Canadian Mineralogist
Vol. 22, pp. 357-365 (1984)

THE PARTITIONING OF NON-APATITE INORGANIC PHOSPHORUS IN SEDIMENTS FROM LAKES ERIE AND ONTARIO

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ABSTRACT

Concentrations of brown Eh-sensitive ferric iron ($EhFe^{3+}$) have been measured, by Mössbauer spectroscopy, in surficial silty clay sediments from several locations in Lakes Erie and Ontario. Concentrations of $EhFe^{3+}$ are well correlated with non-apatite inorganic phosphorus (NAIP) and with 0.1 M NaOH-extractable P. A relationship is derived, $[NAIP] = 0.03 + 0.08[EhFe^{3+}]$, which demonstrates the fractionation of NAIP into $EhFe^{3+}$-adsorbed P and into residual P. (Concentrations [ ] are in wt. % dry sediment.) $EhFe^{3+}$-P is the main source of available P under anoxic conditions; it also represents a readily exchangeable source of phosphate ion for utilization by algae and bacteria. Concentrations of $EhFe^{3+}$ and $EhFe^{3+}$-adsorbed P are poorly correlated with, and possibly independent of, clay (Fe^{2+}) concentrations in these depositional sediments. Redox potentials at the sediment – water interface play a dominant role in determining $EhFe^{3+}$ values.

Keywords: inorganic phosphorus, ferric hydroxides, sediments, Great Lakes.

SOMMAIRE

La concentration d'ions ferriques bruns, amorphes, sensibles au Eh ($EhFe^{3+}$), a été mesurée par spectroscopie Mössbauer dans les sédiments d'argile silteuse à plusieurs endroits des lacs Erié et Ontario. Cette concentration est en bonne corrélation avec celle du phosphore inorganique non-apatitique (NAIP) et celle du P extractible au NaOH (0.1 M). L'équation obtenue, $[NAIP] = 0.03 + 0.08 [EhFe^{3+}]$, exprime le partage du NAIP en P adsorbé sur $EhFe^{3+}$ et P résiduel. (La concentration [ ] s'exprime par le % en poids de sédiment sec.) En milieu pauvre en oxygène, le P–$EhFe^{3+}$ constitue la principale source de P disponible; il représente aussi une source d'ions phosphate facilement échangeables, pouvant être utilisée par les algues et les bactéries. Les concentrations de $EhFe^{3+}$ et de P adsorbé sur $EhFe^{3+}$ concordent mal avec la concentration d'argile (Fe^{2+}) du dépôt sédimentaire, dont elles sont peut-être indépendantes. En chaque endroit, le potentiel rédox à l'interface sédiment – eau joue un rôle dominant dans la détermination de la valeur de $EhFe^{3+}$.

Mots-clés: phosphore inorganique, hydroxydes ferriques, sédiments, Grands lacs.

INTRODUCTION

Anthropogenic loadings of phosphorus have contributed to eutrophication of the lower Great Lakes. The fraction of phosphorus that can be utilized by aquatic plants for growth is termed *bioavailable.* However, measurement of the bioavailable fraction has been compromised by a lack of knowledge of the chemical forms of inorganic phosphorus. This is due mainly to the amorphism or poor crystallinity of the hydrated iron oxides. Detrital apatite is too insoluble to yield significant amounts of dissolved inorganic phosphate ion, the immediately available form of phosphorus. Chemical extraction and algal culture studies of sediments from Lakes Erie and Ontario (Williams *et al.* 1976, 1980) have demonstrated good correlations between concentrations of total iron and non-apatite inorganic phosphorus (NAIP), of NAIP and bioavailable P, and of 0.1 M NaOH-extractable P and bioavailable P. In several sediments, cell uptake of P equals NaOH-extractable P, hence the use of NaOH-extractable P as a measure of bioavailable P (Sonzogni *et al.* 1982). However, chemical speciation of Fe–P compounds was not attempted. Recent Mössbauer spectral work (Manning *et al.* 1981, Manning & Jones 1982) has described the measurement of brown Eh-sensitive ferric iron ($EhFe^{3+}$) in oxidized surface-sediment. Hydrated oxides of $EhFe^{3+}$ are important substrates for adsorption of NAIP and represent the most available source of P, particularly during anoxic regeneration.

The aim of this work is to better define the iron–phosphorus compounds present in oxic surficial muds and, in particular, to partition the NAIP fraction. This should lead to a greater understanding of the available forms of P and of the chemical action of extractants.

EXPERIMENTAL DETAILS

One-metre Benthos gravity cores were extruded and sectioned at 1-cm intervals under Ar or N_2

TABLE 1. DATES AND LOCATIONS OF SEDIMENT CORES

Core	Date	Lake, Basin	Location
1	29 Aug. 1980	Ontario, Niagara	43°24.10'N 79°26.66'W
2	18 Nov. 1980	Ontario, Niagara	43°24.10'N 79°26.66'W
3	14 Oct. 1981	Ontario, Niagara	43°20.00'N 79°30.00'W
4	27 July 1982	Ontario, Niagara	43°18.10'N 79°20.00'W
5	23 July 1981	Ontario, Niagara	43°21.05'N 79°20.16'W
6	9 Sept 1982	Ontario, Niagara	43°01.06'N 79°05.00'W
7	3 July 1981	Ontario, Mississauga	43°33.00'N 78°10.40'W
8	19 Sept 1979	Ontario, Rochester	43°30.70'N 76°54.00'W
9	5 Sept 1980	Erie, Central	41°50.75'N 81°50.82'W
10	25 Sept 1980	Erie, Central	41°50.75'N 81°50.82'W
11	2 Sept 1981	Erie, Central	41°55.75'N 81°53.90'W
12	14 June 1979	Erie, Central	42° 0.20'N 81°36.20'W
13	Aug. 1977	Erie, Central	41°54.20'N 81°41.00'W

within four hours of retrieval. The sections were frozen immediately, freeze-dried, bottled and stored under N_2 at $-20°C$ prior to spectral analysis. The Mössbauer spectra were recorded and computed at Cambridge and McMaster Universities (Manning *et al.* 1981). Values of chi-squared and visual fits over the whole spectral range were used as criteria of goodness of fit.

The locations of the silty-clay sediment cores are listed in Table 1. All Lake Ontario cores displayed a one-to-two-cm-thick uniformly brown oxidized surface layer, the bottom waters were oxic and amphipods were abundant. The Central Basin (Lake Erie) cores showed more tenuous two-to-three-mm-thick brown layers; the 2 Sept. 81 core showed abundant oligochaete activity. Central portions of the cores were selected to eliminate effects of shearing along core-liner walls. Concentrations of NAIP [dithionite–citrate–bicarbonate (DCB) plus NaOH extractable P] and 0.1 M NaOH-extractable P were determined according to Williams *et al.* (1976, 1980). All concentrations are expressed in wt. % of dry sediment.

RESULTS AND DISCUSSION

Representative Mössbauer spectra of Lakes Erie and Ontario sediment are shown in Figures 1 and 2. All spectra contain two prominent doublets in the $+4$ to -4 mm s^{-1} range, one marking Fe^{2+} ions in the chlorite lattice [*IS* (isomer shift) 1.14 mm s^{-1}, *QS* (quadrupole splitting) 2.63 mm s^{-1}, HW (half width) 0.39 mm s^{-1}] and the other, broadened, marking ferric iron (correspondingly, 0.37, 0.65 and 0.56 mm s^{-1}) in a number of different octahedra in amorphous or poorly-crystallized hydrated oxides (Coey *et al.* 1974, Readman *et al.* 1976, Manning *et al.* 1981); all values are good to ±0.02 mm s^{-1}. Isomer shifts are quoted with respect to Fe foil. The spectra for the Lake Ontario sediments display weak absorptions at approximately $+9$, $+5.5$, -4 and -8 mm s^{-1}, marking minor amounts (~5% of Fe_T) of well-crystallized detrital hematite, α–Fe_2O_3. The hematite absorption in the $+4$ to -4 mm s^{-1} region is negligible, and much of it is centred away

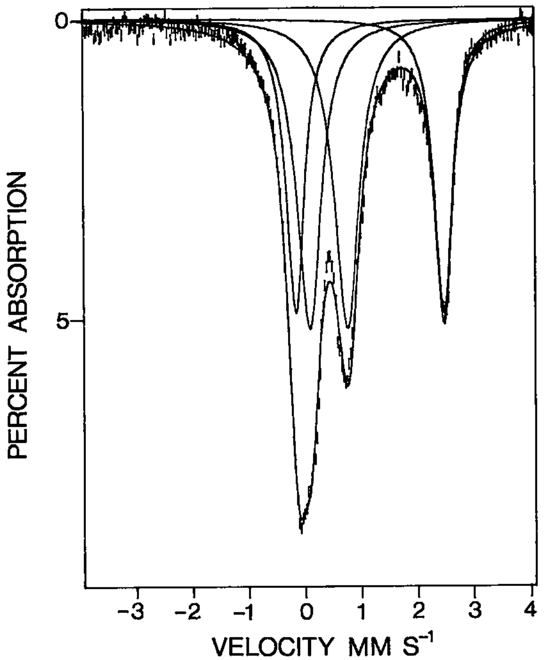

FIG. 1. Mössbauer spectrum of the 1–2-cm fraction of Lake Ontario sediment core. Continuous line represents computed fit based on two doublets. Chi-squared is 736 with 504 degrees of freedom.

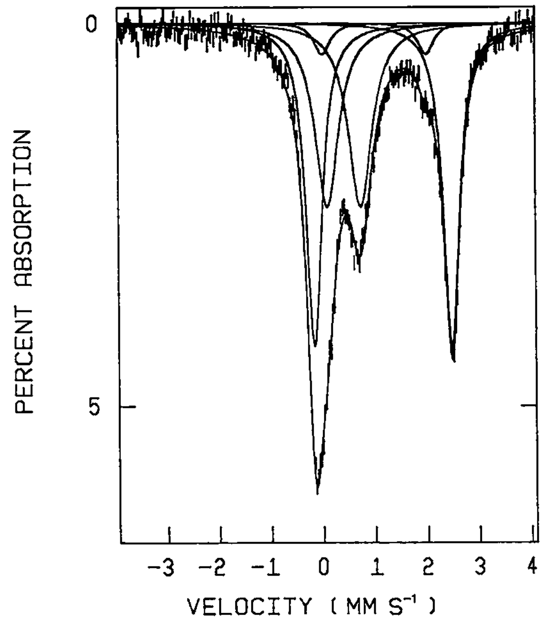

FIG. 2. Mössbauer spectrum of the 1–2-cm fraction of Lake Ontario sediment core. Continuous line represents computed fit based on three doublets (two ferrous). Chi-squared is 675 with 504 degrees of freedom.

from the Fe^{2+} and Fe^{3+} absorptions. Also, a weak second Fe^{2+} doublet ($\sim 5\%$ of Fe_T) marking ferrous ions in a second octahedral site in chlorite can be resolved in most spectra; for it, *IS*, *QS* and *HW* are 1.10, 2.27 and 0.34 mm s^{-1}, respectively. In a two-doublet fit, almost all of the minor Fe^{2+} absorption appears in the main Fe^{2+} envelope. Ferric iron concentrations are not significantly different using either one or two ferrous doublets, but for consistency, ferric iron concentrations listed here are based on one ferrous doublet. Calculated concentrations of ferric iron, normalized to a constant Fe^{2+} (clay) background (Manning & Jones 1982), are listed in Table 2. Table 3 lists comparative concentrations of ferric iron for two cores based on two- and three-doublet fits.

Concentrations ([ ]) of $EhFe^{3+}$ in the oxidized surface layer (OSL) are defined by $[EhFe^{3+}]_{OSL}$ = $[Fe^{3+}{}_T]_{OSL}$ minus $[RFC]_{OSL}$, where *RFC* represents refractory ferric compounds, *i.e.*, ferric compounds that persist in the reduced zone. The method of calculation of $[RFC]_{OSL}$, by extrapolation of [*RFC*] in the reduced zone, has been described (Manning *et al.* 1981, Manning & Jones 1982). All Lake Ontario cores show significant surficial Fe^{3+} enrichment (Table 2, Fig. 3), whereas most Lake Erie cores (*e.g.*, Fig. 3) show insignificant or minor enrichment. Mössbauer data for cores 1, 2, 5 and 9 have been published (Manning *et al.* 1981, 1983, Manning & Jones 1982). For cores 3 (Fig. 3), 4, 7, 12 and 13, $[RFC]_{OSL}$ is the arithmetic mean of [*RFC*] in the reduced zone (see Manning *et al.* 1981); for the remaining cores, except 11, *RFC* concentrations decrease with increasing depth of burial, and regression analysis was used to estimate $[RFC]_{OSL}$ (Manning & Jones 1982). Calculated concentrations of surficial Fe^{2+}, *RFC*s, $EhFe^{3+}$ and extractable P are listed in Table 4. The core pairs 1–2 and 9–10 were

TABLE 2. FERROUS AND FERRIC ION CONCENTRATIONS* IN LAKES ERIE AND ONTARIO SEDIMENTS

Depth cm	%Fe^{2+} meas.	%Fe^{3+} meas.	%Fe^{3+} norm.	%Fe^{2+} meas.	%Fe^{3+} meas.	%Fe^{3+} norm.	%Fe^{2+} meas.	%Fe^{3+} meas.	%Fe^{3+} norm.
		CORE 3			CORE 4			CORE 6	
0- 1	1.26	1.96	1.96	1.66	2.34	2.34	1.39	1.46	1.46
1- 2	1.32	1.96	1.87	1.80	2.20	2.04	1.46	1.27	1.21
2- 3	1.62	1.91	1.49	2.07	1.93	1.54	1.40	1.17	1.16
3- 4	1.77	1.76	1.25	2.03	1.97	1.62	1.57	1.25	1.11
4- 5	1.73	1.80	1.31				1.60	1.22	1.05
5- 6							1.55	1.27	1.13
6- 7	1.69	1.84	1.37	2.09	1.91	1.52	1.63	1.19	1.01
8- 9				2.08	1.92	1.54			
10-11	1.77	1.76	1.25				1.57	1.25	1.11
		CORE 7			CORE 8			CORE 13	
0- 1	1.30	1.98	1.98	1.98	2.06	2.06	1.82	2.21	2.21
1- 2	1.54	1.87	1.59	2.44	2.20	1.78	1.86	2.06	2.02
2- 3	1.72	1.85	1.41	2.38	2.32	1.93			
3- 4				2.34	2.36	2.00	1.85	2.01	1.98
4- 5	1.86	1.99	1.39	2.50	2.29	1.81			
5- 6	1.88	1.97	1.37	2.22	2.09	1.86			
6- 7	1.81	2.04	1.47						
7- 8	1.95	2.21	1.48						
11-13				2.31	2.15	1.85			
15-16							2.07	2.05	1.81
21-22				2.30	2.03	1.75			
28-30				2.40	1.93	1.59			
34-36							2.10	2.01	1.75
38-40				2.49	1.84	1.46			
44-46							2.18	1.98	1.65
		CORE 10			CORE 11			CORE 12	
0- 1	2.32	2.36	2.36	1.77	2.17	2.17	2.55	2.24	2.24
1- 2	2.32	2.16	2.16	1.71	2.13	2.21	2.45	1.93	2.01
2- 3	2.20	2.21	2.32	2.06	1.78	1.53	2.53	2.12	2.14
3- 4	2.03	2.10	2.39	1.86	1.98	1.88	2.57	2.05	2.03
4- 5	2.01	2.18	2.51	1.89	1.95	1.83	2.60	2.07	2.05
5- 6	2.19	2.01	2.13	1.95	1.89	1.72			
6- 7	2.06	2.14	2.41						
7- 8				1.85	1.99	1.90			
9-10				1.84	2.00	1.92			
10-11	2.14	2.06	2.22						
11-12				1.87	1.97	1.87			
13-14	2.18	2.02	2.14	1.86	1.98	1.88			

meas = measured; norm = normalized; * in weight percent

TABLE 3. NORMALIZED FERRIC IRON CONCENTRATIONS* BASED ON TWO- AND THREE-DOUBLET FITS

Depth cm	Core 6		Core 7	
	2-doublet	3-doublet	2-doublet	3-doublet
0- 1	1.46	1.44	1.98	2.01
1- 2	1.21	1.19	1.59	1.58
2- 3	1.16	1.16	1.41	1.38
3- 4	1.11	1.12		
4- 5	1.05	1.08	1.39	1.39
5- 6	1.13	1.16	1.37	1.38
6- 7	1.01	1.03	1.47	1.48
7- 8			1.48	1.49
10-11	1.11	1.08		
[Eh Fe^{3+}]	0.25%	0.23%	0.59%	0.56%

* wt. percent

retrieved, at different times, from the same location (±2 km) in Lakes Ontario and Erie, respectively (Table 1); internally consistent values of $EhFe^{3+}$, NAIP and 0.1 M NaOH-extractable P were obtained (Table 4).

Core 11 is unusual in that it is rather well oxidized compared with other cores from the Central Basin of Lake Erie. Concentrations of $EhFe^{3+}$ and 0.1 M NaOH-extractable P are relatively high, and the oxidized surface-layer is 2 cm thick (Table 2, Fig. 3). It is unclear (Fig. 3, Table 2) whether $[RFC]_{OSL}$ should be based on the mean of the seven deepest points (*i.e.*, ignoring the two-to-three cm value), whence $[RFC]_{OSL}$ is equal to 1.86%, or whether $[RFC]_{OSL}$ equals the $[RFC]$ at 2–3 cm, whence $[RFC]_{OSL}$ is equal to 1.53%. This core was marked by extremely abundant and active oligochaetae, which may have temporarily oxidized the surficial muds and introduced high levels of NAIP, possibly through faeces. The cause of the low concentrations of *RFC*s at 2–3 cm may reflect leaching by feeding oligochaetae.

Phosphorus - $EhFe^{3+}$ correlations

$EhFe^{3+}$ is well correlated with NAIP and with

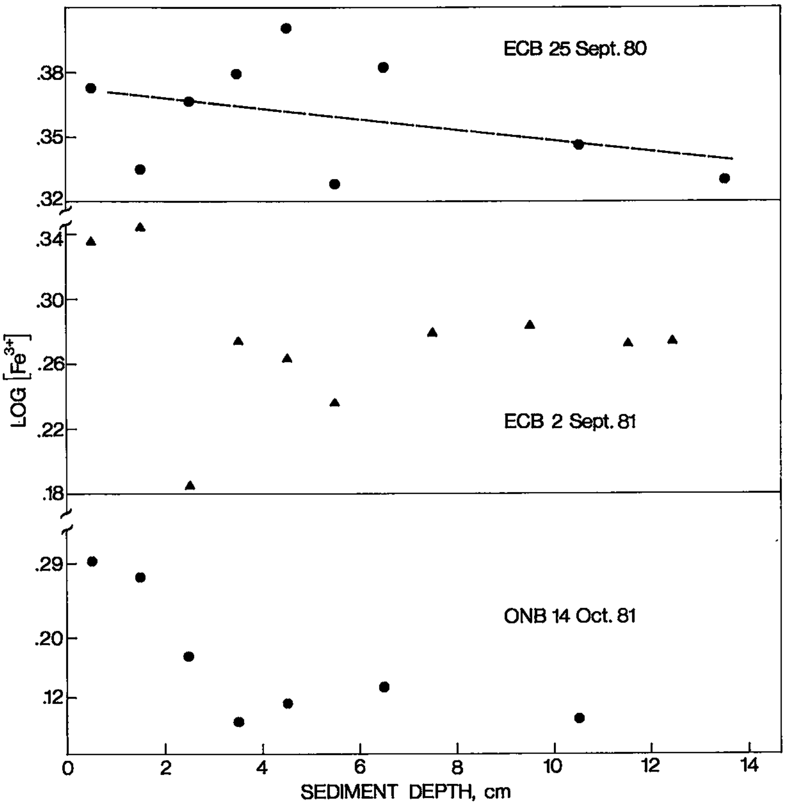

FIG. 3. Plots of normalized ferric iron concentrations (log scale) *versus* depth below sediment—water interface. Note the unusual ferric iron trends in Lake Erie Central Basin (ECB) core retrieved 2 September 1981. ONB represents Ontario, Niagara Basin. A log scale is used for consistency with earlier suggestions (Manning & Jones 1982) of a first-order reduction process.

TABLE 4. IRON* AND EXTRACTABLE PHOSPHORUS CONCENTRATIONS (WT.%) IN LAKE SEDIMENTS

Core	Fe^{2+}	Fe^{3+}_T**	RFC	$EhFe^{3+}$	NAIP	NaOH-P
1	1.30	1.98	1.40	0.58	0.084	
2	1.99	2.29	1.75	0.54	0.083	
3	1.26	1.96	1.30	0.66		0.075
4	1.66	2.34	1.55	0.79		0.059
5	2.43	3.32	~2.74	~0.58	0.075	0.055
6	1.39	1.46	1.21	0.25		0.040
7	1.30	1.98	1.42	0.56		0.063
8	1.98	2.06	1.91	0.15	0.053	
9	1.92	2.13	2.05	0.08	0.036	0.035
10	2.32	2.36	2.36	0.00	0.036	0.034
11	1.77	2.17	?	?		0.080
12	2.55	2.24	2.09	~0.15	0.042	
13	1.82	2.21	2.02	0.19		0.046
14	2.06	1.99	1.99	0		

* After subtraction of 6% of total Fe in hematite in cores 1,2,3,4,6, and 7.

** Concentration in 0 to 1 cm fraction.

0.1 M NaOH-extractable P (Fig. 4), linear regression analysis yielding coefficients of determination (r^2) of 0.97 and 0.84, respectively. Less phosphorus is extracted by NaOH than by dithionite-citrate-bicarbonate reagent, in general agreement with earlier observations (Williams *et al.* 1980) that 0.1 M NaOH extracts ~70% of NAIP. The NAIP - $EhFe^{3+}$ and 0.1 M NaOH-extractable P - $EhFe^{3+}$ curves (Fig. 4) converge at low $EhFe^{3+}$ concentrations but diverge considerably at higher $EhFe^{3+}$ values. The reason for this is unclear, particularly because, with increasing concentration of $EhFe^{3+}$, concentrations of readily available P should increase. Moreover, dissolution of *RFC*-P and iron-bearing silicate compounds by NaOH would release simple amorphous ferric hydroxides similar to those in the oxidized surface layers. The less efficient extraction of P at higher $EhFe^{3+}$ and NAIP concentrations may arise from re-sorption of P on the ferric hydroxide at high pH. Importantly, Figure 4 supports the relationship $[NAIP] = 0.03 + 0.08\,[EhFe^{3+}]$, *i.e.*, NAIP is fractionated into $EhFe^{3+}$ -P and non-Eh-sensitive residual P. Also, $EhFe^{3+}$ adsorbs ~8% of its weight of NAIP (as phosphate ion), which value compares with (a) ~16% measured Berner (1973) for HCl-extractable Fe^{3+} and P in marine sediments; however, Berner considered this value rather high because of discrete ferric phosphate

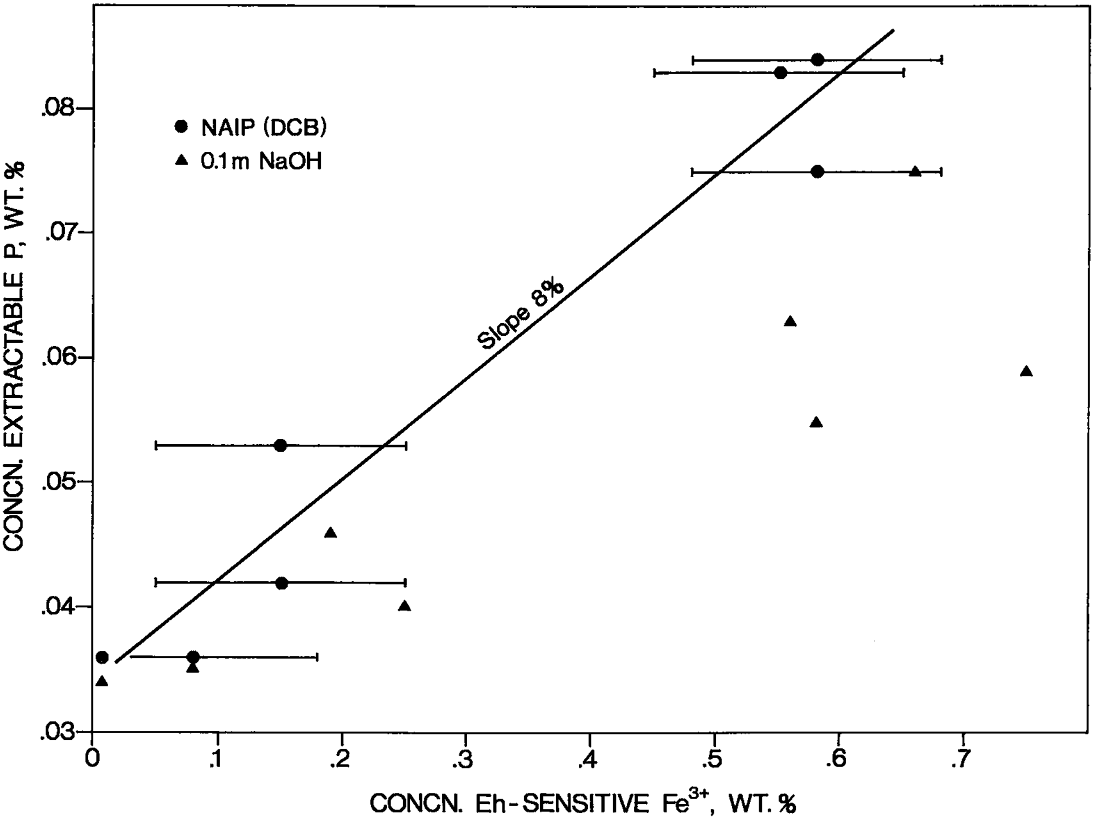

FIG. 4. Plots of concentrations of NAIP and of 0.1 M NaOH-extractable P *versus* concentrations $EhFe^{3+}$.

precipitation, (b) 11% measured (Sholkovitz & Copland 1982) from ferric hydroxide - P cycles in the hypolimnion (pH ~ 7) of Esthwaite Water, (c) ~5% measured by Tipping *et al.* (1981) for ferric hydroxide particles in Esthwaite Water, and (d) 5–10% measured (Stamm & Kohlschutter 1965, Lijklema 1980) for freshly precipitated ferric hydroxide under similar conditions of pH (7.4) and P concentrations to those in the Lakes. Moreover, a red layer present a few cm below the sediment-water interface in some cores from the Niagara Basin (Manning *et al.* 1983) contains, on normalization to Fe^{2+}, an enrichment of ~11%Fe^{3+} and ~0.75% P, corresponding to an adsorption capacity of ~7%. The red oxide has Mössbauer parameters coincident with those of ferrihydrite, $5Fe_2O_3{\cdot}H_2O$ (Coey & Readman 1973, Murad & Schwertmann 1980, Murray 1979), which may have formed at the sediment–water interface under strongly oxidizing conditions.

RFC - Fe^{2+} correlations

Concentrations of *RFC*s and Fe^{3+} are well correlated for Lake Ontario cores excluding core 5 (r^2 0.83), for all Lake Ontario cores (r^2 0.87) and for all cores (r^2 0.80) (Fig. 5). The *RFC* concentration in core 5 may be inflated by the presence of a Fe^{2+}

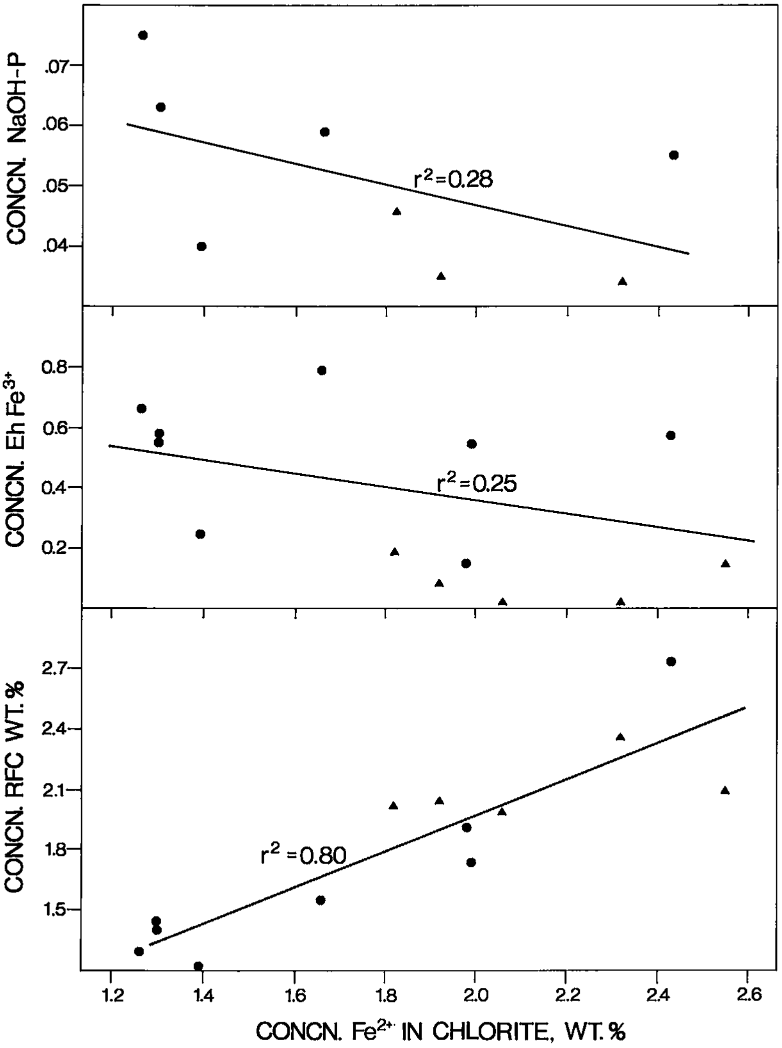

FIG. 5. Plots of concentrations of *RFC*s, of $EhFe^{3+}$, and of 0.1 M NaOH-extractable P *versus* Fe^{2+} (clay) concentrations. Points for Lake Ontario denoted by • and for Lake Erie by Δ.

-PO_4 compound with a ratio of 1:1, containing most of the abundant NAIP (~0.9%: Manning *et al.* 1983). These correlations suggest that most of the ferric iron is located either within the clay (illite) lattice or on the clay surfaces. Consequently, total iron and clay will be strongly correlated in silty clay muds of the Great Lakes (Williams *et al.* 1976); $EhFe^{2+}$ is usually a minor portion of total Fe.

$EhFe^{3+}$ - Fe^{2+} and P - Fe^{2+} correlations

Concentrations of $EhFe^{3+}$ and Fe^{2+} (r^2 0.24; for Lake Ontario cores, r^2 is 0.02; Fig. 5), NAIP and Fe^{2+} (r^2 0.21) and 0.1 M NaOH-extractable P and Fe^{2+} (r^2 0.27; Fig. 5) are poorly correlated. Surprisingly, all correlations are negative, in contrast to the strong positive correlations measured for total Fe, NAIP and clay in Lake Erie sediments (Williams *et al.* 1976). Most Lake Ontario cores are well oxidized and also have relatively low Fe^{2+} contents; Central Basin cores, on the other hand, are relatively poorly oxidized and have relatively high Fe^{2+} contents (Fig. 5). Consequently, the points plotted in Figure 5 tend to fall into two opposite "quadrants", thus generating a negative correlation. A negative $EhFe^{3+}$ -Fe^{2+} correlation is difficult to comprehend because much of the $EhFe^{3+}$ represents precipitation of pore-water Fe^{3+}derived from the breakdown of ferric-iron-bearing clays in the reduced zone. In view of the poor fits to the curves, it is likely that concentrations of $EhFe^{3+}$ and $EhFe^{3+}$ -P are largely independent of Fe^{3+} (clay) concentrations; redox conditions at the surface of the silty-clay sediment are of greater importantce in determining $EhFe^{3+}$

General discussion

$EhFe^{3+}$ is the sole detectable species of iron strongly and positively correlated with NAIP and with 0.1 M NaOH-extractable P. The reasonable slope (8 ± 1.5%) of the NAIP - $EhFe^{3+}$ plot (Fig. 4) confirms that the partitioning of NAIP is based on sound assumptions. In oxic sediments, therefore, most of the NAIP is formed by the precipitation of pore-water ferrous ion in the presence of phosphate ion, *i.e.*, according to the classical picture (Mortimer 1941).

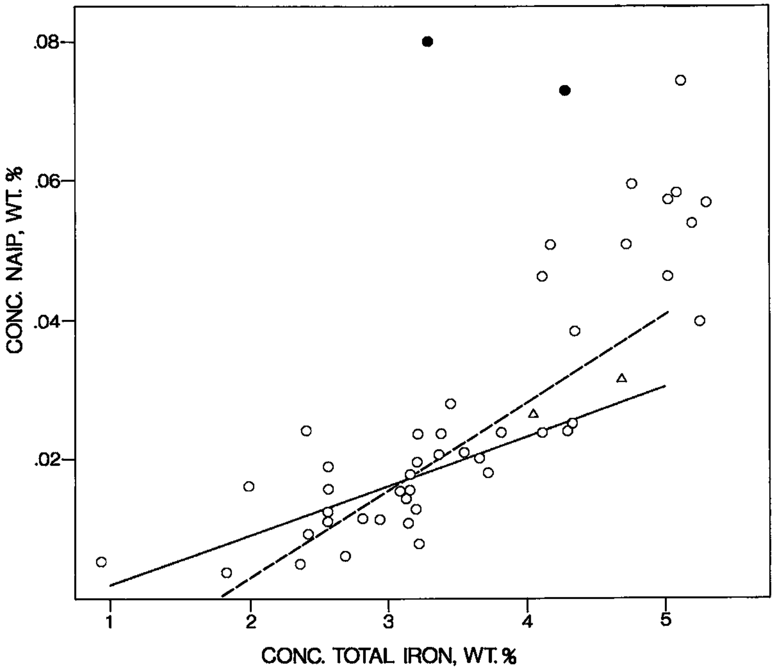

Fig. 6. A plot of concentrations of NAIP *versus* total Fe for the top 3 cm of Lake Erie sediments (after Williams *et al.* 1976). Included are our corresponding data for cores 9 and 10 (Lake Erie) and 1 and 2 (Lake Ontario). The continuous line represents a least-squares regression analysis of NAIP on total Fe for 34 points with < 0.032% NAIP. The dashed line represents a least-squares regression of total Fe on NAIP. These 34 points are relatively low in organic C and in clay fraction.

Our cores 1, 2, 3 and 7, containing high $EhFe^{3+}$ concentrations, also contained high surficial Mn concentrations, *e.g.*, 0.3 to 0.8% Mn *versus* ~0.1% in the reduced zones, whereas the Central Basin cores were relatively low in Mn_T (~0.1%) and showed minor Mn and Fe^{3+} artificial enrichment. These Mn trends follow those of Kemp & Thomas (1976); they attributed the trends to differences in redox potentials. In core 11, high concentrations of $EhFe^{3+}$ and extractable P are not matched by high Mn (0.1% Mn throughout the core), suggesting that Mn has little role in the binding of NAIP (Bortleson & Lee 1974). Black (8% Mn) and red (10% Fe) layers in one Niagara Basin core contain, respectively, 0.20% P and 1.08% P (Manning *et al.* 1983).

The strong correlations between Fe^{3+}, NAIP, and clay measured for the top 3 cm of Lake Erie sediments (Williams *et al.* 1976) are based on samples encompassing a wide range of sand–silt–clay compositions. Most of their samples contained < 0.03% NAIP, < 45% clay and were relatively low in organic C. These samples are too low in NAIP to appear in Figure 4. Their NAIP - total iron (Fig. 6), NAIP - organic C, NAIP - HCl-extractable Fe and NAIP - clay plots, although well correlated, are curvilinear, NAIP values increasing rapidly at higher concentrations of the other variable. If our NAIP (0.7% P over top 3 cm) and total Fe values for Lake Ontario cores 1 and 2 are included in their corresponding plots, curvilinearity is accentuated (Fig. 6). In well-oxidized sandy low-organic-matter near-shore sediments, release of Fe to the pore waters is relatively slow, causing minor precipitation and buildup of $Fe(OH)_3$ at the sediment–water interface: NAIP concentrations are relatively independent of redox conditions, and most of the NAIP is probably *RFC*-P. In higher-Fe, higher-organic-matter silty clay sediments of the depositional basins, however, ferrous iron is released relatively rapidly to the pore waters from reduction of clays and *RFC*s, leading to the precipitation of $EhFe^{3+}$ as hydrated oxide, in concentrations dependent upon the redox potential at the surface. Consequently, plots of NAIP *versus* clay, total Fe, and organic C for sediments with wide-ranging sand–silt–clay compositions will be biphasic, *i.e.*, curvilinear. Considering the data of Williams *et. al.* (1976) for those Lake Erie depositional locations with clay > 45%, organic P > 0.013% and NAIP > 0.03% (Fig. 6, *i.e.*, values corresponding to those in our Fig. 4), and including the NAIP and total Fe values for cores 1 and 2, the regression coefficient (r^2) for NAIP on total Fe is 0.092, indicating a poor fit.

The measurement of $EhFe^{3+}$ and adsorbed P is a more expensive and time-consuming method than dithionite–citrate–bicarbonate or 0.1 M NaOH extraction. However, the method offers improved speciation and a basis for an understanding of the action of these extractants.

The dithionite-citrate-bicarbonate reagent is insufficiently specific in its dissolution of iron compounds to be useful in determining available P. NaOH can dissolve silicates, amorphous forms of which might well contain phosphate ion. The replacement of brown ferric hydroxides by black reduced ferrous sulfides has been demonstrated photographically during seasonal anoxia in the Central Basin surficial muds (Burns & Ross 1972). Calculations of P regenerated from such sediments based on $EhFe^{3+}$ adsorbed P (0 to 0.2% $EhFe^{3+}$ yielding 0 to 2 μmoles P L^{-1} for a 3-m-thick hypolimnion, for four points in Table 3 and Fig. 4) and on 0.1 M NaOH extraction from the top cm (3 to 4.5 μmoles P L^{-1}) are clearly at variance. Measured releases in 1970 were 0 to 4 μmoles P L^{-1} (Burns 1976). Interestingly, for well-oxidized muds containing, say, 0.6% $EhFe^{3+}$ (Fig. 4), $EhFe^{3+}$ -P contains ~60% of NAIP, whereas 0.1 M NaOH extracts ~60% of NAIP, in rather good agreement. For relatively poorly oxidized muds, say, ~0.2% $EhFe^{3+}$ agreement (see above) is poor. NaOH extraction may mimic the localized high pH generated by ammonia released as an excretory product by organisms, but release of carboxylic acids might be expected to buffer this and also solubilize phosphate. The efficient extraction of *RFC*-P (non-$EhFe^{3+}$ P) by 0.1 M NaOH requires further study, especially because *RFC*-P may be siliceous and not readily available. Presumably, dissolution of amorphous ferric aluminosilicates by NaOH would form a ferric hydroxide similar in composition to the brown surficial compound.

ACKNOWLEDGEMENTS

We thank Professors W.J. Jones and J.M. Thomas for use of equipment, and M.N. Charlton, K.R. Lum, A. Murdoch, J.O. Nriagu, and staff of Technical Operations, National Water Research Institute, for their assistance. We also acknowledge the useful suggestions of the referees.

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Received May 6, 1983, revised manuscript accepted August 5, 1983.