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FERRIC HYDROXIDES IN SURFICIAL SEDIMENTS OF THE GREAT LAKES AND THEIR ROLE IN PHOSPHORUS AVAILABILITY: A MÖSSBAUER SPECTRAL STUDY

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ABSTRACT

Sections of sediment cores, retrieved from beneath oxic water of the Niagara Basin of Lake Ontario and from beneath anoxic water of the Central Basin of Lake Erie were freeze-dried and analyzed for ^{57}Fe by Mössbauer spectroscopy. Concentrations of total ferric ion and of refractory ferric compounds in the brown oxidized microzone were measured, the latter by the extrapolation of data from the underlying reduced zone; the difference in concentrations was attributed to brown, Eh-sensitive hydrated ferric oxide $Fe(OH)_3$. Approximately 18% of the total Fe, or 0.73% Fe^{3+} (dry wt. sediment), in the top 1 cm of the Niagara Basin core is in $Fe(OH)_3$, compared with ~2% in the Central Basin core. Roughly estimated $Fe(OH)_3$-adsorbed phosphorus concentrations in the Niagara Basin core are in good agreement with non-apatite inorganic phosphorus concentrations. The method may be extended to the measurement of bioavailable phosphorus in surficial muds.

Keywords: sediments, ferric hydroxides, phosphate adsorption, Mössbauer spectroscopy, Great Lakes.

SOMMAIRE

Des sections de carottes de sédiment, recueillies au-dessous des eaux riches en oxygène du bassin de Niagara (lac Ontario) et au-dessous des eaux pauvres en oxygène du bassin central du lac Erié, ont été liophylisées et le ^{57}Fe dosé par analyse spectrale Mössbauer. On a mesuré les concentrations totales des ions ferriques et des composés ferriques réfractaires présents dans la microzone brune oxydée. Dans le deuxième cas, on a extrapolé les données obtenues pour la zone réduite sous-jacente; on a attribué les différences en concentrations à l'oxyde ferrique hydraté $Fe(OH)_3$, qui est sensible au Eh. Environ 18% du Fe total, soit 0.73% de Fe^{3+} par rapport au poids sec de sédiment, se présente sous forme de $Fe(OH)_3$ dans la partie supérieure (1 cm à partir de la surface) de la carotte prélevée dans le bassin de Niagara, au lieu de ~2% dans la carotte prélevée dans le bassin central. Les concentrations de phosphore adsorbé sur le $Fe(OH)_3$, mesurées approximativement, concordent bien avec les concentrations de phosphore inorganique autre que l'apatite. On commente une extension possible de cette méthode à la mesure du phosphore biodisponible dans les boues de surface.

Mots-clés: sédiments, hydroxydes ferriques, adsorption des phosphates, analyse spectrale Mössbauer, Grands Lacs.

INTRODUCTION

Sediments underlying oxic waters of the Great Lakes display a brown oxidized microzone (OMZ) a few mm to 1 cm thick. During the August–September anoxia in the Central Basin of Lake Erie, the brown surficial color is replaced by the black of reduced ferrous sulfides, and, coincidentally, phosphate, Fe, Mn and Si are released to the hypolimnion (Burns & Ross 1972). Iron concentrations in muds of the Great Lakes are strongly correlated with total phosphorus and with non-apatite inorganic phosphorus (NAIP) (Williams *et al.* 1976a, b); measured P releases during summer anoxia in the Central Basin of Lake Erie and in the Bay of Quinte, Lake Ontario, have been attributed to reduction and dissolution of ferric phosphate moieties (Burns & Ross 1972, Lean & Charlton 1976). Phosphorus release upon the reduction of ferric phosphate complexes has been postulated for many years (Mortimer 1942). The brown color probably represents a hydrated ferric oxide, here termed simply $Fe(OH)_3$; its presence as an amorphous stain on clay particles (Mudroch & Zeman 1975) promotes adsorption of phosphate (Mortimer 1942, Syers *et al.* 1973, Mackereth 1966, Williams *et al.* 1976a), heavy metals (Gibbs 1973) and possibly trace organic constituents. Clearly, $Fe(OH)_3$ plays an important role in pollutant interactions at the sediment–water interface. Here, we describe the results of a Mössbauer spectral analysis of oxic muds from the Western Basin of Lake Ontario and anoxic muds from the Central Basin of Lake Erie; we demonstrate significant enrichments of Eh-sensitive $Fe(OH)_3$ in oxic sediments. This paper represents an early attempt at placing the ferric iron–phosphate interactions at the sediment–water interface on a more quantitative basis.

EXPERIMENTAL DETAILS

One-metre Benthos gravity cores were retrieved from beneath 110 m of oxic water in the Niagara Basin of Lake Ontario (43°24.10′N, 79°26.66′W) on August 29, 1980, and from beneath 7 m of anoxic hypolimnion in the Central Basin of Lake Erie (41°50.51′N, 81°50.51′W, total water depth 25 m) on September 5, 1980. The silty clay cores were extruded and sectioned under nitrogen, and the sections were frozen immediately and placed in a freeze-drier, all within 24 hours of retrieval. Bottled residuals were stored under N_2 at –20°C. The Niagara Basin core displayed a uniform rich brown, 1-cm-thick microzone (Eh = +0.3 v at 0–1 cm and +0.02 v at 1–2 cm, pH = 7.4) overlying a mainly light grey core, whereas the Lake Erie core displayed a tenuous 0.1-cm-thick brown surface overlying mottled dark/light grey mud. Cores were sectioned at 1 cm intervals, corresponding to the estimated thickness of the OMZ in the Niagara Basin core, based on color and Eh properties. Central portions of the sections were selected for analysis to eliminate shearing along core-liner walls. Pollen dating of cores (Kemp *et al.* 1974) has placed the ~1840 Ambrosia horizons at ~15 cm and ~28 cm depths in the Niagara and Central Basin cores, respectively. Procedures for determining NAIP concentrations have been described (Williams *et al.* 1976a); these yielded 0.084% NAIP in the Niagara Basin 0–1 cm fraction and 0.035% in the Central Basin fraction.

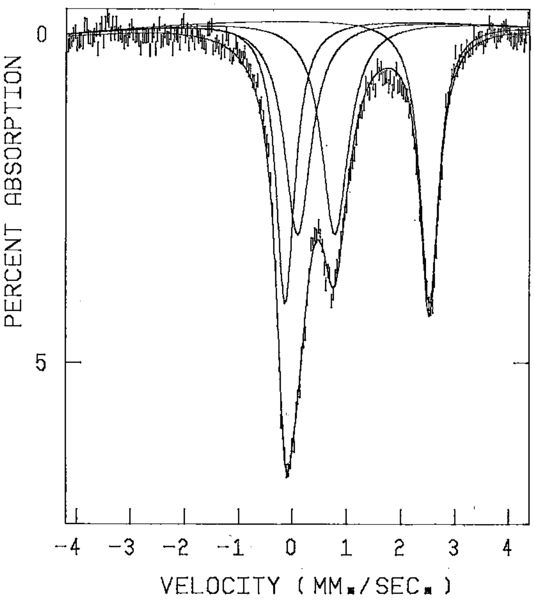

FIG. 1. Room-temperature Mössbauer spectrum of Niagara Basin sediment. Continuous lines depict the two doublets and the overall computed fit.

Mössbauer spectra were recorded at McMaster and Cambridge universities and computed using Stone's (1967) programs. Peak halfwidths and areas within a given doublet were constrained to be equal. Chi-squared values and visual examination were used as criteria for goodness of fit. The spectrometers were calibrated periodically with iron foil.

RESULTS AND DISCUSSION

Spectral assignments

Figure 1 presents a representative Mössbauer spectrum of dried sediment from the Great Lakes. All spectra are described adequately by two doublets (see Coey 1975, Readman *et al.* 1976, Manning & Ash 1978), one marking ferrous ions in chlorite (with isomer shift 1.14 mm s^{-1}, quadrupole splitting 2.63 mm s^{-1} and half width 0.41 mm s^{-1}) and the other, considerably broadened, marking amorphous ferric

TABLE 1. % Fe^{3+} OF TOTAL Fe* IN NIAGARA BASIN (N.B.) AND CENTRAL BASIN (C.B.) MUDS

Depth cm	0-1	1-2	2-3	3-4	4-5	5-6	6-7	7-8	11-12	13-14
%Fe^{3+}, N.B.	60.4	51.2	52.4	52.9	51.7	49.9	52.0	52.1		52.6
%Fe^{3+}, C.B.	52.5	51.3	51.3	50.3	49.7	50.9	50.6		49.0	

* Total Fe = 4.05%

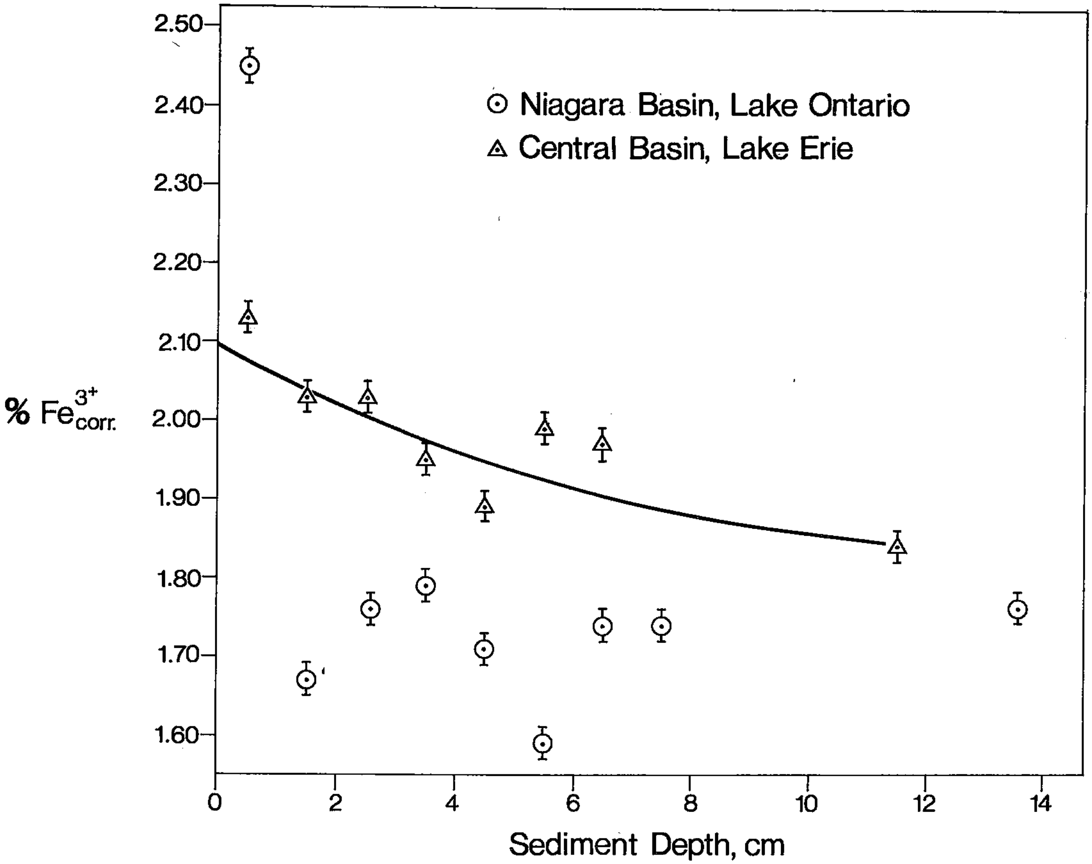

FIG. 2. A plot of corrected Fe^{3+} concentrations *versus* depth below the sediment–water interface for Niagara and Central Basin cores. Continuous line represents exponential fit of Lake Erie data. The 0–1 cm and 2–3 cm Central Basin points are the average of two spectral determinations.

compounds (with corresponding values of 0.37 mm s^{-1}, 0.65 mm s^{-1} and 0.59 mm s^{-1}); all values are good to ±0.02 mm s^{-1}. Ferric concentrations are presented in Table 1 and Figure 2; in the latter, they are normalized against conservative Fe^{2+}–chlorite concentrations (*e.g.*, $Fe^{2+} = 1.60\%$ by wt. of dry sediment at 0–1 cm in the Niagara Basin core) in order to compensate for loss on burial of organic C, Ca and Mg carbonates, *etc.* Both cores contain refractory ferric compounds (RFCs) in their reduced zones (beneath the OMZ) in concentrations greatly exceeding those that can reasonably be placed in clay lattices. The RFC fraction may be composed mainly of amorphous ferric aluminosilicates (Nriagu 1978, Manning & Ash 1978, Manning *et al.* 1980) formed at the sediment–water interface from $Fe(OH)_3$ and hydrated alumina and silica (from bloom collapses). Pyrite is very rare in Great Lakes sediments (Dell 1975). At depths greater than a few cm below the sediment–water interface, most Great Lakes cores are light grey, indicating suppression in RFCs of the charge-transfer and magnetic-domain-ordering processes that cause intense color in ferric oxides (Rossman 1975). Ferric-iron-bearing silicates are weakly colored (Manning *et al.* 1980). The brown head developed in a core is evidence, consequently, for a different redox-dependent hydrated ferric oxide.

The profiles of Fe^{3+} concentration *versus* sediment depth (Fig. 2) for the cores from the two basins are remarkably different, that for the Centrral Basin being similar to the profile derived earlier for another Central Basin core (Manning & Ash 1978). The Niagara Basin plot describes a core with a relatively ferric-iron-rich OMZ overlying a reduced zone in which Fe^{3+} concentrations do not change significantly with depth of burial (time). Because chlorite is derived from long-term stable geological processes, it would appear that ferric loadings to the Niagara Basin, and presumably to the lower Great Lakes generally, are fairly constant on a time scale of centuries; decreasing ferric concentrations with increasing depth of burial in the Central Basin core (see also Manning & Ash 1978) reflect diagenesis. Total iron concentrations in Lake Erie cores, below the top few cm, do not change significantly with depth (Kemp *et al.* 1976). Central Basin cores, beneath the OMZ, show a five-to-ten-cm-thick dark grey to black mottled zone, indicative of reducing conditions; the data in Figure 2 suggest that minor reduction of RFCs occurs in the top 1 cm of mud during the few weeks of summer anoxia.

The marked enrichment in ferric iron in the top cm of the Niagara Basin core (Fig. 2) corresponds to a rich brown OMZ and to the high Eh. Moreover, Fe^{3+} enrichment in the anoxic Central Basin core clearly is relatively insignificant. Therefore, the surficial enrichment in ferric iron in the Niagara Basin core is redox-related, and its disappearance in the reduced zone indicates rapid reduction and dissolution of the ferric moiety, with consequent migration of ferrous ion upward into the OMZ and reprecipitation. We attribute the enrichment to $Fe(OH)_3$.

Calculation of $Fe(OH)_3$ concentrations

RFCs are probably formed at or very near the sediment–water interface where concentrations of biogenic silica are relatively high (Nriagu 1978, Manning *et al.* 1980). Apart from bioturbation in the top few mm of sediment, ferric hydroxides are considered immobile in the OMZ; it can be assumed, within experimental error, that $Fe(OH)_3$ and RFCs are uniformly distributed across the OMZ. If the RFC concentration can be estimated, the $Fe(OH)_3$ concentration in the OMZ is obtained by the difference in concentration between total Fe^{3+} and RFCs. No significant reduction of RFCs occurs in the grey reduced zone of the Niagara core (Fig. 2). Therefore, RFC concentrations in the OMZ can be estimated, within experimental error, by averaging all points in Figure 2 except that for the 0–1 cm fraction; this yields 1.72% Fe in RFC and a dramatic 0.73 ± 0.15% Fe^{3+} in $Fe(OH)_3$ (wt. % of dry sediment). Fitting the Central Basin curve (Fig. 2) to the correct function is difficult, but the curve is shallow, and the extrapolation is not great. The decay of RFCs in sulfide-rich cores (Manning *et al.* 1979) seems to follow a first-order reaction. Hence the fitting of the plot of RFC concentration against time to an exponential curve (Wentworth 1965) and extrapolation of the curve to the underside of the OMZ will yield the RFC concentration in the OMZ; this yields, for the Central Basin core, 2.05% Fe^{3+} in RFCs and a low 0.08 ± 0.04% Fe^{3+} in $Fe(OH)_3$. Moreover, no significant $Fe(OH)_3$ enrichments have been observed in sulfide-rich muds (Manning & Ash 1979, Manning *et al.* 1979). Consequently, significant $Fe(OH)_3$ enrichments seem to occur in oxic surficial muds.

Bioavailable phosphorus in sediments

NAIP in Great Lakes sediments is well correlated with bioavailable P (Williams *et al.* 1980); $Fe(OH)_3$-adsorbed P is probably the main single source of available P (Manning *et al.* 1980). With a knowledge of $Fe(OH)_3$ concentrations and with suitable P-adsorption isotherms, this source of bioavailable P can be measured. However, at this early stage in the Mössbauer studies of sediments, it is best to use the published $Fe(OH)_3$-adsorption capacities to demonstrate that the $Fe(OH)_3$ concentrations measured for the Niagara Basin are realistic. Freshly precipitated ferric hydroxide, at a pH value below its isoelectric point of 8.5, adsorbs 5% of its weight of P (as phosphate: Stamm & Kohlschütter 1965). A corresponding value of 8% can be estimated for volcanogenic hydrated ferric oxides in marine sediments (Berner 1973). The agreement is rather good and suggests that the impurity ions do not critically affect the P-adsorption capacity. Assuming similar P-adsorption capacities for $Fe(OH)_3$ and for the above hydroxides and an average capacity of 6.5%, the calculation of $Fe(OH)_3$-adsorbed P in the Niagara Basin core proceeds as follows:

Vol. of top 1 cm of mud over 1 m^2	10^4 cm^3,
Wt. of solid in 10^4 cm^3	10^3 g,
Wt. of Fe in $Fe(OH)_3$	7.3 ± 1.5 g,
Wt. of $Fe(OH)_3$	14 ± 3 g,
Wt. of $Fe(OH)_3$-adsorbed P	0.90 g,
Wt. of NAIP	0.84 ± 0.1 g.

The error in $Fe(OH)_3$-adsorbed P is probably ±30%. The agreement in NAIP and $Fe(OH)_3$-adsorbed P suggests that the $Fe(OH)_3$ concentrations are reasonable. Because RFC concentrations in both Niagara and Central Basin cores differ by only 15%, it is tempting to assign the difference in NAIP concentrations (0.084% in Niagara Basin *versus* 0.035% in the Central Basin) mainly to differences in $Fe(OH)_3$ concentrations.

The above calculation assumes that all the Fe^{3+} enrichment in the top 1 cm is $Fe(OH)_3$. More than one Eh-sensitive ferric moiety, possibly a whole range of compounds spanning the $Fe(OH)_3$–RFC compositional range, may be formed in the OMZ. However, surficial sediments in Lake Ontario contain high concentrations of amorphous silica (Nriagu 1978), and the ferric aluminosilicate precipitates formed are expected to be highly siliceous (Hem *et al.* 1973, Willey 1975). The oxic–anoxic boundary in the Niagara Basin core is sharply defined from both the Mössbauer (Fig. 2) and Eh measurements, whereas a wide compositional range of ferric aluminosilicates would yield a gently sloping reduction curve. Consequently, most of the Eh-sensitive ferric ions seem compositionally close to $Fe(OH)_3$.

The reasonable agreement between NAIP and $Fe(OH)_3$-adsorbed P suggests that the binding capacity of $Fe(OH)_3$ is close to saturation. However, it is conceivable that significant amounts of NAIP are tied up in RFCs and in poorly crystallized apatite in fish bone. Thus, NAIP concentrations in the top 1 cm of Central Basin muds are not reduced to close to zero. Fish bone, so far as is known, has not been observed microscopically in Great Lakes sediments. Divers from the Canada Centre for Inland Waters very rarely observe dead fish on offshore muds of the Great Lakes, *e.g.*, in the Central Basin. Bearing in mind that 1 cm of surficial mud amounts to five or ten years' deposition and that fish carcasses decay in a few weeks, it is unlikely that much NAIP is in fish bone.

The distribution of NAIP between $Fe(OH)_3$ and RFC is an important problem because $Fe(OH)_3$-adsorbed P is bioavailable, whereas RFC-adsorbed P is released below the OMZ and then precipitated as vivianite (Nriagu & Dell 1974). Much of the 0.035% NAIP measured in the top 1 cm of the Central Basin core may be RFC-adsorbed P. The high NAIP and $Fe(OH)_3$ concentrations determined for the Niagara Basin core show that the basin is an important sink for NAIP, but the above calculation suggests that a considerable part of the $Fe(OH)_3$ adsorption capacity is now being utilized. Sediments from other basins in the lower Great Lakes do not show the same elevated $Fe(OH)_3$ concentrations (P.G.M., unpubl. data) or NAIP concentrations (Williams *et al.* 1976a, b); it would seem that increased loading of NAIP to the lower lakes would compromise the P-adsorption capacity of the sediment.

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