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MÖSSBAUER SPECTRAL STUDIES OF IRON-ENRICHED SEDIMENTS FROM HAMILTON HARBOR, ONTARIO

P. G. MANNING
National Water Research Institute, Box 5050, Burlington, Ontario L7R 4A6

W. JONES
Physical Chemistry Laboratories, University of Cambridge,
Lensfield Road, Cambridge, U.K. CB2 1EP

T. BIRCHALL
Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1

ABSTRACT

Mössbauer spectroscopic methods have been applied to the determination of iron compounds in freeze-dried sediment residuals from two locations in Hamilton Harbor, Ontario. Surficial sediments from the deep basin contain the following major compounds, the iron contents of which have been determined as weight % of the dry sediment: amorphous ferric-bearing refractory material (4.3 wt. % Fe), hematite (2.9%), chlorite (2.6%) (Fe^{2+}), wüstite (1.2%) and siderite (0.7%). The wüstite and most of the hematite and ferric compounds are derived from the iron- and steel-making facilities located on the shore of the harbor. Unpolluted muds would contain 3–4% total Fe. None of the compounds poses an obvious environmental problem. The refractory ferric material may be compositionally similar to the ferric material commonly observed in the reduced zones of sediments, including those of the Great Lakes. It is proposed that it is an amorphous ferric aluminosilicate that can fix a large fraction of the non-apatite inorganic phosphate and take it harmlessly to depth. Dissolution of the complex in the reduced zone would lead to vivianite formation.

Keywords: Mössbauer spectra, iron, sediments, steel mills, Hamilton Harbor.

SOMMAIRE

On a appliqué les méthodes spectroscopiques Mössbauer pour déterminer les composés de fer des résidus de sédiments lyophilisés provenant de deux endroits du port de Hamilton, en Ontario. Les sédiments superficiels du bassin profond contiennent les composés principaux suivants: matériau ferrique réfractaire amorphe (4.3% Fe en poids dans les sédiments secs), hématite (2.9%), chlorite (2.6%, Fe^{2+}), wüstite (1.2%) et sidérite (0.7%). La wüstite et la majeure partie de l'hématite et des composés ferriques proviennent des installations de fabrication du fer et de l'acier situées sur le rivage du port. Les boues non polluées contiennent un pourcentage total de Fe de 3 à 4 pour cent. Aucun de ces composés ne pose de problème environnemental manifeste. Le matériau ferrique réfractaire pourrait être, au point de vue de sa composition, similaire aux matériaux ferriques que l'on trouve dans les zones réduites de sédiments, y compris celles des Grands lacs. Nous émettons l'hypothèse que c'est un silicate d'aluminium ferrique amorphe pouvant fixer une grande partie du phosphate inorganique non apatite et le transporter sans danger dans les eaux profondes. La dissolution du complexe dans la zone réduite entraînerait une formation de vivianite.

Mots-clés: spectroscopie Mössbauer, fer, sédiments, aciéries, port de Hamilton.

INTRODUCTION

Non-apatite inorganic phosphorus (NAIP) in sediments is strongly correlated with iron (Williams *et al.* 1976a, Bortleson & Lee 1974, Mortimer 1941), and release of phosphorus (as phosphate) to overlying waters during anoxia has been attributed to reduction and dissolution of $Fe(OH)_3$–PO_4 complexes (Lean & Charlton 1976, Manning 1977). Mössbauer spectral studies of sediments have grown increasingly popular and problem-oriented in recent years (Coey *et al.* 1974, Coey 1975a, 1975b, Readman *et al.* 1976, Perlow *et al.* 1974, Manning 1977, Manning & Ash 1978, 1979, Manning *et al.* 1979). Chlorite and amorphous ferric-bearing hydrated oxides seem ubiquitous; interest in the latter stems from their refractory nature and potentially important phosphate-fixing capacity (Manning & Ash 1978). Approximately 50% of the iron in Lake Erie muds is

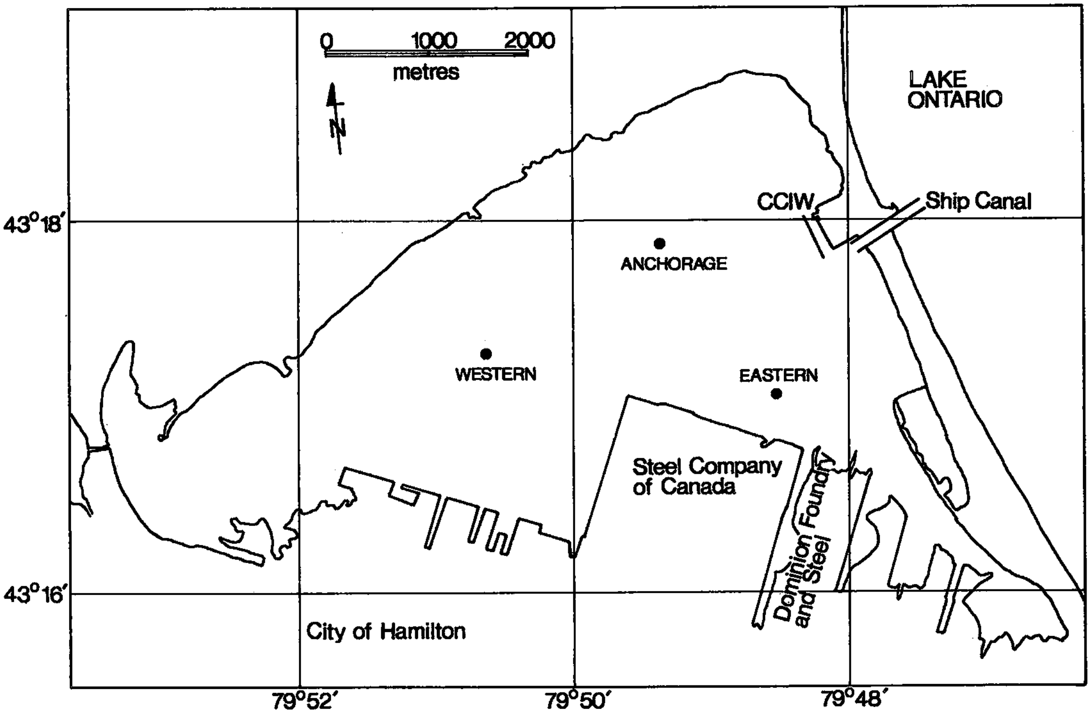

FIG. 1. Location of sampling stations in Hamilton Harbor, Ontario.

present in the refractory ferric compounds (RFCs), which persist in the reduced zone for centuries and which could carry adsorbed phosphate to depth. The RFCs are a distinct moiety (Manning & Ash 1978) from the Eh-sensitive "ferric hydroxide" popularly considered responsible for the brown color of the oxidized microzone (Mortimer 1941, Burns & Ross 1972, Williams *et al.* 1976a, b). Although RFCs and "$Fe(OH)_3$" do not have distinctive Mössbauer signatures, the method is nevertheless well suited to the study of RFCs because of their greater abundance and stability.

Hamilton Harbor is a natural embayment separated from the western end of Lake Ontario by a sandbar, which is traversed by a ship canal (Fig. 1). The harbor waters are highly eutrophic, with a summer Secchi depth of ~ 1 m. Situated on the harbor are the Ontario cities of Hamilton (population 300,000) and Burlington (population 110,000) and the iron- and steel-making facilities of the Steel Company of Canada and the Dominion Foundries and Steel Company. Harbor sediments are heavily polluted by iron and phosphorus, and also by Mn, Pb and Zn and by chemical oxygen demand (Ontario Ministry of the Environment 1977). The ~13% Fe content of the freeze-dried surficial muds (Mudroch & Zeman 1975) reflects heavy loading from the steel mills, but the constituent compounds have not been identified. Iron and phosphorus concentrations in the harbor muds are strongly correlated (R.L. Thomas, priv. comm.), and most of the phosphorus is acid-extractable (Ontario Ministry of the Environment 1977), suggesting that most of the phosphate is adsorbed on amorphous ferric hydroxides.

Here, we report the results of a Mössbauer study of Hamilton Harbor muds. The aims are (1) to quantify the major iron compounds and (2) to identify more adequately the ferric compounds and their capacity to fix elevated levels of phosphate.

EXPERIMENTAL DETAILS

Sixty-cm Benthos gravity cores were obtained in October and November 1978 from two locations in the harbor (43°17'15"N, 79°50'42"W and 43°17'00"N, 79°48'30"W), in the western (deep part, 25 m) and eastern (12 m) parts of the harbor, respectively. The cores were dark grey to black with minor areas of light grey mottling but no obvious laminations. The cores were extruded and sectioned within two hours under nitrogen; the fractions were frozen immediately and then placed in a freeze-dryer. The dried residuals were bottled under nitrogen and stored in a freezer. Oxidation on processing is therefore considered minimal.

Mössbauer spectra were recorded at room temperature and at 77K and over different velocity ranges using equipment at Cambridge and McMaster universities. Spectra were computer-fitted using the programs of Stone (1967). Lorentzian line shapes were assumed, and area ratios and half-widths of peaks in a quadrupole doublet were constrained to be equal. Such assumptions may not be perfectly valid, but constraints are probably justified in complicated spectra involving amorphous natural materials. Chi-squared values and visual fits were used as criteria for goodness of fit.

Results of total Fe, total S and some organic-C and inorganic-C analyses are listed in Table 1; some supportive data from a third core in the anchorage part of the harbor are included. Pyrite framboids were observed in the dried sediments under reflected light in an optical microscope, but the chemical analyses indicate that $< 10\%$ of total Fe is in FeS_2.

Pb–210 dating methods were used to determine continuity of sedimentation in both cores; dredging, shipping activities and slumping would yield misleading time intervals. The eastern core displays undisturbed sedimentation over the last 80 years (surface to 8 cm), with a present-day rate of 1.33 mm yr^{-1}; corresponding values for the western core are 40 years (0 to 7 cm) and 2 mm yr^{-1}.

The mineralogical analysis of a core taken close to our eastern station is 37% illite, 25% quartz, 8% dolomite, 6% chlorite, with lesser amounts of mixed-layer clays, feldspars and kaolinite (Mudroch 1974). Sediments from Lakes Erie and Ontario are of similar composition (Thomas *et al.* 1972, Kemp *et al.* 1976). X-ray-diffraction analyses were performed on the heavy-mineral fractions of several samples using a 57.3 mm Debye-Scherrer camera. The limit of detection of a compound is 5–10% of the total sample.

RESULTS AND DISCUSSION

Spectral interpretations and assignments

Representative room-temperature Mössbauer spectra of Hamilton Harbor sediment residuals are shown in Figures 2–4. All spectra are complicated, showing evidence of at least five doublets, some of which are easily identified. From their peak energies, doublets C and F mark, respectively, Fe^{2+} in chlorite and Fe^{3+} in mainly amorphous hydrated oxides (Coey *et al.* 1974, Readman *et al.* 1976, Manning & Ash 1978, 1979). Chlorite is abundant in harbor muds (Mudroch & Zeman 1975). Doublet S is relatively well defined in Figure 3, with peak energies corresponding to those of siderite, $FeCO_3$ (Readman *et al.* 1976). An X-ray-diffraction analysis of the heavy-mineral fractions confirmed siderite. Doublet H is sharply defined in Figure 2, at energies (~0.84 and +1.77 mm s^{-1}) matching hematite, α–Fe_2O_3 (Ruskov & Tomov 1975). Hematite was confirmed by X-ray diffraction and by measurement of the four outer lines (at –8.0, –4.3, +5.2 and +8.5 mm s^{-1}) in an expanded velocity spec-

TABLE 1. TOTAL Fe AND TOTAL S CONTENTS OF SECTIONS OF HAMILTON HARBOR SEDIMENT CORES

Eastern core			Western core			Anchorage core****		
Depth	%Fe	%S	Depth	%Fe	%S	Depth	%Fe	%S
0-1*	9.3	0.39	0-1***	11.7	0.07	0-1	12.5	0.97
1-2**	11.8	0.51	3-4	16.6	1.17	2-3	4.3	0.26
2-3	12.6	0.53	17-19	11.7	0.88	6-7	4.1	0.25
4-5	6.9	0.42	28-30	6.1	0.54	8-9	3.6	0.18
21-33	3.1	0.26						
33-35	3.9	0.26						
40-41	4.3	0.33						
54-56	8.2	0.21						

* % Org-C = 5.4, % Inorg. C = 2.2

** % Org-C = 2.9, % Inorg. C = 0.9

*** % Org-C = 6.0, % Inorg. C = 1.6

**** 43°17'50"N 79°49'24"W

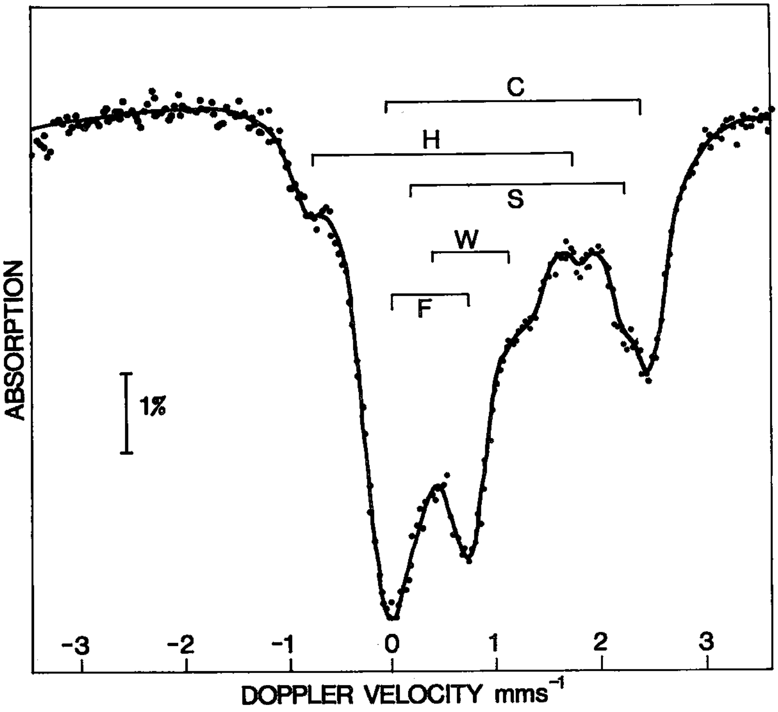

FIG. 2. Room-temperature Mössbauer spectrum of 0–1 cm freeze-dried fraction of eastern core. Continuous curve represents computed fit based on five doublets: C = Fe^{2+} in chlorite, F = ferric compounds (mainly), S = siderite, H = hematite and W = wüstite. Chi-squared = 256 with 208 degrees of freedom.

trum. The magnetic pattern does not match that of magnetite, Fe_3O_4 (Ruskov & Tomov 1975), and no magnetite was detected by X-ray diffraction; hematite is therefore present in far greater concentrations than magnetite.

Doublet W has not been observed in sediment spectra; it is prominent in Figure 4 at energies (0.52 and 1.32 mm s^{-1}) unlike those of Fe^{2+} or Fe^{3+} ions in silicates or carbonates. The doublet does not correlate with pyrite (Manning *et al.* 1979), and there is insufficient sulfur to generate sufficient FeS for its intensity. Doublet W is clearly anthropogenic. Significantly, the doublet disappears at 77K, and a six-line magnetic pattern develops, spread over greater velocities. The paramagnetic → magnetic transition in wüstite, $Fe_{1-x}O$, occurs at 198K (Koch & Fine 1967, Greenwood & Howe 1972b). The presence of wüstite was confirmed by X-ray diffraction. Wüstite forms a scale when hot iron or steel contacts air. The hot rolling mill is located close to the southeast corner of the Steel Company complex, and elevated levels of wüstite in the eastern core are thus explicable. The wüstite "doublet" (Greenwood & Howe 1972a) is slightly asymmetric because of the spectral interference from one ferric and two ferrous doublets; however, this leads to only minor errors in our computations.

Calculated values of isomer shift (*IS*), quadrupole splitting (*QS*) and half-width (*HW*) for the five iron compounds are listed in Table 2, and iron concentrations (computed from areal ratios and total Fe concentrations) are presented in Table 3 and in Figure 5. All Mössbauer parameters are in generally good agreement with accepted values for the five compounds (*e.g.*, Readman *et al.* 1976, Ruskov & Tomov 1975, Manning & Ash 1978), and hence assignments are confirmed.

Ferric iron concentrations in the harbor muds are too high for significant amounts to be placed in clay-mineral lattices (Manning & Ash 1978). No iron-rich crystalline phases other than wüstite, hematite, chlorite and side-

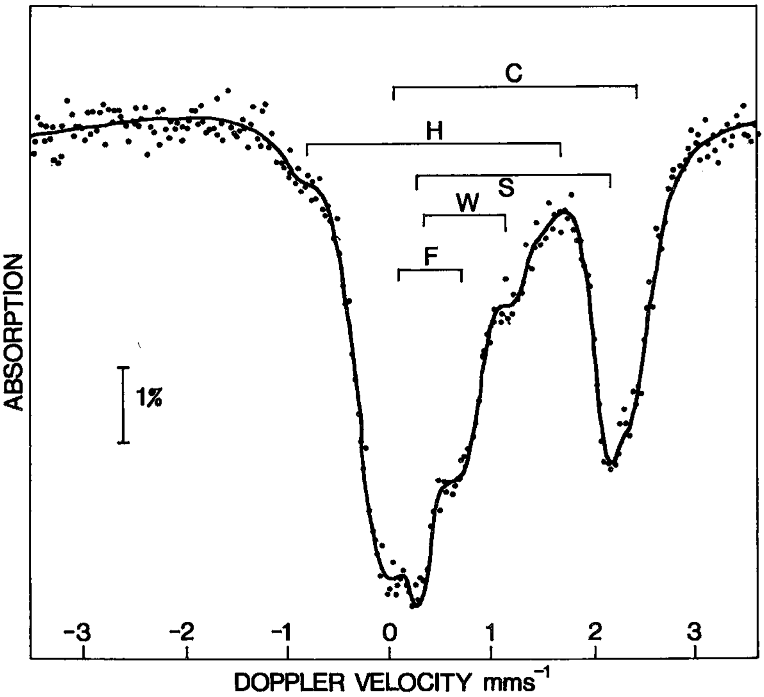

FIG. 3. Room-temperature Mössbauer spectrum of 4–5 cm freeze-dried fraction of eastern core. Continuous curve represents computed fit. Doublets are C = chlorite, F = mainly amorphous ferric compounds, S = siderite, H = hematite and W = wüstite. Chi-squared = 303 with 208 degrees of freedom.

rite were detected by X-ray diffraction of the heavy-mineral fraction, but abundant amorphous material was indicated. The ferric ions are also very persistent in these reducing muds; hence most of the absorption represents refractory amorphous material. Several compounds could contribute to the spectral envelope: (a) amorphous "$Fe(OH)_3$". This is material precipitated from solution and similar compositionally to the brown "ferric hydroxide" in oxic surficial sediments. However, the Eh regime in Hamilton Harbor surficial muds (−100 mV; see Mudroch & Zeman 1975) argues against significant amounts of "$Fe(OH)_3$". None of our cores showed a brown oxidized microzone. (b) pyrite. FeS_2 concentrations were estimated by introducing a sixth doublet and constraining its parameters to those of pyrite (IS = 0.31 mm s^{-1}, QS = 0.61 mm s^{-1}, HW = 0.29 mm s^{-1}; Manning & Ash 1979, Manning *et al.* 1979). On the basis of computations of the better spectra, FeS_2 comprises <10% of the total ferric envelope. (c) super-paramagnetic (~100 Å sized) hematite. Such small particles of large surface-area are probably rapidly reduced in high-sulfide muds. (d) amorphous ferric aluminosilicates. The refractory amorphous ferric compounds (RFCs) in Great Lakes sediments (Manning 1977, Manning & Ash 1978) and in the strongly reducing muds of Hamilton Harbor, Moira Lake (Manning & Ash 1979) and Lake St. George (Manning *et al.* 1979) suggest compositionally and genetically similar material. The light grey mottling in several harbor cores and the very light grey, almost creamy, color of parts of some Lake Erie cores suggest that the RFCs are not highly colored. The oxides and hydroxides of ferric iron are usually intensely colored, *e.g.*, hematite (red), magnetite and wüstite (black) and "$Fe(OH)_3$" (brown). Color is generated by one or more of $O^{2-} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer processes and Fe^{3+}–Fe^{3+} antiferromagnetic interaction (Rossman 1975); in contrast, ferric-rich silicates are often green (Manning 1973). Ferric ions in a silicate or an aluminosilicate will have

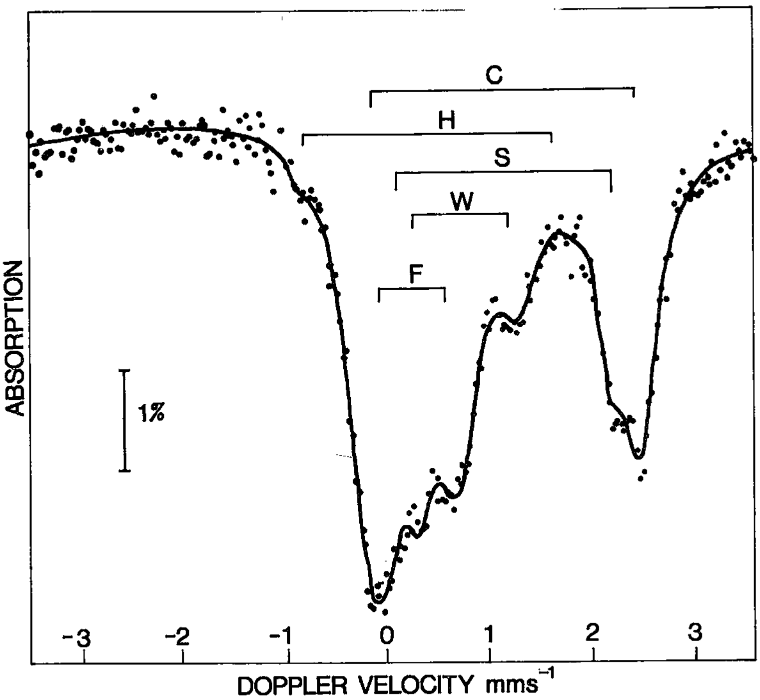

FIG. 4. Room-temperature Mössbauer spectrum of 54–56 cm freeze-dried fraction of eastern core. Continuous curve represents computed fit. Doublets are C = chlorite, F = mainly amorphous ferric compounds, S = siderite, H = hematite and W = wüstite. Chi-squared = 273 with 208 degrees of freedom.

TABLE 2. MÖSSBAUER PARAMETERS AND ASSIGNMENTS OF MAJOR IRON COMPOUNDS IN HAMILTON HARBOR SEDIMENTS

Doublet	IS	QS	HW	Assignment
C	1.14	2.67	0.46	Fe^{2+}, chlorite
S	1.23	1.90	0.30*	Fe^{2+}, siderite
F	0.38	0.76	0.54	Fe^{3+}, amorphous
H	0.46	--	0.27	hematite, Fe_2O_3
W	0.92	0.79	0.60	wüstite, $Fe_{1-x}O$

All values in mms^{-1}; estimated error ±0.03 mms^{-1}. IS values relative to iron foil.

*Siderite half-width constrained in most computations at value derived from computation of Eastern core 4-5 cm fraction (Fig. 3). This HW agrees with that of Readman et al. (1976).

TABLE 3. IRON CONCENTRATION IN WESTERN CORE FRACTIONS. VALUES IN % DRY WT. SEDIMENT

Iron Compound	0-1 cm	17-19 cm	28-30 cm
Fe^{2+}, chlorite	2.6 (2.0)	3.2	2.1
Fe^{2+}, siderite	0.7 (0.5)	0.8	0.4
Fe^{3+}, amorphous	4.3 (2.5)	5.4	2.8
hematite, Fe_2O_3	2.9 (2.5)	1.4	0.4
wustite, $Fe_{1-x}O$	1.2 (1.8)	0.9	0.4

Values in brackets are for Eastern core 0-1 cm fraction

greater separations and less scope for Fe–Fe interactions; consequently, color is less intense.

Nriagu (1978) has summarized published work on the coprecipitation of silica and alumina and of silica and iron from solution. With supportive thermodynamic evidence, he proposed that amorphous ferric aluminosilicates are formed at the sediment–water interface; diatom frustules and the dissolution of clay minerals supply the hydrated silica and alumina. We propose that the refractory nature of the RFCs is explicable in terms of a range of compositionally variable ferric aluminosilicates that are formed at the sediment–water interface. The precipitation of RFCs would undoubtedly bring down some phosphate, Mn and other heavy metals (Gibbs 1973). Supporting this hypothesis are the observed, and measured, releases of Fe, P, Mn and Si from Lake Erie muds during summer anoxia (Burns & Ross 1972). Our model for the RFCs suggests that Al is also released. Furthermore, complex compounds of Fe, Al, Si, Ca and P have been detected in soils and sediments (Sawhney 1973).

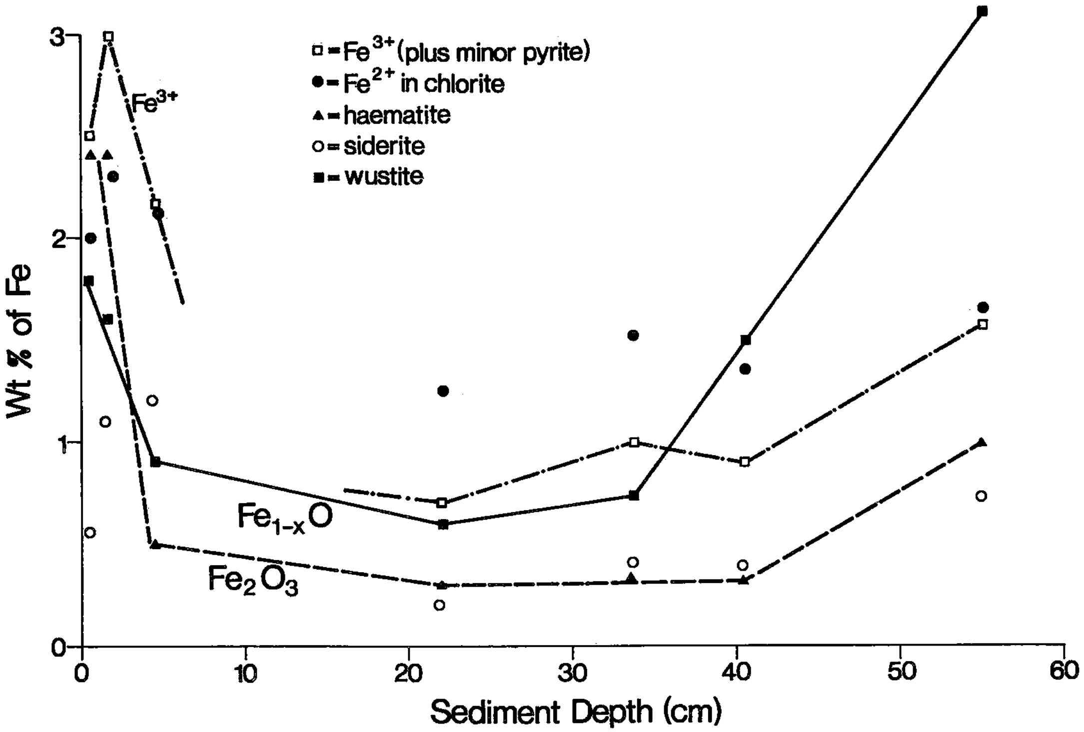

FIG. 5. Calculated concentrations of Fe compounds as a function of depth in freeze-dried fractions of the eastern core.

Background Fe concentrations in the harbor

Harbor muds are compositionally similar to those of Lakes Erie and Ontario (Mudroch 1974, Kemp *et al.* 1976, Thomas *et al.* 1972); hence, anticipated harbor backgrounds are ~4% total Fe with Fe^{3+}:Fe^{2+} (in chlorite) ~1 (Manning & Ash 1978). Total Fe in the undisturbed silty clay (7–8 cm fraction) of the eastern core is ~4%; however, values of ~3% are widespread (Table 1) and may be more representative. The open-water sediments of Coote's Paradise, a marsh- and woodland-bounded bay that drains into the western end of the harbor, contain ~3.5% Fe (Mudroch & Capobianco 1979). Clearly, background levels in the harbor muds are 3–4% Fe.

Iron loadings

Collation of data in Table 3 and Figure 5 and estimated background levels demonstrate that the major Fe pollutants in the upper sediments are ferric iron > hematite > wüstite for both eastern and western cores and probably for silty clay muds of the harbor generally. Some hematite may be derived from the red soils found along the north shore. However, the rapid increase in hematite levels in the top 20 cm of sediment in the eastern core can only be due to industrial activity. Iron loadings to the harbor have decreased over the top 4 cm (Table 1), corresponding to ~20–30 years of deposition, but anthropogenic loading is still three to four times higher than the background.

The RFCs, hematite and wüstite are persistent in the sediments but pose no obvious environmental problems. The RFCs are ecologically the most significant iron compounds in the muds because of their potential benefit in removing phosphate and heavy metals (Gibbs 1973) through adsorption and coprecipitation.

General discussion

The importance of iron in sediments relates to its role in the cycles of phosphate, sulfur and heavy metals (Gibbs 1973). The refractory nature of the RFCs is paramount, because reduction of the ferric iron and the consequent dissolution and release of phosphate and heavy metals in the reduced zone of sediments (rarely

>1 cm below the sediment–water interface) are slow. Ferrous and phosphate ions released to the pore waters would reprecipitate as insoluble vivianite, and iron–phosphorus correlations would be retained. $Fe(OH)_3$ is unstable at the low Eh values characteristic of the harbor sediments, and with abundant Fe^{3+} (from natural and anthropogenic sources) and hydrated silica and alumina (from diatom frustules and from the dissolution of clay minerals), relatively high RFC concentrations and consequently high P retentions are anticipated. Thus, RFC concentrations in harbor muds (3–4% Fe in top 1 cm) exceed those in Lake Erie muds (~1.8%; Manning & Ash 1978). If this model is correct, during summer anoxia only minor amounts of adsorbed P can be released to the water. No summer P release coincident with anoxia was observed in two studies (Ontario Ministry of Environment 1977); however, Harris (1976 and priv. comm.) believes that phosphorus is released in pulses during anoxia, but not in concentrations approaching the 1–3 μmoles l^{-1} measured for hypolimnion of the Lake Erie Central Basin (Burns & Ross 1972). Lenses of cold Lake Ontario water penetrate the bottom waters of the harbor periodically, so that the Central Basin is probably a better location for studying anoxic phosphorus release.

The relative amounts of ferric iron and of phosphate tied up in the brown Eh-sensitive "$Fe(OH)_3$" and in the RFCs are crucial to determining phosphate release from sediments during anoxia. Surficial muds in the Lake Erie Central Basin release significant amounts of phosphorus to the overlying water during summer anoxia (Burns & Ross 1972) but, according to the current model, most of this P is derived from reduction and dissolution of "$Fe(OH)_3$". The photographs of Burns & Ross (1972) clearly show a 0–1 cm yellow-brown layer, colored presumably by "$Fe(OH)_3$", which is replaced in August by black patches of amorphous Fe–S compounds. Deep basins, such as the Central Basin, are favored areas of RFC formation because they are sinks for the fine-grained clay minerals that dissolve to yield hydrated silica and alumina. Inshore areas of the Great Lakes and, in particular, large embayments, with sandy bottoms and low RFC production, are likely to be more susceptible to elevated phosphorus nutrient loads, and therefore would not be representative of the eutrophic state of the lake as a whole.

Can we estimate the phosphorus-fixing capacity of the RFCs? Iron and phosphorus are strongly correlated in harbor muds (R.L. Thomas, priv. comm.), and ~75% of total P is acid-extractable and is probably associated mainly with amorphous ferric-bearing compounds (Ontario Ministry of Environment 1977). In surficial muds of the harbor's western basin, the measured 4% Fe^{3+} in RFCs fixes, say, 0.35% P (total P ~0.5%), for an Fe:P atomic ratio ~6. Lake Erie Central Basin muds contain ~2% Fe^{3+} in RFCs (Manning & Ash 1978), with a presumed capacity of ~0.18% P. Measured NAIP levels in Central Basin muds are ~0.035% (Williams *et al.* 1976b), suggesting that these muds can adsorb considerably more phosphorus. Freshly precipitated "$Fe(OH)_3$" can adsorb P (as phosphate) in the ratio Fe:P ~ 11 (Stamm & Kohlschutter 1965).

The current model highlights the importance of clays in fixing phosphate through RFC formation. The choice of ferric iron or alum to precipitate phosphate artificially in a fertilized lake is then predicated on whether the availability of ferric iron or hydrated alumina limits RFC formation. Hydrated silica, in view of its abundance, probably is not limiting.

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