

MÖSSBAUER SPECTRAL STUDIES OF LAKE ERIE SEDIMENTS

P.G. MANNING

*Nutrient Dynamics Section, Canada Centre for Inland Waters,
Environment Canada, Box 5050, Burlington, Ontario L7R 4A6*

L.A. ASH

*Edward Davies Chemical Laboratories, University College of Wales,
Aberystwyth, Dyfed, U.K. SY23 1NE*

ABSTRACT

Transmission Mössbauer spectra of freeze-dried sediment residuals from the central basin of Lake Erie are reported. The spectra are best-fitted with two quadrupole doublets; the first has the following parameters: isomer shift = 1.14 mm s⁻¹, relative to Fe foil, quadrupole splitting = 2.67 mm s⁻¹, and half-width = 0.39 mm s⁻¹; it is typical of ferrous ions in chlorite. The other (with corresponding parameters of 0.39, 0.64 and 0.64 s⁻¹) reflects ferric ions, most of which are in amorphous hydrated ferric oxides but with smaller amounts in illite and chlorite. Total ferrous : ferric ratios increase with sediment depth, from a value of 0.82 at 0-1 cm to 1.10 at 44-46 cm. The geochemistry of Fe in the Lake Erie sediments has not changed significantly since European settlement (~ 130 years BP). Consequently, the nature of ferric-phosphate interaction and the ability of the sediments to fix phosphate under oxic conditions remain unaltered.

SOMMAIRE

Nous présentons les spectres Mössbauer que donnent, par transmission, les résidus après séchage par congélation de sédiments prélevés dans le bassin central du lac Érié. Ces spectres s'interprètent pour le mieux par deux doublets quadrupoles. Le premier possède un déplacement isomérique de 1.14 mm s⁻¹ par rapport au fer en feuille, un doublement quadrupolaire de 2.67 mm s⁻¹ et une demi-largeur de 0.39 mm s⁻¹, paramètres typiques des ions ferreux dans la chlorite. Le second dont les paramètres correspondants sont 0.39, 0.64 et 0.64 mm s⁻¹, indique des ions ferriques, pour la plupart dans les oxydes ferriques hydratés amorphes, mais aussi (en moindre proportion) dans l'illite et la chlorite. Le rapport Fe²⁺/Fe³⁺ d'un sédiment augmente, avec la profondeur à laquelle on le trouve, de 0.82 (0-1 cm) à 1.10 (44-46 cm). La géochimie du fer dans les sédiments du lac Érié n'a pratiquement pas changé au cours des quelque 130 années écoulées depuis l'arrivée des Européens. Par conséquent, l'interaction entre le Fe ferrique et le phosphate reste immuable, tout comme la

capacité des sédiments de stabiliser le phosphate en milieu oxygéné.

(Traduit par la Rédaction)

INTRODUCTION

It has long been recognized that lake sediments can remove phosphate ions from the overlying waters, thus rendering these ions unavailable for algal growth (Fitzgerald 1970, Burns & Ross 1972, Lean & Charlton 1976). Provided oxic conditions are maintained in the bottom waters, relatively high phosphate concentrations can occur in sediments of oligotrophic lakes (Williams & Mayer 1972). However, the buffering action of muds breaks down during periods of hypolimnion anoxia, when phosphate ions are released to the overlying waters (Mortimer 1941, Mackereth 1966, Burns & Ross 1972, Lean & Charlton 1976). Phosphate regeneration from sediments was observed and measured in Lake Erie in the summer of 1970 (Burns & Ross 1972) following deposition of a 2-3 cm carpet of decomposing algae, and in the Bay of Quinte, Lake Ontario, in the summer of 1974 (Lean & Charlton 1976). Mössbauer spectrometry of the Bay-of-Quinte muds (Manning 1977) demonstrated a coincidence in the reduction of ferric ions in the upper few cm of sediment and phosphate regeneration, seemingly confirming that insoluble ferric phosphate complexes are destroyed under anoxic conditions (Mortimer 1941, Mackereth 1966, Burns & Ross 1972, Lean & Charlton 1976). Because a reasonable correlation exists between phosphate and iron in Lake Erie sediments (Kemp *et al.* 1976), a determination of the principal iron-bearing compounds is desirable. Recent Mössbauer studies of lake sediments have demonstrated the widespread occurrence of amorphous ferric hydroxides (Coe *et al.* 1974, Coe 1975a, Readman *et al.* 1976, Manning 1977), and such compounds are probably the important phosphate binders in sediments.

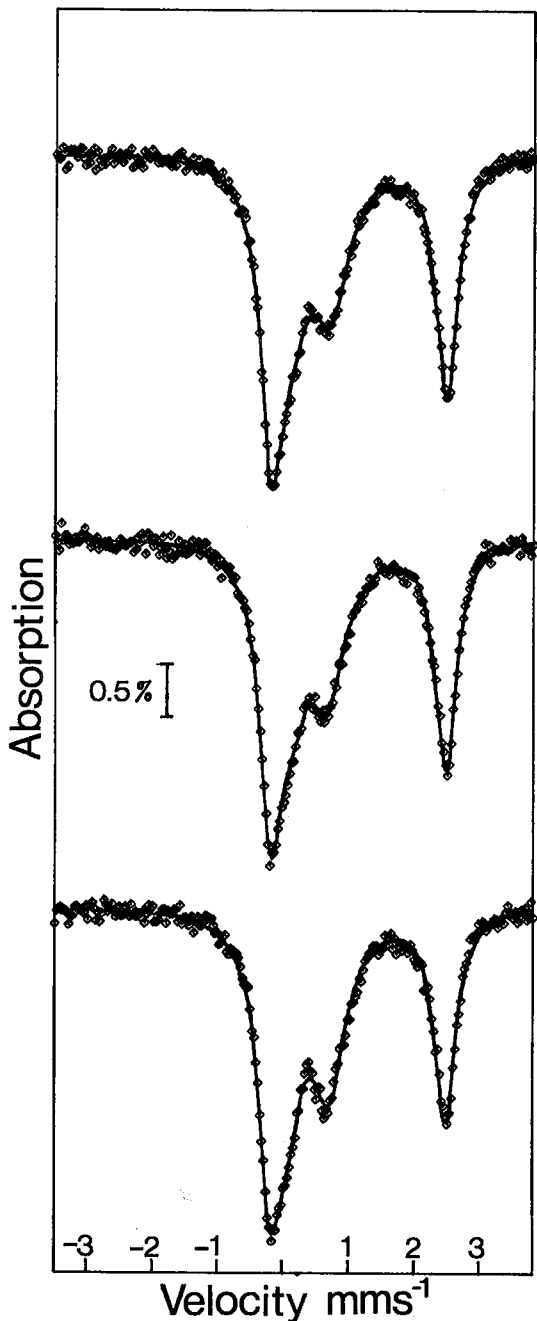


FIG. 1. Room-temperature Mössbauer spectra of Lake Erie sediment residuals. Upper curve is the 0–1 cm fraction, middle curve the 15–16 cm fraction, and the lower curve the 44–46 cm fraction. Chi-squared values are, respectively, 300 with 240 degrees of freedom, 313 with 240 degrees of freedom, and 290 with 240 degrees of freedom. Sediments contain 4.5% Fe and $\sim 0.1\%$ S (Kemp *et al.* 1976).

This article describes the Mössbauer spectra of freeze-dried fractions of a 50 cm core taken from the central basin of Lake Erie in August 1977. As is usually the case in summer, the hypolimnion waters were anoxic, and no brown oxidized microzone was observed in the top few mm of sediments; all fractions were grey. The sampling position, latitude $41^{\circ}54'12''$, longitude $80^{\circ}41'00''$, is close to station G-16 used by Kemp *et al.* (1976) in their central-basin-sediment studies; at that time, too, hypolimnion waters were anoxic.

EXPERIMENT DETAILS

Sediment cores were collected using a single Benthos gravity corer. The corer was allowed to settle before striking the sediment surface, and was then lowered slowly so as to minimize disturbance of the surface. The cores were sectioned immediately and the samples sealed and frozen on board ship. The sediments were freeze-dried on return to the laboratory and the residuals stored in a vacuum desiccator. All fractions were grey in color, with the deeper sediments being slightly darker. No black patches indicative of precursor sulfides (Berner 1970) were observed, nor was there a brown microzone in the top few mm of the core. The sediments contain 4.5% Fe and $\sim 0.1\%$ S, dry weight of sediment.

Transmission Mössbauer spectra of freeze-dried residuals were obtained as described earlier (Manning & Tricker 1975). Experimental envelopes were fitted using the computer program written by Stone (1967) and assuming Lorentzian line shapes. Halfwidths and area ratios of each peak of a quadrupole doublet were constrained to be equal. Chi-squared tests and visual examination of the spectra were used to obtain a good fit.

RESULTS AND DISCUSSION

Three representative Mössbauer spectra of Lake Erie sediment residuals are shown in Figure 1. The spectra are almost identical to each other and are also similar to spectra measured for sediment residuals from the Bay of Quinte, Lake Ontario (Manning 1977). The peak at ~ 2.4 mm s $^{-1}$ occurs at an energy characteristic of octahedrally-bonded ferrous ions (Bancroft 1973); the other peak of the doublet contributes to absorption at ~ 0 mm s $^{-1}$. The peak at

$\sim 0.7 \text{ mm s}^{-1}$, with its counterpart at $\sim 0 \text{ mm s}^{-1}$, probably reflects ferric ions in octahedral coordination. The Fe:S atomic ratio in Lake Erie sediments is sufficiently high (~ 40 ; Kemp *et al.* 1976) that pyrite absorptions, which are expected to overlap with ferric absorptions, can be ignored. Calculated values of isomer shift (IS), quadrupole splitting (QS) and half-width (HW), based on a two-doublet fit, are listed in Table 1.

TABLE 1. CALCULATED MÖSSBAUER PARAMETERS (IN mm s^{-1}) FOR IRON COMPOUNDS IN LAKE ERIE SEDIMENT FRACTIONS.

Sediment fraction, cm	Doublet II			Doublet I			Fe ²⁺ :Fe ³⁺
	IS	QS	HW	IS	QS	HW	
0-1	0.38	0.66	0.62	1.14	2.67	0.39	0.82
1-2	0.41	0.64	0.63	1.14	2.67	0.39	0.90
3-4	0.39	0.65	0.68	1.14	2.66	0.39	0.92
15-16	0.39	0.60	0.64	1.14	2.67	0.39	1.01
34-36	0.40	0.63	0.63	1.14	2.67	0.39	1.04
44-46	0.40	0.63	0.65	1.14	2.67	0.40	1.10

IS = isomer shift (relative to Fe foil); QS = quadrupole splitting, and HW = peak half-width.

Estimated error in IS and QS = $\pm 0.02 \text{ mm s}^{-1}$

The IS, QS and HW values for doublet I undoubtedly reflect ferrous ions in octahedral coordination, probably in a field of oxygen and OH ions. The constancy in the Mössbauer parameters over the length of the core suggests that the ferrous ions are in a well-crystallized material. The parameters are similar to those reported for Fe²⁺ ions in chlorite (Coey 1975a, b), whereas the QS value is significantly different from that reported for Fe²⁺ in illite (Coey 1975b), the principal clay mineral in Lake Erie sediments (Thomas 1969). Kaolinite rarely contains significant amounts of ferrous ions (Coey 1975b, Deer *et al.* 1962). Chlorite comprises $\sim 20\%$ of the clay-mineral fraction in Lake Erie muds (Thomas 1969), confirming that most Fe²⁺ ions are in a chlorite lattice.

The IS and QS values measured for doublet II (Table 1) are typically those of ferric ions in an octahedral field of oxygen and OH ions (Bancroft 1973). The very broad absorptions (HW $\sim 0.65 \text{ mm s}^{-1}$) indicate the presence of ferric ions in a wide variety of different octahedra. Chlorites are generally much richer in ferrous than in ferric iron (Deer *et al.* 1962); hence, only a minor proportion of the ferric absorptions can arise from chlorite. The calculated Mössbauer parameters are significantly different from those reported for ferric ions in kaolinite and illite (Coey 1975b). Moreover, Al:Fe ratios for most kaolinites (Deer *et al.* 1962)

are $\sim 100:1$; if this ratio holds for Lake Erie kaolinites, and as these sediments contain $\sim 9\%$ Al, then clearly ferric ions in kaolinite form an almost negligible part of the total ferric iron concentration ($\sim 2\%$). The Mössbauer parameters are similar to those reported for amorphous ferric gels (Mathalone *et al.* 1970); hence, it seems reasonable to suggest that most of the ferric absorption arises from amorphous hydrated ferric oxides, with a smaller but probably significant contribution from illite. Amorphous ferric compounds have been postulated for sediments from different lakes (Coey *et al.* 1974, Coey 1975a, Readman *et al.* 1976, Manning 1977).

Ferrous: ferric ratios are listed in Table 1. Reduction of ferric iron occurs relatively rapidly in the upper 5 cm of sediment, but at greater depth the rate of reduction is more gradual. Because the concentrations of ferrous and ferric ions that can partake in redox reactions are not known, Eh values cannot be calculated. For station G-16 (Kemp *et al.* 1976), Eh values were negative for the upper 3 cm of sediment-water admixture, but below this, Eh values were constant and close to zero. Presumably, the rate of reduction of ferric iron depends on the rate of electron transfer in the solid; fine-grained materials, having the largest surface areas, are those most easily reduced, and this reduction occurs in the upper few cm.

Under conditions of hypolimnion anoxia in the central basin, Burns & Ross (1972) calculated a release of $240 \mu\text{mol P m}^{-2} \text{ day}^{-1}$. The current Mössbauer analysis shows a ferric iron content in the top 1 cm of sediment of $\sim 1.5 \text{ moles m}^{-2}$. If anoxia persisted for 60 days and if one assumes that one "reactive" ferric ion fixes one phosphate, then 1% of total Fe³⁺ was used in fixing the released phosphate.

The Ambrosia horizon at station G-16 (Kemp *et al.* 1976) occurs at a sediment depth of $\sim 30 \text{ cm}$, corresponding to deposition ~ 130 years BP. Our Mössbauer results for fractions 34-36 and 44-46 cm show that the geochemistry of Fe in the upper few cm of sediment has not changed significantly over the last 130 years; the differences in Fe²⁺:Fe³⁺ ratios for the current 0-1 cm, 34-36 cm and 44-46 cm fractions is simply a product of diagenesis. Consequently, the nature of the ferric-phosphate interaction at the sediment-water interface has not changed since pre-settlement days.

Surprisingly, high concentrations of ferric ions are bound in poorly crystallized or amorphous material, even in the deeper sediment

fractions. Ferric ions can be placed into three categories: (a) ferric ions in fine-grained amorphous material located mainly in the oxidized microzone. These ions are efficient binders of phosphate but are rapidly reduced under hypolimnion anoxia, causing phosphate release; (b) ferric ions in amorphous or poorly crystalline materials which are reduced over hundreds of years. This group may represent "aged", possibly polymerized ferric hydroxides; significant amounts of adsorbed phosphates are fixed and rendered unavailable during the aging process. The reduced ferric phosphate is converted mainly into vivianite. In sulfide-rich sediments, however, reduction and dissolution of ferric phosphates and fine-grained goethite and chlorite proceed more rapidly (Berner 1970). Pyrite formation implies a permanent loss of phosphate-fixing sites in such strongly reducing sediments; (c) ferric ions that are relatively inert, i.e., those in well-crystallized chlorite and illite.

ACKNOWLEDGMENTS

We thank Mr. Henry Wong and the crew of the LIMNOS for assistance in coring, and professor J.M. Thomas and Dr. W. Jones for the use of the Mössbauer and computing facilities. We are grateful to Drs. N.M. Burns and J.D.H. Williams for useful discussions and to Dr. D.R.S. Lean and K. Burnison for reading the manuscript.

REFERENCES

- BANCROFT, G.M. (1973): *Mössbauer Spectroscopy. An Introduction for Inorganic Chemists and Geochemists*. McGraw-Hill, London.
- BERNER, R.A. (1970): Sedimentary pyrite formation. *Amer. J. Sci.* 268, 1-23.
- BURNS, N.M. & ROSS, C. (1972): Oxygen-nutrient relations within the central basin of Lake Erie. In *Nutrients in Natural Waters* (H.E. Allen & J.R. Kramer, eds.), John Wiley & Sons, New York.
- COEY, J.M.D. (1975a): Iron in a post-glacial lake sediment core; a Mössbauer effect study. *Geochim. Cosmochim. Acta* 39, 401-415.
- (1975b): The clay minerals: use of the Mössbauer effect to characterize them and study their transformation. *Proc. Int. Conf. Mössbauer Effect (Cracow)*, 333-354.
- , SCHINDLER, D.W. & WEBER, F. (1974): Iron compounds in lake sediments. *Can. J. Earth Sci.* 11, 1489-1493.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals. 3. Sheet Silicates*. Longmans, London.
- FITZGERALD, G.P. (1970): Aerobic lake muds for the removal of phosphorus from lake waters. *Limnol. Oceanogr.* 15, 550-555.
- KEMP, A.L.W., THOMAS, R.L., DELL, C.I. & JAQUET, J.M. (1976): Cultural impact on the geochemistry of sediments in Lake Erie. *J. Fish. Res. Board Can.* 33, 440-462.
- LEAN, D.R.S. & CHARLTON, M.N. (1976): A study of phosphorus kinetics in a lake ecosystem. In *Environmental Biogeochemistry* (J.O. Nriagu, ed.), *Proc. 2nd Int. Symposium* (1975) 1, Ann Arbor Sci., Ann Arbor, Michigan.
- MACKERETH, F.J.H. (1966): Some chemical observations on post-glacial lake sediments. *Roy. Soc. London Phil. Trans* 250B, 165-213.
- MANNING, P.G. (1977): Mössbauer spectral studies of ferric phosphate interaction in sediments underlying oxic lake waters. *Can. Mineral.* 15, 422-426.
- & TRICKER, M.J. (1975): Optical-absorption and Mössbauer spectral studies of iron and titanium site-populations in vesuvianites. *Can. Mineral.* 13, 259-265.
- MATHALONE, Z., RON, M. & BIRAN, A. (1970): Magnetic ordering in iron gel. *Sol. State Comm.* 8, 333-336.
- MORTIMER, C.H. (1941): The exchange of dissolved substances between mud and water in lakes. *J. Ecol.* 29, 280-329.
- READMAN, P.W., COEY, J.M.D., MOSSER, C. & WEBER, F. (1976): Analysis of some lake sediments from Greece. *J. Phys. (Paris)* 37, (*Colloq.* 6), 845-848.
- STONE, A.J. (1967): Appendix In Bancroft, G.M., Maddock, A.G., Ong, W.K. & Prince, R.H.: Mössbauer spectra of Fe(III) acetylacetonates. *J. chem. Soc.* 1967A, 1966-1971.
- THOMAS, R.L. (1969): A note on the relationship of grain size, clay content, quartz and organic carbon in some Lake Erie and Lake Ontario sediments. *J. Sed. Petrology* 39, 803-809.
- WILLIAMS, J.D.H. & MAYER, T. (1972): Effects of sediment diagenesis and regeneration of phosphorus with special reference to Lakes Erie and Ontario. In *Nutrients in Natural Waters* (H.E. Allen & J.R. Kramer, eds.), John Wiley & Sons, New York.

Received May 1978; revised manuscript accepted August 1978.