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MÖSSBAUER SPECTRAL STUDIES OF FERRIC PHOSPHATE INTERACTION IN SEDIMENTS UNDERLYING OXIC LAKE WATERS

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ABSTRACT

Mössbauer spectra were obtained of freeze-dried sediment samples from the Bay of Quinte, a shallow eutrophic bay on the northern shore of Lake Ontario. Spectra were measured on sections from the upper 6 cm of sediment collected beneath 4 m of oxic water during late July and August, a period covering a massive release of phosphate from the sediments to the overlying waters (Lean & Charlton 1976). The spectra comprise two resolvable doublets which mark ferrous and ferric ions in octahedral coordination. Fe^{3+}:Fe^{2+} ratios for the 0-2 cm sections of core decreased from late July (ratio=2.8) to late August (ratio=2.2), showing that the release of phosphate is coincident with the reduction of sediment-bound ferric ions. For fractions of core collected in late August, Fe^{3+}:Fe^{2+} ratios increased in the order 0-2 cm (ratio=2.23), 2-4 cm (=2.51), 4-6 cm (=2.71); in contrast, Fe^{3+}:Fe^{2+} ratios for 0-2 cm, 2-4 cm, and 4-6 cm fractions collected in mid-June were equal. Calculated values of isomer shift (IS) and of quadrupole splitting (QS) are: for Fe^{3+}, IS=0.37 mm s^{-1} and QS=0.67 mm s^{-1}, and for Fe^{2+}, IS=1.13 mm s^{-1} and QS=2.53 mm s^{-1}. These results are consistent with the theory that, for most of the year, ferric phosphate complexes are a sink for phosphate ion, but under the reducing conditions generated by the decay of the load or organic matter deposited in early summer, the complexes are unstable and phosphate is released. The ferric ions are present on exchangeable cation sites in amorphous hydrated ferric oxides or in clay minerals.

SOMMAIRE

Des échantillons de sédiments provenant de la baie de Quinte, baie eutrophe peu profonde sur la rive nord du lac Ontario, ont été séchés à froid, puis étudiés par spectroscopie Mössbauer. Les spectres mesurés ont été obtenus sur des sections prélevées, de fin juillet à fin août, dans la couche supérieure (épaisse de 6 cm) de sédiments submergés par 4 m d'eau oxique. Pendant cette période de l'année, les sédiments dégagent dans l'eau une grande quantité de phosphate (Lean & Charlton 1976). Les spectres comprennent deux doublets résolus, caractéristiques d'ions ferriques et ferreux en coordination octaédrique. Le rapport ionique Fe^{3+}/Fe^{2+}, déterminé dans les sections du tiers supérieur de la carotte (0-2 cm), décroît en fonction du temps de 2.8 (fin juillet) à 2.2 (fin août), preuve que le dégagement de phosphate accompagne la réduction des ions ferriques liés aux sédiments. Ce même rapport, déterminé dans les carottes prélevées à la fin d'août, croît avec la profondeur. 2.23 (0-2 cm), 2.51 (2-4 cm), 2.71 (4-6 cm), tandis qu'il reste constant pour les carottes de la mi-juin. Les valeurs calculées du déplacement isomère (IS) et du dédoublement quadripolaire (QS) sont les suivantes: pour Fe^{3+}, IS = 0.37 mm s^{-1} et QS = 0.67 mm s^{-1}; pour Fe^{2+}, IS = 1.13 mm s^{-1} et QS = 2.53 mm s^{-1}. Ces résultats sont compatibles avec la théorie qui veut que, pendant presque toute l'année, les complexes de phosphate ferrique constituent un réservoir d'ions phosphate, mais que, dans le milieu réducteur créé par la décomposition des dépôts organiques du début de l'été, les complexes aillent occuper les sites du cation échangeable dans des oxydes ferriques hydratés ou dans des minéraux argileux.

(Traduit par la Rédaction)

INTRODUCTION

The importance of phosphate in the accelerated eutrophication of lakes has stimulated much research into the elucidation of phosphate compartments in lakes. Phosphate ion is a limiting nutrient in many inland waters. Dramatic increases in phosphate loadings of lakes in recent years have caused considerable deterioration in water quality, brought about in large measure through the promotion of algal growth and the consequent consumption of oxygen by decaying algae. It has been claimed (Fitzgerald 1970) that muds may remove phosphate ions from waters that remain oxic and that such phosphate becomes unavailable for algal growth. However, the formation of sediment-bound ferric phosphate complexes which break down under anoxic conditions also has been recognized for many years (Mortimer 1942; Mackereth 1966).

Burns & Ross (1972) have shown that a massive algal bloom in Lake Erie in July 1970 was followed by the deposition of a 2 to 3 cm-thick layer of algae on the lake floor; subsequent algal decomposition led to anoxic conditions and release of phosphate to the overlying waters, and further massive blooms occurred when these phosphate-rich waters were mixed with surface waters in September. Lean & Charlton (1976) studied similar events in the Bay of Quinte, which is a shallow eutrophic bay on the northern shore of Lake Ontario, using three triangular-shaped enclosures of cross-sectional area 25 m^2. The enclosures were installed in 4 m of water, and at this site the overlying waters neither stratified nor became anoxic. Corral I received no external phosphate nor nitrate input, Corral II received phosphate only, and Corral III received both phosphate and nitrate. Enrichment began on 24 May 1974 with rates of 0.88 gP $m^{-2}yr^{-1}$ and 11 gN $m^{-2}yr^{-1}$. Nutrients were added weekly, except during mid-summer when daily additions were made. From October 1973 through July 1974, the concentrations of total phosporus in the overlying waters were approximately equal in all three corrals and averaged 40 mgP l^{-1}, but in early August phosphate levels increased dramatically in Corral III, reaching 380 mgP l^{-1} by the end of August. This value exceeded the quantity of phosphorus added to the water during this event by ~50% and clearly demonstrated the release of phosphate from the sediments. This release stimulated an algal bloom, and chlorophyll concentrations in the water followed the increasing trend in total phosphate.

The release of phosphate under anoxic conditions has been ascribed (Mortimer 1942; Mackereth 1966; Lean & Charlton 1976; Burns & Ross 1972) to the reduction of sediment-bound ferric ions which are present in ionic association with phosphate and possibly organic matter; ferrous phosphate complexes are weaker than ferric phosphate. Redox processes in sediments may be implied in extreme cases by observations of color changes, from the yellows and light browns of hydrated ferric oxides in the oxidized layer to the black of reduced iron sulfides. However, the reduction of ferric ions coincident with phosphate dissolution, and the nature of the complexes involved, have not been studied using modern quantitative spectroscopic methods.

The facility with which Mössbauer techniques may be applied to identify Fe-bearing minerals in sediments under favorable conditions has been demonstrated (Coey 1975a,b; Coey *et al.* 1974; Perlow *at al.* 1974); Fe^{2+} in chlorite and Fe^{3+} in well-crystallized iron oxides are readily identified. Ferric ions in silicates and in amorphous oxides are more difficult to differentiate because all absorb in the same region of the energy spectrum.

This article describes a Mössbauer spectral study of a series of three Bay of Quinte sediments sampled at the upper 0-2 cm level on 27 July 1974, 8 August and 27 August 1974, a series of three at the 0-2 cm, 2-4 cm and 4-6 cm levels from the same core on 13 June 1974, and a series of three at the 0-2 cm, 2-4 cm and 4-6 cm levels on 27 August 1974. The first series gives a direct indication of reduction in the most active zone whereas the other two series permit a comparison of Eh profiles during August and during less biologically-active periods of the year. Total Fe concentrations are ~3% (dry weight) and are constant at least over the upper 6 cm of sediment.

EXPERIMENTAL DETAILS

Sediment cores were obtained weekly by Lean & Charlton (1976), as part of their program, using a Kajak-Brinkhurst corer (Guelph Instruments). The cores were sectioned immediately on extrusion into 0-2 cm, 2-4 cm, 4-6 cm, etc., fractions. The fractions were centrifuged for 10 mins. in capped 50 ml-capacity centrifuge tubes to remove pore water. The sediment and pore water occupied approximately 60% of the volume of the tubes and, in those tubes tested, the pore water remained anoxic. The pore waters were removed by pipette and the residue frozen immediately. The residues were later freeze-dried and stored as dry solids in capped vials. The Bay of Quinte sediments are rich in organic matter (>10% dry weight) and this, together with the rapid treatment of the cores, suggests that oxidation of the specimens after sampling is probably not serious.

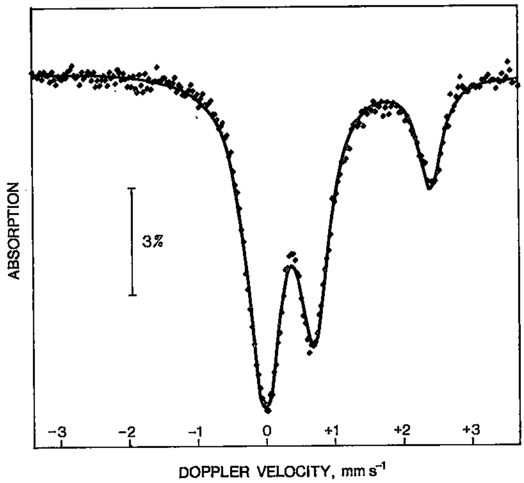

FIG. 1. Room-temperature Mössbauer spectrum of Bay of Quinte sediment sample at 4-6 cm core-depth on 27 August 1974. Total counts per channel 0.7×10^6. Chi-squared = 240 for 240 degrees of freedom.

TABLE 1. Fe^{3+}:Fe^{2+} RATIOS AND MÖSSBAUER SPECTRAL LINE HALF-WIDTHS FOR Fe^{3+} AND Fe^{2+} IONS IN SECTIONS OF BAY OF QUINTE SEDIMENTS

Date, 1974	Section, cm	Fe^{3+}:Fe^{2+}*	Line half-width** mm s^{-1}	
			Fe^{3+}	Fe^{2+}
13 June	0-2	2.65	0.53	0.41
13 June	2-4	2.60	0.54	0.47
13 June	4-6	2.59	0.52	0.45
27 July	0-2	2.80	0.52	0.45
8 August	0-2	2.67	0.54	0.42
27 August	0-2	2.23	0.53	0.50
27 August	2-4	2.51	0.54	0.46
27 August	4-6	2.71	0.52	0.43

* Estimated error ±4%; ** estimated error ±0.02 mm s^{-1}.

For Fe^{3+} ions, IS = 0.37 mm s^{-1} and QS = 0.67 mm s^{-1}; for Fe^{2+} ions, IS = 1.13 mm s^{-1} and QS = 2.53 mm s^{-1}. IS values relative to Fe foil.

Mössbauer spectra of freeze-dried, powdered sediment residuals were run on equipment at the Chemistry Department, University College of Wales, Aberystwyth; experimental procedures followed those described in earlier work (Manning & Tricker 1975). Computer analysis was performed on the University of Manchester Regional Computer Centre CDC 6600 machine using fitting programs written by Stone (1967).

RESULTS AND DISCUSSION

A representative Mössbauer spectrum of the Bay of Quinte sediments is shown in Figure 1. Ferric:ferrous concentration ratios for eight fractions measured are in the range 2.2 to 2.8. From its position in the spectrum, the main doublet with peaks at the Doppler velocities ~0 mm s^{-1} and 0.8 mm s^{-1} represents absorption by high-spin ferric ions (Bancroft 1973). There may be some contribution to absorption from Fe (II) in pyrite, but Fe:S ratios in comparable Lake Erie sediments are ~40:1 (Kemp *et al.* 1976), hence the pyrite contribution is probably small. The Mössbauer parameters measured from spectra of the eight sediment fractions are isomer shift (IS) = 0.37±0.02 mm s^{-1} (relative to Fe foil) and quadrupole splitting (QS) = 0.67±0.02 mm s^{-1}, quoted as averaged values. The IS value is strongly indicative of ferric ions in octahedral fields (Bancroft 1973). The rather large half-widths (~0.55 mm s^{-1}, Table 1) reflect ferric ions in a variety of different sites, which in light of the geochemistry of ferric ions are probably distorted octahedra. Mössbauer parameters for paramagnetic ferric ions fall in too narrow a range to be diagnostic of the parent compound, but the IS and QS values are similar to those of Fe^{3+} ions in X-ray amorphous ferric oxides (Coey *et al.* 1974). The principal clay mineral in the Bay of Quinte sediments is illite (R. L. Thomas, private comm.), but the published QS value for Fe^{3+} in illite (=0.52 mm s^{-1}; Coey 1975b) seems significantly different from the QS value measured here.

The absorption at ~2.2 mm s^{-1} is the high-velocity component of the ferrous doublet, the low-velocity component contributing to absorption at ~0 mm s^{-1}. Calculated values of IS=1.13 mm s^{-1} and QS=2.53 mm s^{-1} are consistent with ferrous ions in octahedral fields. The half-widths of the peaks (0.4 to 0.5 mm s^{-1}, Table 1) suggest that the ferrous ions are located in two or more octahedra of different symmetry. The calculated values of IS and of QS are similar to published values for Fe^{2+} in some trioctahedral sheet-silicates; e.g. chlorite (Table 1) IS=1.15 mm s^{-1} and QS=2.63 mm s^{-1} (Coey 1975b).

Fe^{3+}:Fe^{2+} ratios measured for the 0-2 cm, 2-4 cm, and 4-6 cm fractions sampled on 13 June 1974 are approximately equal and are probably indicative of the trend in Eh for the upper 6 cm during less biologically-active periods of the year. If the uppermost 1 cm of sediment could be sampled reliably, the presence of a more strongly oxidized zone could possibly be demonstrated. As it is, the difference in Fe^{3+}:Fe^{2+} ratios measured for the 13 June fractions is probably within experimental error. These data also suggest that oxidation of the sediments on processing is not a serious problem, because it is unlikely that all would oxidize extensively to the same degree.

Ferric:ferrous concentration ratios (Table 1) for the 0-2 cm fractions decrease in the order 27 July, 8 August, and 27 August, reflecting a significant degree of reduction of ferric ions. Values of Fe^{3+}:Fe^{2+} for the 27 August fractions increase in the order 0-2 cm, 2-4 cm, and 4-6 cm, which is in contrast to the trend exhibited by the 13 June fractions. Generally, in periods of low biological activity, the upper few cms of sediment are oxidized and characterized by brown ferric oxides (Mortimer 1942; Burns & Ross 1972). Measurements of sediment–water intermixtures in the Western Basin of Lake Erie (Kemp *et al.* 1976) show that Eh values decrease with depth over the upper few cms. This is supported by visual and photographic evidence (Burns & Ross 1972) of brown oxides at the surface which overlie black iron sulfides; in June, the oxidized layer was ~1 cm thick whereas in September the layer had disappeared. The Fe^{3+}:Fe^{2+} ratio for the 4-6 cm section of 27 August is slightly smaller than the 0-2 cm 27 July value, suggesting that reduction occurs mainly in the upper 6 cm of sediment. Therefore, the reduction of sediment-bound ferric ions coincident with release of phosphate would seem to be proved.

Reduction of Fe^{3+} occurs in a period of days. Bearing in mind the relatively low temperatures characteristic of sediments, in contrast to the elevated temperatures required to reduce Fe^{3+} in ceramic formation in the presence of organic matter (Hess & Perlman 1974), it would seem that most of the Fe^{3+} ions are not incorporated within a silicate structure. Mössbauer studies of reduction spots in purple slates from North Wales (Manning 1975) show that the decay of an organic-rich nucleus in ancient sediments caused reduction of ferric ions in hydrated oxides but not ferric ions in chlorite. The ferric ions that are reduced in the Bay of Quinte sediments would therefore seem to be present as amorphous hydrated ferric oxides or are present in cation sites within colloidal clays. Spectra measured at 77°K did not reveal a magnetic six-line pattern, indicating that, if oxides, the particle sizes are <200Å across (Gangas *et al.* 1973).

Significantly, the decrease in Fe^{3+}:Fe^{2+} values for the 4-6 cm, 2-4 cm, and 0-2 cm 27 August fractions is accounted for largely in the increased width of the ferrous absorption. This broadening probably reflects the recently-produced ferrous ions. Mössbauer resonance implies that these ferrous ions are insoluble. Also, there is no evidence of Fe^{2+}–S or Fe^{2+}–SH interaction. If the parent ferric complexes are oxides or hydroxides, then presumably the daughter ferrous ions are associated with refractory organic matter. The parent Fe^{3+} compound would then seem to be a mixed-ligand complex of the type (phosphate) M^{3+} (organic ion), where M^{3+} represents Fe^{3+} as an oxide or hydroxide. Soluble complexes of the type (phosphate)M(carboxylate anion) are of enhanced stability (Ramamoorthy & Manning 1974). Alternatively, the parent ferric ions could be on cation exchange sites within colloidal clays. The Mössbauer absorptions of the freshly-produced ferrous ions are centered on, but are broader than, those of the "background" ferrous ions, hence it would seem that all ferrous ions measured here are on readily exchangeable sites; the principal difference is that the freshly-produced ferrous ions are in a greater variety of distorted octahedral sites. Measurements of half-widths could be useful in following the ageing or "annealing" of sediments.

The Mössbauer data show that approximately 5% to 10% of the Fe^{3+} in the 0-2 cm section of core had been reduced by 27 August. The total weight of iron in such a section of 1 m^2 cross-section is ~500 g and that of Fe^{3+} is ~350 g or 7 moles. If 1 mole of Fe^{3+} fixes 1 mole of PO_4, the fixing capacity of the 0-2 section is 700 g PO_4 m^{-2}. A 7.5% reduction of Fe^{3+} would then release 50 g PO_4 m^{-2} to the overlying waters, which compares with experimentally measured release of 1.5 g PO_4 m^{-2}. The phosphate-fixing capacity of the sediment does not appear to be exhausted.

A particularly interesting feature of the current work is the demonstration that, even though the overlying waters remain oxic in July and August, in the upper few cm of sediments the reduction of ferric ion caused by the decay of algae is coincident with the release of phosphate, which then becomes available for the growth of further algal blooms. Much of the phosphate in sediments is probably tied up as ferric phosphate complexes and also as Al^{3+} phosphate complexes which presumably are stable under anoxic conditions. Increasing the Al:Fe ratio in sediments in small lakes might reduce phosphate release in August, but in general a decrease in organic matter loading is suggested.

It should be stressed that the current study does not prove direct bonding between ferric and phosphate ions in sediments. Nevertheless, the strong correlation of iron and phosphate in sediments with depth (Mortimer 1942; Mackereth 1966) is usually accepted as evidence for some form of interaction. Ferric ion in these sediments is the most abundant cation that can be reduced, and it seems reasonable to infer bonding between ferric ions and phosphate.

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REFERENCES

BANCROFT, G. M. (1973): *Mössbauer Spectroscopy*. McGraw-Hill, London.

BURNS, N. M. & ROSS, C. (1972): Oxygen-nutrient relationship within the central basin of Lake Erie. *In* Project Hypo (N. W. Burns, ed.), *C.C.I.W. U.S.E.P.A. Tech. Rep.* TS-05-71-208-24.

COEY, J. M. D. (1975a): Iron in post-glacial sediment core: a Mössbauer effect study. *Geochim. Cosmochim. Acta* **39**, 401-416.

——— (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**, 1489-1491.

DAMIANI, V. & THOMAS, R. L. (1974): The surficial sediments of the Big Bay Section of the Bay of Quinte, Lake Ontario. *Can. J. Earth Sci.* **11**, 1562-1576.

FITZGERALD, G. P. (1970): Aerobic lake muds for the removal of phosphorus from lake muds. *Limnol. Oceanogr.* **15**, 550-555.

HESS, J. & PERLMAN, I. (1974): Mössbauer spectra of Fe in ceramics. *Archeometry* **16**, 137-152.

GANGAS, N. H., SIMOPOULOS, A., KOSTIKAS, A., YASSOGLOU, N. J. & FILIPPAKIS, S. (1973): Mössbauer studies of small particles of iron oxides in soils. *Clays Clays Minerals* **21**, 151-160.

KEMP, A. L. W., THOMAS, R. L., DELL, C. I. & JACQUET, 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 Biochemistry (J. O. Nriagu, ed.). Ann Arbor Science, Ann Arbor, Michigan.

MACKERETH, F. J. H. (1966): Some observations on post-glacial lake sediments. *Phil. Trans.* **250**, 165-213.

MANNING, P. G. (1975): Mössbauer studies of the reduction spots in Welsh purple roofing slates. *Can. Mineral.* **13**, 358-360.

——— & TRICKER, M. J. (1975): Optical-absorption and Mössbauer spectral studies of iron and titanium site-population in vesuvianites. *Can. Mineral.* **13**, 259-265.

MORTIMER, C. H. (1942): The exchange of dissolved substances between mud and water in lakes. *J. Ecol.* **29**, 280-329.

PERLOW, G. J., POTZEL, W. & EDDINGTON, D. (1974): Serial study of lake Michigan sediments by Mössbauer spectroscopy. *J. Physique* **35**, C6 547-548.

RAMAMOORTHY, S. & MANNING, P. G. (1974): Formation and stabilities of quaternary complexes of Fe^{3+} in solutions of phosphate, fulvate and simple carboxylate ligands. *Inorg. Nucl. Chem. Lett.* **10**, 109-114.

STONE, A. J. (1967): Appendix. *J. Chem. Soc.* **1976A**, 1966-1971.

WEAVER, C. E., WAMPLER, J. M. & PECUIL, T. E. (1967): Mössbauer analysis of Fe in clay minerals. *Science* **156**, 504-508.

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