is constant with time (Nriagu *et al.* 1979). The supported  $^{210}\text{Pb}$  activities were taken as the measured background-activities ( $= 0.4 \text{ pCi g}^{-1}$ ) for the Niagara Basin.

Concentration of excess  $^{210}\text{Pb}$  activity is plotted against sediment depth in Figure 1. The  $^{210}\text{Pb}$  profile for the 27 July 1982 core shows an obvious discontinuity coincident with the appearance of the sandy, brown, 9- to 17-cm portion of the core. Presumably, soon after its formation, the red layer was covered rapidly by the  $\sim 8$  cm of dredged material or by underwater slump. The excision of

this sandy section of the core from the plot (Fig. 1) indicates that the red layer is overlain by  $\sim 83$  years of silty clay deposition, in reasonable agreement with the ages ( $\sim 53$ ,  $\sim 60$  and  $\sim 70$  years) measured for the other cores. Formation of the red layer in all cores was probably concurrent and occurred  $65 \pm 15$  years ago. The plots (Fig. 1) further suggest that the layers were formed over a short period of a few years.

Sequential extractions of phosphorus were performed on the 7 July 1982 core using slight modifications of the method of Tessier *et al.* (1979), namely: (1) extraction by a 0.75 M LiCl + 0.25 M

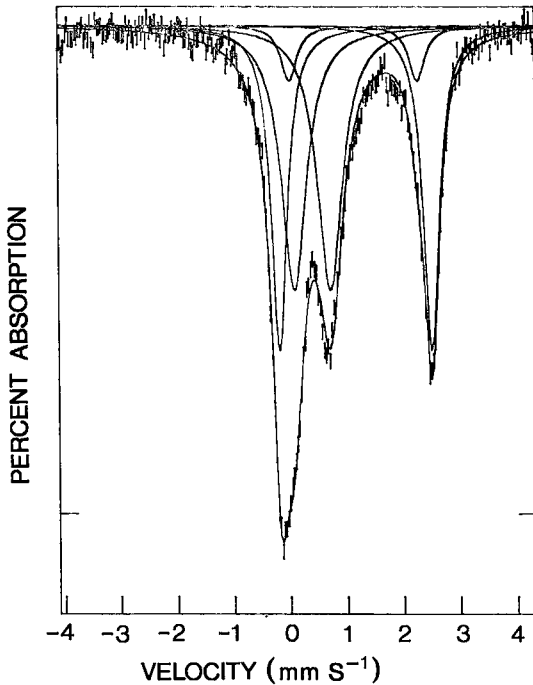


FIG. 2. Mössbauer spectrum of 1- to 2-cm section of Niagara Basin core, recorded at room temperature. Individually computed peaks and final envelope are presented as continuous lines. Chi-squared is 680 with 500 degrees of freedom.

CsCl mixture in 60% CH<sub>3</sub>OH, for readily exchangeable ions; (ii) extraction by NaOAc followed by 0.1 M NH<sub>2</sub>OH·HCl in 0.01 M HNO<sub>3</sub>, for ions associated with Mn oxides; (iii) extraction by 1 M NH<sub>2</sub>OH·HCl in 25% acetic acid, for ions associated with iron and manganese oxides; (iv) extraction by 0.1 M sodium pyrophosphate, for labile associations of organic matter. Concentrations of extractable P listed in Table 2 refer to steps (i), (ii) and (iii). The modifications are intended as an aid to improved selectivity (Lum & Edgar 1983).

Concentrations of non-apatite inorganic phosphorus were measured in selected sections by sequential extraction with dithionite-citrate-bicarbonate and 0.1 M NaOH reagents (Williams *et al.* 1976).

## RESULTS AND DISCUSSION

### Mössbauer spectra

The room-temperature Mössbauer spectrum of the 1- to 2-cm-sediment residual (Fig. 2) is representative, qualitatively, of all sections of the 27 July 1982 core, showing in the range of +4 to -4 mm s<sup>-1</sup> the major quadrupole doublets marking Fe<sup>2+</sup> in chlo-

rite (outer doublet) and Fe<sup>3+</sup> ions in silicates and in amorphous hydrated oxides a (broadened innermost doublet) (Manning *et al.* 1981, Manning & Jones 1982). The ferric-ion envelope comprises absorptions of (a) brown Eh-sensitive "ferric hydroxide" in the oxidized surface-layer and (b) ferric ions that are present in the oxidized and reduced zones of sediments (Manning *et al.* 1981, Manning & Jones 1982). The concentration of Fe<sup>3+</sup> ions in (b) is strongly correlated with clay concentration (Manning *et al.* 1984), the principal forms being ferric ions in clay lattices, ferric ions in hydrated oxides coating clay surfaces, and ferric ions in amorphous aluminosilicates formed surficially from the coprecipitation of brown "ferric hydroxide", hydrated silica and hydrated alumina (Nriagu 1978).

A weak Fe<sup>2+</sup> doublet, marking Fe<sup>2+</sup> ions in the second octahedral layer in chlorite, is easily resolved in all spectra (Fig. 2) except in that of the high-Fe<sup>3+</sup> red layer. Spectra recorded over a wide range of energy display additional peaks of magnetically ordered well-crystallized hematite (α-Fe<sub>2</sub>O<sub>3</sub>), the two weak innermost peaks of the six-line pattern being obscured by the major Fe<sup>2+</sup> and Fe<sup>3+</sup> absorptions (Manning *et al.* 1983). Computation of spectra showed ~7% total iron contained in each of hematite and the minor Fe<sup>2+</sup> ion. Calculated Mössbauer spectral parameters and ferrous and ferric iron concentrations are listed in Table 4.

The Mössbauer spectra of the 0- to 1-cm section and of the red layer (17 to 17.2 cm), recorded at 4 K, show prominent broad six-line magnetic patterns (Figs. 3, 4). Approximately 50% of total Fe in the top cm and ~85% of total Fe in the red layer are magnetically ordered at 4 K (Table 4). In the 23 July 1981 core (Manning *et al.* 1983), the iron in the 0- to 1-cm section remains paramagnetic at 4 K. Calculated Mössbauer parameters for the magnetically ordered oxides are listed in Table 4. The relatively high value of the ferric ion quadrupole splitting at 298 K, the value of the hyperfine field (~460 kOe) at 4 K and the temperature dependence of ordering suggest that the oxide in the red layer is ferrihydrite 5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O (Coe & Readman 1973, Murad & Schwertmann 1980, Manning *et al.* 1983).

TABLE 4. MOSSBAUER PARAMETERS MEASURED FOR IONS IN LAKE ONTARIO SEDIMENT

Temp.	Ion	IS mm s <sup>-1</sup>	QS mm s <sup>-2</sup>	HW mm s <sup>-1</sup>	H kOe
298 K	Fe <sup>2+</sup> , major	1.11	2.65	0.36	
298 K	Fe <sup>2+</sup> , minor	1.00	2.20	0.37	
298 K	Fe <sup>3+</sup>	0.38	0.62	0.53	
298 K	Fe <sup>3+</sup> , red oxide	0.38	0.75	0.52	
4 K	Magn. Oxide (0-1 cm sect.)	0.30	-	>0.71	485
4 K	Magn. Oxide (17-17.2 cm sect.)	0.29	-	>0.96	463

IS = isomer shift, relative to Fe foil. QS = quadrupole splitting. HW = half width. All values ±0.02 mm s<sup>-1</sup>. Fe<sup>2+</sup> (major):Fe<sup>2+</sup> (minor) ~7. α-Fe<sub>2</sub>O<sub>3</sub> contains ~7% of total Fe. H = 458 kOe for red layer oxide in 23 July 1981 core.

### Iron profiles

Ferrous ion concentrations increase with increasing depth of burial over the top 9 cm of the 27 July 1982 core (Table 1), reflecting loss of calcium carbonate and organic matter (Kemp & Thomas 1976, Manning & Jones 1982). The normalization of the concentrations of  $\text{Fe}^{3+}$  ion over the top 9 cm (Table 1), using  $\text{Fe}^{2+}$  concentrations as conservative indicators (Manning & Jones 1982), demonstrates the surficial enrichment in Eh-sensitive  $\text{Fe}^{3+}$  ion of 0.65%, i.e., 2.06% minus 1.41%, where 1.41%  $\text{Fe}^{3+}$  is the mean of ferric ion concentrations from 2 to 9 cm depth; this enrichment agrees well with those measured for nonlayered cores (Manning & Jones 1982, Manning *et al.* 1984). Moreover, concentrations of non-apatite inorganic P are consistent with the magnitude of this enrichment in  $\text{Fe}^{3+}$  ion and also with total concentrations of P (Table 1; Manning & Jones 1982, Manning *et al.* 1984). Trends in the concentrations of total Ca, Pb, Al and Mn, above the red and black layers, are very similar to those in non-layered cores (Tables 1 to 3; Kemp & Thomas 1976, Manning *et al.* 1983, 1984). Compositionally, deposition since layer formation has been representative of the Niagara Basin and of most of Lake Ontario.

The sediment immediately underlying the red layers in the present core (and in several others) is invariably a uniform very light grey, in marked contrast to the mottled grey of reduced muds in Lakes Ontario and Erie. Concentrations of  $\text{Fe}^{3+}$  ions are significantly reduced in the very light grey zones of the 23 July 1981 (Manning *et al.* 1983) and 27 July 1982 (Table 1) cores, whereas Al is impoverished in the 23 July 1981 core (Manning *et al.* 1983). Also, total Al and total Fe concentrations are relatively low beneath the red layer in the 7 July 1982 core (Table 2). It is, therefore, likely that a high proportion of the  $\text{Fe}^{3+}$ , Mn, P and Al ions concentrated in the red and the black layers is derived from the reduction of illite and amorphous ferric aluminosilicates in the very light grey zone, with consequent upward mobilization to, and precipitation at, the oxic horizon. The magnitude of losses of the  $\text{Fe}^{3+}$  ion over 3 to 4 cm of the very light grey zone and of the Fe concentrations in the ~0.5-cm-thick red layer are consistent (Table 1).

However, the release of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  from clay lattices and aluminosilicates is not considered a common process in Great Lakes sediments; Al is often used as a conservative element for procedures of normalization of concentration (Kemp *et al.* 1976, Kemp & Thomas 1976). Approximately 20% of the  $\text{Fe}^{3+}$  ion is lost in the reduced zone of cores from an area of high sedimentation of Lake Ontario and from the Rochester Basin of Lake Ontario (Cores 6 and 8, Manning *et al.* 1984). Mostly, however, Lake

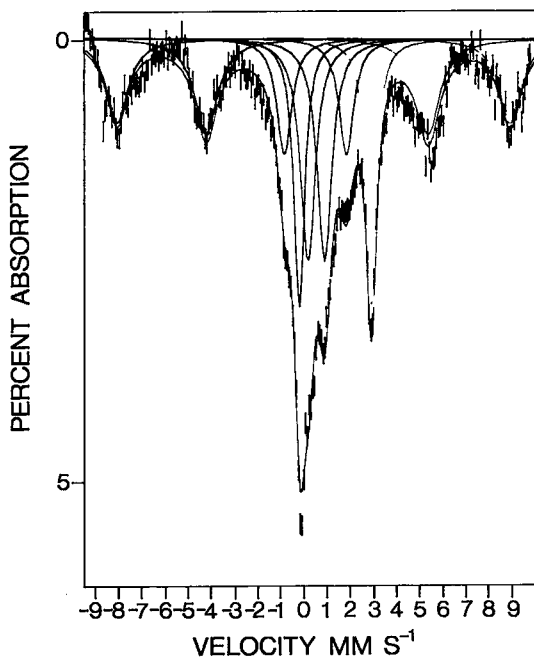


FIG. 3. Mössbauer spectrum of 0- to 1-cm section of 27 July 1982 core recorded at 4 K. Continuous lines represent individually computed peaks and final overall fit; 50% of total Fe is magnetically ordered.

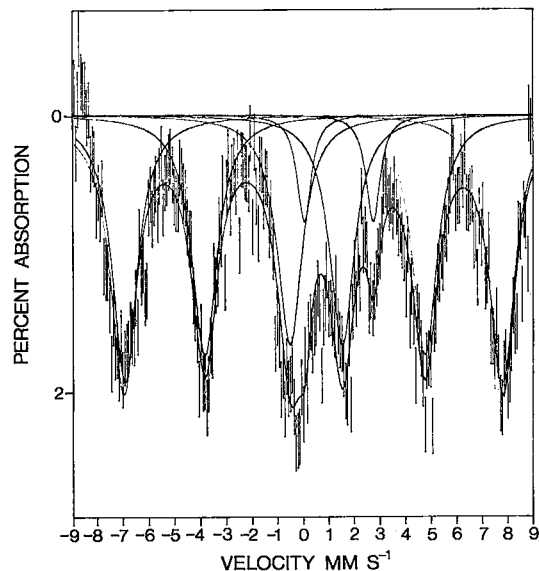


FIG. 4. Mössbauer spectrum of red layer (17 to 17.2 cm) section of 27 July 1982 core recorded at 4 K. Continuous lines represent computed peaks and overall fit; 85% of total Fe is magnetically ordered.

Ontario cores display little or no loss of  $\text{Fe}^{3+}$  ion in the reduced zone (Manning *et al.* 1981, 1984, Manning & Jones 1982). Abstraction of ferric ions from clay lattices can occur in anoxic marine sediments by reaction with sulfide ion (Drever 1971), Mg ions reoccupying the vacant sites. Significantly, Mg concentrations are elevated beneath the red layer in the 27 July 1982 core (Table 1). Ferric ions are completely removed from clay sites in anoxic sulfide-rich Lake St. George sediments (Manning *et al.* 1979). Elevated concentrations of sulfide are derived from the metabolism of organic matter by sulfate-reducing bacteria. Consequently, the abstraction of  $\text{Fe}^{3+}$  and Al ions from illite in these very light grey zones reflects past conditions of sediment anoxia, enhanced possibly by sulfide production. The absence of black ferrous sulfides as a remnant of sulfide formation is, however, puzzling; light grey to black mottling is characteristic of reduced Lake Ontario muds.

#### *Phosphorus profiles*

Phosphorus concentrations are considerably elevated in all the red layers (Tables 1 to 3) but are insignificantly elevated in the black Mn-rich layers (Table 2; Manning *et al.* 1983). The enrichment in normalized concentrations of P in the red layer in the 27 July 1982 core (Table 1) is 0.53 minus 0.07% P, or 0.46% P; the  $\text{Fe}^{3+}$  ion enrichment is 5.66 minus 1.41%  $\text{Fe}^{3+}$ , or 4.25%  $\text{Fe}^{3+}$ . Hence, the  $\text{Fe}^{3+}$  in the oxide of the red layer adsorbs ~11% of its weight of P, in reasonable agreement with the value of ~7% measured for the 23 July 1981 core (Manning *et al.* 1983) and with the ~8% measured for brown surficial Eh-sensitive "ferric hydroxide" (Manning & Jones 1982, Manning *et al.* 1984), averaged over seven cores.

Phosphorus is particularly abundant in the red layers of the 7 July 1982 and 26 October 1982 cores (Tables 2, 3), in marked contrast to the low values of P measured in the overlying Mn-rich layer. Hence, phosphorus is strongly associated with ferric ion in the red layer (Tables 1 to 3; Manning *et al.* 1983). Minor amounts of phosphorus are extracted by the method of Tessier *et al.* (1979) (Table 2; Manning *et al.* 1983) from both the brown surficial Eh-sensitive "ferric hydroxide" and the red layer. Hence, the value of the method in assessing crystalline and amorphous forms of P must be questioned. In contrast, almost all the P contained in the red oxide and in the "ferric hydroxide" is non-apatite inorganic P and extractable using the dithionite-citrate-bicarbonate reagent (Tables 1, 3).

#### *Mn profiles*

Mn concentrations are elevated in the oxidized surface-layer (Tables 1 to 3; Manning *et al.* 1983),

beneath which concentrations steadily decrease until the sharp increase at the black layer is attained (Table 2; Manning *et al.* 1983). Above the black horizon the Mn profiles are those expected for Lake Ontario muds (Kemp & Thomas 1976). The dramatic concentration of Mn in the very thin black layer attests to an intense redox gradient and quiescent conditions at the time of precipitation. Mn concentrations are at, or below, background levels in the very light grey layer.

#### *Origin of the red layer*

Redox processes are strongly implicated in the formation of the red layers. Firstly, ferrihydrite is precipitated naturally as a reddish stain when percolating groundwaters containing ferrous ions and organic matter meet an oxygen-rich environment, *e.g.*, in freshwater springs and in drainage ditches (Coe & Readman 1973, Schwertmann & Taylor 1977, Schwertmann & Fischer 1973, Murray 1979). The restriction of brown surficial Eh-sensitive ferric ion to the oxidized surface-layer (Table 1; Manning *et al.* 1983) indicates that oxygen does not diffuse in significant concentrations to a depth exceeding 2 cm of sediment. Hence, the red layer, occurring at depths of up to 18 cm, probably formed at the sediment-water interface and has since been buried. The strong cementing action of ferrihydrite (Schwertmann & Taylor 1977) promotes encrustation, and the increased order in crystals promotes resistance against reduction on burial. Extensive magnetic ordering in the 0- to 1-cm section of the 27 July 1982 core (Fig. 3) demonstrates that increased ordering in crystals does occur during early diagenesis under surficial conditions; however, it is not known whether a minor red layer is now being formed, or whether ordering does occur frequently at the surface but is insufficiently intense to promote cementation and increased resistance to reduction. The ordered surficial oxide also has a similar P-adsorption capacity to that of brown Eh-sensitive ferric hydroxide (Manning & Jones 1982, Manning *et al.* 1984). Conceivably, the brown Eh-sensitive ferric hydroxide is a precursor to ferrihydrite.

As an alternative, the red layers may be actively accreting, with two simple variations: firstly, the layers are immobile with respect to the clay background, and secondly, the layers are continuously dissolving and reprecipitating so as to maintain a fairly constant separation from the sediment-water interface. The action of Mn- and Fe-precipitating bacteria is inferred. The layers are characterized more by similar age than by constant distance from the interface, and a relatively dry crust further argues against the second variation. The first variation does not explain the loss of color and of ferric iron in the very light grey zone.

Hence, the layers are best considered fossil surficial horizons of high redox potential. This could not have arisen from a period of low production of organic matter in the Great Lakes because cultural eutrophication since ~1840 implies increased organic loadings to the lake. More easily envisaged are changes in rates of sedimentation over relatively small areas of the lake. Over, say, five years or so of very low sedimentation, the continuous supply of organic matter to the bottom is halted, and organic matter contained in the top 2 cm will be oxidized by diffusing molecular oxygen. Iron, manganese and phosphate ions percolating upward in the pore water are now precipitated under conditions of low inputs of foreign organic and inorganic ions. Crystallization to ferrihydrite will be promoted by (a) greater time in the oxic zone, (b) lower concentrations of adsorbed foreign ions (Schwertmann 1966), (c) high concentrations of  $\text{Fe}^{3+}$  ions derived from the reduction of underlying silicates, and (d) lower concentrations of hydrated alumina and silica that would remove "ferric hydroxides" as aluminosilicates (Nriagu 1978). Moreover, under low-energy conditions, Mn ions will precipitate as a thin layer at higher Eh levels, *i.e.*, at the immediate sediment-water interface. The very light grey layer is easily explained in terms of the elevation of Eh sufficiently over the top 3 or 4 cm to dissolve black ferrous sulfides during the period of low sedimentation.

#### General discussion

If abstraction of ferric iron from illite and from amorphous aluminosilicates is a measure of relatively strong reducing conditions, then surficial muds over this ~100-km<sup>2</sup> area of the Niagara Basin are now more strongly oxidized than they were > 65 years ago. We attribute this change, which probably implies a higher P-binding capacity, to changes in sedimentation patterns locally. Between ~1840 and ~1910, sedimentation may have been greatly influenced by land-clearing subsequent to colonial settlement along the shores.

The red layer may have formed contemporaneously with the ferromanganese-coated sands along the north shore of Lake Ontario. However, the coatings are enriched in trace elements (Cronan & Thomas 1972), whereas the layer contains background levels of, for example, Pb and Zn (Manning *et al.* 1983). Hence the coatings are still accreting heavy metal ions. The long-term stability of the layers and coatings is important because deteriorating quality of water would cause reduction and dissolution, with consequent release of massive quantities of P and trace metal ions to the overlying water. This would promote further eutrophication.

On the basis that eutrophication causes increased production of organic matter and, in turn, reduced

redox potentials at the sediment-water interface, we can conclude that the trophic status of the Niagara Basin has improved since pre-red-layer times. This is in marked contrast to the trend for the Great Lakes generally; cultural eutrophication has been pronounced in both Lakes Erie and Ontario. Conceivably, much of the nutrient input to the Niagara Basin, possibly from the Niagara River, may have been diverted naturally ~65 years ago to the detriment of the eastern Rochester and Kingston basins.

Approximately 5000 tonnes of P is contained in the ~100 km<sup>2</sup> of red layer in the Niagara Basin. This is comparable to the current annual load of P to Lake Ontario (8500 tonnes, Great Lakes Water Qual. Board 1981). A red layer also occurs in sediments of the central Mississauga Basin (Sly & Thomas 1974). If dissolved, the P would pose a major nutrient problem, as the P would be highly bioavailable. The Mössbauer spectra reveal no vivianite peaks; consequently, reduction and dissolution of the red oxide have hitherto been minimal.

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