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THE BINDING CAPACITY OF FERRIC HYDROXIDES FOR NON-APATITE INORGANIC PHOSPHORUS IN SEDIMENTS OF THE DEPOSITIONAL BASINS OF LAKES ERIE AND ONTARIO

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ABSTRACT

Mössbauer spectrometry has been used to measure the distribution of iron between ferrous and ferric forms in freeze-dried sections of two silty-clay sediment cores retrieved from the Niagara Basin of Lake Ontario and the Central Basin of Lake Erie. The ferric fraction in the oxidized surface layer is further divided by a kinetic method into brown amorphous Eh-sensitive $Fe(OH)_3$ and into amorphous refractory compounds, possibly aluminosilicates. Chemically derived concentrations of non-apatite inorganic phosphorus, measured for the same sections, are compared with these ferric values and show that the $Fe(OH)_3$-based phosphate-adsorptive capacities of the sediments in, and in areas around, the two cores are probably saturated. The data suggest that the P-adsorptive capacities of silty clay sediments encompassing large areas of the depositional basins of the two lakes are fully utilized and have been for many years. This saturation may have contributed importantly to eutrophication in recent years.

Keywords: phosphorus, ferric hydroxides, sediments, Great Lakes, Mössbauer spectroscopy.

SOMMAIRE

On a déterminé, par spectrométrie Mössbauer, la répartition du fer entre états ferreux et ferrique dans les sections liophylisées de deux carottes d'argile silteuse provenant des bassins Niagara (lac Ontario) et Central (lac Erié). La fraction ferrique du niveau oxydé de surface est elle-même fractionnée, par méthode cinétique, en $Fe(OH)_3$ brun, amorphe, sensible au Eh, et en matériaux réfractaires amorphes (aluminosilicates?). Dans ces sections, les concentrations de phosphore dérivées chimiquement, mais non de l'apatite, comparées aux quantités de Fe^{3+}, montrent que la capacité des sédiments d'adsorber le phosphore, par le biais du $Fe(OH)_3$, à proximité des carottes a probablement atteint la saturation. Les données indiquent que la capacité d'adsorption des sédiments argileux silteux est pleinement utilisée sur une grande superficie des bassins de déposition des deux lacs, et ce depuis nombre d'années. Il se peut que cette saturation ait contribué de façon notable à l'eutrophication récente des lacs.

(Traduit par la Rédaction)

Mots-clés: phosphore, hydroxydes de fer ferrique, sédiments, Grands Lacs, spectrométrie Mössbauer.

INTRODUCTION

Chemical fractionation and algal culture studies of oxic Great Lakes sediments suggest that bioavailable phosphorus (orthophosphate) is contained within the non-apatite inorganic phosphorus (NAIP) fraction and adsorbed on ferric hydroxides (Williams *et al.* 1976a, b, 1980). The main binder is probably surficial brown amorphous Eh-sensitive hydrated ferric oxide, termed $Fe(OH)_3$; its concentration cannot be measured directly by Mössbauer methods because of the far greater abundance of amorphous refractory ferric compounds (RFCs) (Manning *et al.* 1980, 1981). However, using a model for early diagenesis based on the extrapolation of Mössbauer-derived RFC concentrations from the anoxic zone to the brown oxidized surface-layer (OSL), significant concentrations of Eh-sensitive ferric ion [*i.e.*, $Fe(OH)_3$] were measured for oxic surficial muds from Lake Ontario, coincident with high NAIP concentrations [0.73% Fe in $Fe(OH)_3$, 0.083% NAIP: Manning *et al.* 1981]. For anoxic sediments from Lake Erie, the corresponding values are 0.1% Fe and 0.035% NAIP. Oxic muds are known to be efficient phosphate binders (Mortimer 1941, Mackereth 1966, Fitzgerald 1970).

Here, we present a refinement of previous work (Manning *et al.* 1981) and a more detailed discussion and interpretation of results, with the aim of determining the degree to which the NAIP-binding capacity of $Fe(OH)_3$ in the sediments has been utilized. A silty clay sediment core was retrieved from beneath 110 m of oxic well-mixed water of the Niagara Basin of Lake Ontario at 43°24.10′N, 79°26.66′W on 18 November 1980. The previous core (Manning *et al.* 1981) came from the same location, but on that occasion (29 August 1980) the basin was strongly stratified. Comparative data are also included for a core from the Central Basin of Lake Erie, sampled at 41°50′45″N 81°50′50″W on 26 September 1979, a few days after turnover; this again is the same location as previously studied (Manning *et al.* 1981). Positional reproducibility from year to year is ±0.5 km. The two cores may not be representative of conditions at the sediment–water interface the width of the basin, but they are probably representative of conditions over large areas of silty clay sediment.

EXPERIMENTAL DETAILS

One-metre Benthos gravity cores were extruded and sectioned (at 1 cm intervals) under argon, the sections frozen immediately and placed in a freeze-drier, all within 24 hours of retrieval. Bottled residuals were stored under Ar at –20°C. The Niagara Basin core displayed a 1-to-2-cm-thick brown OSL (Eh +0.3 v) in contrast to the tenuous 2-to-3-mm-thick surficial layer in the Lake Erie core; the underlying muds were a mottled light and dark grey. Central portions of the sections were selected to eliminate shearing along core-liner walls. Concentrations of NAIP and apatite–P were determined according to Williams *et al.* (1976a).

Mössbauer spectra were recorded at Cambridge University and computed using Stone's (1967) programs. Peak half-widths and areas within a quadrupole doublet were constrained to be equal. Chi-squared values and visual ex-

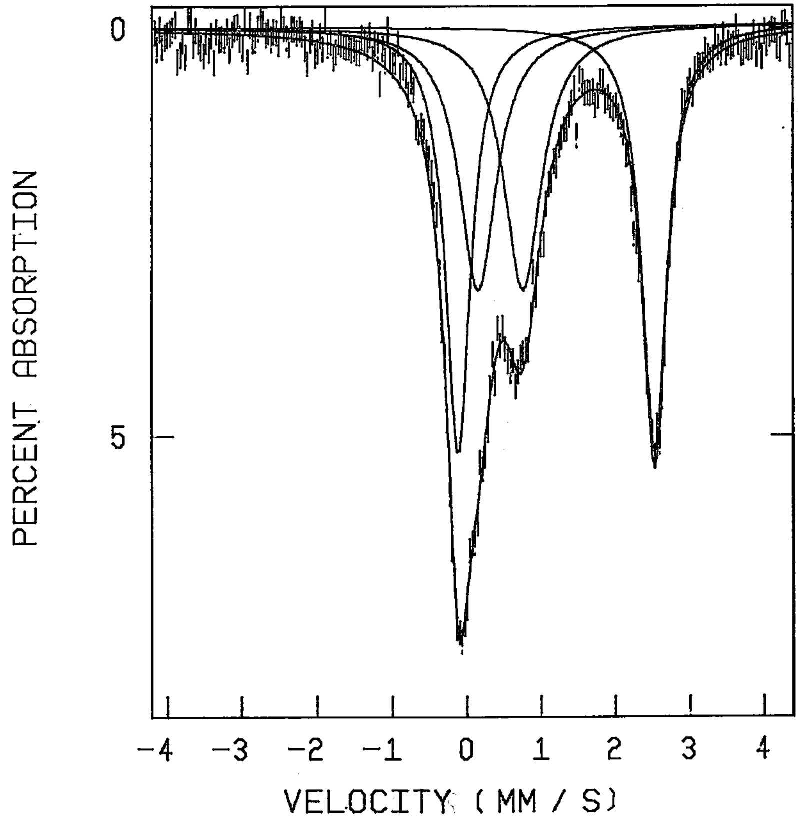

FIG. 1. Room-temperature Mössbauer spectrum of 5 to 6 cm section of sediment core from the Niagara Basin retrieved on 18 November 1980. The computed fit based on two doublets is shown.

amination of computed fits were used as criteria for goodness of fit. The spectrometers were calibrated against Fe foil. Concentrations are expressed as wt.% of dry sediment.

RESULTS AND DISCUSSION

Spectral assignments

A representative Mössbauer spectrum of sediment from Lakes Erie and Ontario is shown in Figure 1. All spectra are qualitatively similar and can be fitted adequately assuming two doublets (Coey *et al.* 1974, Readman *et al.* 1976, Manning & Ash 1978, Manning *et al.* 1981); one marks ferrous ions, mainly in chlorite (isomer shift 1.14 mm s^{-1}, quadrupole splitting 2.63 mm s^{-1}, and half-width 0.39 mm s^{-1}) and the other, broadened, marks amorphous ferric compounds (correspondingly, 0.37, 0.65 and 0.56 mm s^{-1}). All values are good to ±0.02 mm s^{-1}. Calculated ferric ion concentrations are listed as a function of core depth in Table 1, together with the concentrations normalized against a constant Fe^{2+} in chlorite background (*i.e.*, 2.12% Fe^{2+} at 0 to 1 cm). Normalizing is required to compensate for loss on burial of organic matter and calcium carbonates, *etc.* (Kemp *et al.* 1976, Kemp & Thomas 1976).

Figure 2 presents a logarithmic plot of normalized ferric concentrations against sediment depth (*i.e.*, time) for the Niagara Basin core. The profile is reminiscent of that derived earlier for a core from the same location (Manning *et al.* 1981), showing slowly changing RFC concentrations in the reduced zone and enhanced total ferric concentrations in the OSL. Assuming, according to our simple hypothesis, a first-order decay process for the RFCs (Manning *et al.* 1981) and extrapolating a fitted line to the underside of the OSL, say to 1.5 cm depth, then the concentration of Eh-sensitive Fe^{3+} in the top 1 cm is 2.43% Fe minus 1.88% Fe, or 0.55% Fe (wt.% dry sediment). The systematic error based on counting statistics, on the reproducibility of results for one sample, and in the placing of the underside of the OSL, is ~0.05% Fe, but random errors are difficult to assess, *e.g.*, sample oxidation on processing, annual differences in sedimentation characteristics, and formation of vivianite (see below). Uncertainty regarding the order of the RFC decay process does not introduce great error because of the low slope of the RFC curve and the short extrapolation. The enhanced Fe^{3+} concentrations for the 0 to 1 cm and 1 to 2 cm sections (Fig. 2) are mutually supportive and indicate an OSL of ~2 cm thickness; insignificant reduction of RFC is expected within the OSL. The current value of 0.55% Fe in $Fe(OH)_3$ is in very reasonable agreement with that derived for the earlier Niagara Basin core (0.73% Fe, 0.084% NAIP: Manning *et al.* 1981).

In contrast to the Niagara Basin core, but supporting an earlier analysis of cores from the same two locations in Lakes Ontario and Erie (Manning *et al.* 1981), OSL Fe^{3+} enrichment is clearly absent in the Central Basin core (Table 2). Although this core was retrieved a few days after turnover, oxic conditions are not re-established in the surficial muds. The NAIP concentration in the top cm (0.033%) agrees well with that measured (0.035%) in the earlier Central Basin core (Manning *et al.* 1981). Significantly, the top few cm of mud in the highly eutrophic Bay of Quinte, Ontario, contain 72.6% Fe^{3+} (of total Fe) at 0 to 2 cm, 72.2% at 2 to 4 cm, and 72.1% at 4 to 6 cm (Manning 1977), reflecting the small surficial enrichments of redox-dependent ferric moieties in these organic-matter-rich (15% C: Charlton 1975) low-redox muds. Clearly, real, signi-

TABLE 1. FERRIC ION CONCENTRATIONS AND NORMALIZATION FACTORS FOR NIAGARA BASIN SEDIMENTS

Depth cm	wt.% Fe_T	Wt.% Fe^{3+}	wt.% Fe^{3+}_{norm}	Fe^{2+}N.F.	Al N.F.	K N.F.
0-1	4.55	2.43	2.43	1.00	1.00	1.00
1-2	5.23	2.72	2.30	0.85	0.95	0.94
2-3	4.81	2.27	1.89	0.84	0.88	0.88
3-4	5.08	2.37	1.85	0.78	0.80	0.83
4-5	4.93	2.19	1.69	0.77	0.80	0.84
5-6	5.03	2.33	1.83	0.79	0.78	0.81
6-7	4.93	2.27	1.81	0.80	0.80	0.81
10-11	4.75	2.16	1.77	0.81	0.75	0.76
13-14	4.75	2.09	1.67	0.80	0.75	0.75

Fe_T = total iron. Fe^{3+}_{norm} = normalized concentration of ferric iron.
N.F. = normalization factor.

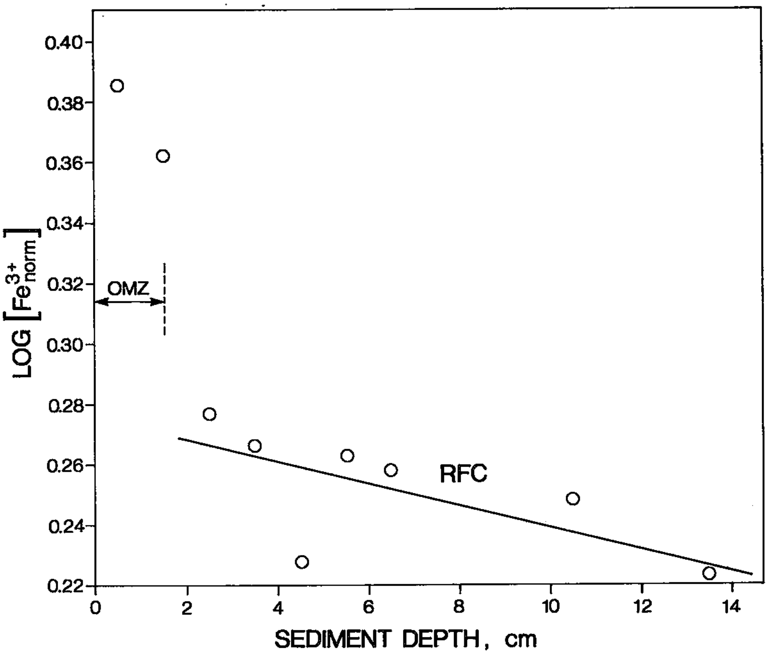

FIG. 2. A plot of normalized ferric ion concentrations (logarithmic scale) *versus* depth below the sediment–water interface for the Niagara Basin core. Solid line describes an assumed first-order fit.

ficant and consistent enrichments in Eh-sensitive Fe^{3+} are present in these Niagara Basin muds.

What ferric compounds comprise the brown Eh-sensitive Fe^{3+} fraction? Of the simpler phosphates, strengite is unlikely to form in freshwater sediments, and rockbridgeite is of hydrothermal origin (Moore 1970, Nriagu & Dell 1974); moreover, there is insufficient NAIP to react with but a minor portion of the Fe^{3+}. Natural small particles of amorphous ferric hydroxides precipitated from fresh waters are well characterized (Coey & Readman 1973, Tipping *et al.* 1981). The brown color of the OSL strongly suggests a hydrated oxide rather than an aluminosilicate (Manning *et al.* 1980, 1981). The presence of small superparamagnetic (< 100 Å) crystals of a magnetically ordered material such as hematite cannot be eliminated; however, hematite would impart a reddish hue to the OSL. Hence, most of the Eh-sensitive surficial Fe^{3+} is probably amorphous $Fe(OH)_3$.

TABLE 2. FERRIC ION CONCENTRATIONS IN A LAKE ERIE CENTRAL BASIN SEDIMENT CORE

Depth cm	wt.% Fe^{2+}	wt.% Fe^{3+}	Norm. Factor	wt.% Fe^{3+}_{norm}
0-1	2.06	1.99	1.0	1.99
1-2	2.02	2.03	1.02	2.07
2-3	2.025	2.025	1.02	2.07
3-4	2.09	1.96	0.985	1.93

Total iron = 4.05%

Correlation coefficients

Chemical extraction studies of Lake Erie sediments (Williams *et al.* 1976a, b) have demonstrated strong correlations between NAIP, total Fe, HCl-soluble Fe and clay content, but it is not known whether the correlations are based on physical or chemical relationships. The work of Williams *et al.* (1976a, b) is compromised because (a) the top 3 cm of mud sampled reduces the significance of $Fe(OH)_3$, (b) their NAIP–total Fe correlations are heavily clay-dependent; indeed, ~50% of the total Fe is lattice-bound in chlorite, and (c) their approach cannot explain the large differences in NAIP between muds from the Central Basin (Lake Erie) and Niagara Basin (Lake Ontario). We have defined the Fe and P compartments and have attempted to relate some of them quantitatively. We propose that $Fe(OH)_3$ occurs as an amorphous stain on clay surfaces and that this stain is the principal substrate for NAIP; the more clay, the greater the number of $Fe(OH)_3$ sites and hence the greater the capacity for binding NAIP. Significantly, the ionic ratio of Fe:P released during anoxia of the Central Basin of Lake Erie (~3: Burns & Ross 1972) is consistent with $Fe(OH)_3$:P ~3, but inconsistent with RFC:NAIP ~ 12.

Logan *et al.* (1979) considered that NaOH extracts labile and short-term P, whereas dithionite extracts potentially available P, *e.g.*, P released during extended anoxia. This idea is consistent with NaOH-P = $Fe(OH)_3$-P and with dithionite-P = RFC-P. The zero point of charge of $Fe(OH)_3$ is at pH 8.5 (Stamm & Kohlschutter 1965); hence, in NaOH solution, dissolution of $Fe(OH)_3$-P is expected. Amorphism, small size of particles, large surface-area and presence as a stain on clay particles promote rapid reduction and dissolution of Fe $(OH)_3$-P. Advantages of the current Mössbauer method are that it is nondestructive and that complexed species are better defined compositionally and quantitatively.

$Fe(OH)_3$–adsorbed P relationships

The relatively low sedimentation rates in the Niagara Basin (Kemp *et al.* 1974) promote the mineralization of deposited organic matter and delay the onset of reducing conditions. The brown OSL in Niagara Basin cores is commonly ~2 cm thick compared to the few mm to 1 cm for most other cores from the lower Lakes. Consequently, Niagara Basin muds are efficient sinks for phosphate, consistent with the high surficial enrichments in $Fe(OH)_3$ and high concentrations of NAIP measured at this one location.

When $Fe(OH)_3$–phosphate complexes reach the reduced zone, reduction and consequent dissolution of ferrous and phosphate ions occurs. The Fe:P ratio in the $Fe(OH)_3$–adsorbed P moiety is greater than in vivianite (Stamm & Kohlschutter 1965, Lijklema 1980, Berner 1973, Tipping *et al.* 1981, Manning *et al.* 1981), and it is probable in these low-S muds that most of the ferrous ions are mobile. Vivianite crystals are present in the reduced zones of Great Lakes cores (Nriagu & Dell 1974), but the vivianite Mössbauer envelope is superimposed on and is "swamped" by that of Fe^{2+} in chlorite. Therefore, vivianite would inflate the normalizing factor and invalidate the quantitative value of the plot in Figure 2. Assuming that all the NAIP in the reduced portion of the Niagara Basin core is in vivianite, the amount of ferrous ion in vivianite can be calculated and subtracted from the overall concentration of Fe^{2+}; this correction is ~ 5% of total Fe^{2+}. Attempts to quantify such small amounts from the Mössbauer spectra were unsuccessful or inconsistent. The correction effectively raises the RFC portion of the curve in Figure 2 by 0.075 log units, yielding a concentration of $Fe(OH)_3$ in the top cm of 0.43% Fe. Surficial Fe^{3+} enrichment still exists. However, it is unrealistic to expect quantitative conversion of NAIP to vivianite because much of the NAIP is probably in refractory compounds, *e.g.*, the anoxic muds of the Central Basin in Lake Erie contain 0.035% NAIP, and yet $Fe(OH)_3$ is close to zero (Manning *et al.* 1981, this work). The $Fe(OH)_3$ concentration in the Niagara Basin core is reasonably 0.5 ± 0.1% Fe^{3+}.

Apatite concentrations in the Niagara Basin core (Table 3), when normalized, show significant surficial enhancement. This may reflect increased land erosion in recent years, but this effect is probably covered by chlorite normalization. Alternatively, apatite is formed authigenically, the higher surficial levels reflecting the increased phosphorus loadings of recent years or the precipitation of upwardly mobile phosphate ion (or both). Much of this authigenic apatite is probably amorphous, poorly crystallized or fine grained, and as such would be extracted in the NAIP fraction.

TABLE 3. PHOSPHORUS CONCENTRATIONS IN SECTIONS OF NIAGARA BASIN SEDIMENT CORE

Depth cm	NAIP	$NAIP_{norm}$	Ap-P	$Ap\text{-}P_{norm}$	Org-P	$Org\text{-}P_{norm}$
0-1	0.083	0.083	0.038	0.038	0.034	0.034
1-2	0.077	0.065	0.039	0.037	0.032	0.027
2-3	0.059	0.050	0.038	0.032	0.024	0.020
3-4	0.066	0.051	0.038	0.030	0.026	0.020
4-5	0.046	0.035	0.041	0.032	0.023	0.018
5-6	0.055	0.043	0.039	0.031	0.021	0.017
6-7	0.022	0.018	0.039	0.031	0.025	0.020
7-8	0.055	0.044	0.039	0.031	0.023	0.018

Concentrations as wt. % P in freeze-dried sediment. Values normalized against Fe^{2+} in chlorite.

Table 1 also lists normalization factors, based on Al and K concentrations in the 0 to 1 cm section, for a Niagara Basin core retrieved from the same location in 1971 (Kemp & Thomas 1976); Al and K are bound mainly in clay minerals and are reliable conservative elements (Kemp *et al.* 1976). Bearing in mind errors in the analyses, the agreement between the Fe^{2+}, Al and K factors is rather good, confirming that reduced iron species do not contribute significantly to the chlorite Mössbauer envelope. Low-spin ferrous sulfides would absorb within the main envelope (Manning & Ash 1979), but sulfide concentrations (~0.1%) in the anoxic zone are too low to bind significant amounts of ferrous ion.

Most of the NAIP entering the reduced zone of Niagara Basin sediments is retained within that zone (Table 3). We cannot say how that NAIP is distributed between RFCs, vivianite, authigenic apatite or $Al(OH)_3$, *etc.* In Central Basin muds, NAIP concentrations decrease from 0.035% at 0 to 1 cm to 0.018% at 3 to 4 cm (this work) to 0.01% at depths (~28 cm) corresponding to colonial development in ~ 1850 (Williams *et al.* 1976b). If NAIP is retained as efficiently in reduced muds of the Central Basin as in muds of the Niagara Basin, then precolonial surficial muds of the Central Basin were relatively low in NAIP and in $Fe(OH)_3$; *i.e.*, low redox conditions are a characteristic of these surficial muds.

The binding of 0.083% NAIP by 0.96% $Fe(OH)_3$ (or 0.5% Fe^{3+}) indicates that Niagara $Fe(OH)_3$ binds ~ 9% of its weight of NAIP (as phosphate). Corresponding values of ~ 5% have been measured for freshly precipitated $Fe(OH)_3$ (Stamm & Kohlschutter 1965, Lijklema 1980) and ~ 8% for marine-rise sediments (Berner 1973). Part of the NAIP is probably tied up in refractory inorganic compounds, *e.g.*, RFCs, but this is unlikely to be more than the 0.035% NAIP measured for anoxic Central Basin cores. If, for the Niagara Basin, $Fe(OH)_3$-adsorbed P equals 0.05%, then $Fe(OH)_3$ binds ~ 5% of its weight of NAIP. This value is probably on the low side because not all Eh-sensitive surficial Fe^{3+} is in $Fe(OH)_3$. Consequently, the $Fe(OH)_3$ P-binding capacity of large areas of Niagara Basin sediment is approaching saturation. Because total phosphorus concentrations in waters of the Niagara and Central Basins are similar (Burns & Ross 1972, Dobson 1981), the low $Fe(OH)_3$ and NAIP values for the two Central Basin cores suggest that the NAIP-binding capacity of the sediments at this one location is saturated. However, higher sedimentation rates and more rapid burial of organic matter suggest that this conclusion is probably valid for most basins of Lakes Erie and Ontario. Has this saturation been the major cause of eutrophication of the lower Great Lakes? As phosphate loadings to the lower lakes increased following colonial settlement in 1850, most of the increase was tied up by the sediments. Nevertheless, organic production was stimulated, generating lower Eh conditions on deposition and cutting into $Fe(OH)_3$ concentrations at the sediment–water interface. This developed into a vicious circle of ever-increasing phosphate loading and ever-diminishing capacities of the sediments to cope with the NAIP.

This study ignores the P-binding capacity of amorphous $Al(OH)_3$. However, hydrated alumina is silicified in sediments (Curtis 1977, Curtis & Spears 1968), leading to amorphous aluminosilicates and ferric aluminosilicates, possibly the RFCs. Because of excess silica (Nriagu 1978), most of the Al is probably tied up in the aluminosilicates; there is no evidence for significant coprecipitation of Al with $Fe(OH)_3$ in Esthwaite water (Tipping *et al.* 1981). The effect of "impurity" ions on the P-binding capacity of $Fe(OH)_3$ is not great and is reflected in Berner's value for marine-rise sediments.

Anoxic release

Three sources of anoxic P release are expected: 1) $Fe(OH)_3$, giving rapid release, 2) RFCs, giving slow release, and 3) the summer's and previous autumn's unmetabolized organic detritus. Lean & Charlton (1976) measured a P release of 377 μg P L^{-1} in their 4-m-deep corrals in the Bay of Quinte, equivalent to a release of 1.5 g P per m^2 of sediment, and corresponding to mud levels of ~ 30 g $Fe(OH)_3$ per m^2 or ~ 16 g Fe^{3+} per m^2. If this P is released from the top cm of sediment containing 1 kg of solid and 28 g total Fe, then ~ 50% of total Fe is in $Fe(OH)_3$. This is unacceptable because surficial Fe^{3+} enrichment in Bay of Quinte muds is one or two % of total Fe (see above). RFC–P amounts to ~ 0.3 g P m^{-2}, based on current analyses of Lakes Erie and Ontario core; hence, most of the P released from Bay of Quinte muds is derived from decomposing organic matter and not from sediment iron compounds. In the Central Basin of Lake Erie, late summer release of anoxic P stimulates an autumn algal bloom, which eventually settles out under conditions of decreasing water temperatures. Decomposition is probably slow over the winter months but is undoubtedly relatively rapid in the ~ 11 °C hypolimnion temperatures of late summer. Burns & Ross (1972) estimated that ~ 50% of the P released in the Central Basin is organic in origin.

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