The Canadian Mineralogist
Vol. 32, pp. 459-468 (1994)

FORMS OF IRON AND THE BIOAVAILABILITY OF PHOSPHORUS IN EUTROPHIC AMISK LAKE, ALBERTA

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ABSTRACT

Mössbauer spectral studies indicate that the main forms of iron in the reducing bottom sediments of eutrophic Amisk Lake, Alberta, are pyrite and ferric ions in structural positions in clay minerals. Minor concentrations of hydrated ferric oxides occur in the suspended particulate matter. Pyrite is formed within the sediments by the reaction of sulfide ion with clay-bound ferric ions. The large volume of seasonally anoxic water and strong formation of pyrite in the sediments serve to efficiently remove poorly crystalline hydrated ferric oxides from the water column. The concentrations of hydrated ferric oxides in the water are insignificant relative to those of phosphorus; consequently, most of the internally regenerated inorganic phosphorus is readily available for algal growth. Amisk Lake is probably naturally eutrophic.

Keywords: bioavailable phosphorus, eutrophication, iron deficiency, lake, Alberta.

SOMMAIRE

Nos études des spectres de Mössbauer indiquent que les formes principales du fer dans les sédiments réducteurs du fond du lac Amisk (Alberta), eutrophique, seraient la pyrite et le fer ferrique piégé dans les sites structuraux des argiles. Des concentrations mineures d'oxydes ferriques hydratés se trouvent dans les particules en suspension. La pyrite doit son origine dans ces sédiments à une réaction des ions sulfurés avec le fer ferrique des argiles. L'apport important saisonnier d'eau anoxyque et la forte production de pyrite dans les sédiments assurent l'élimination efficace des oxydes ferriques hydratés à faible cristallinité en suspension. La concentration des oxydes ferriques hydratés dans l'eau est insignifiante comparée à la concentration de phosphore. Par conséquent, la plupart du phosphore inorganique regénéré de façon interne serait biodisponible pour la croissance d'algues. Le lac Amisk serait tout probablement naturellement eutrophique.

(Traduit par la Rédaction)

Mots-clés: phosphore biodisponible, eutrophication, déficience de fer, lac, Alberta.

INTRODUCTION

Amisk Lake is a deep hardwater and highly eutrophic prairie lake situated 175 km northeast of Edmonton, Alberta (Fig. 1). Approximately 90% of the drainage basin is forested and, apart from minor agricultural and cottage activity, the watershed is undeveloped. Drainage from local Orthic Grey Luvisol soils ensures that Amisk Lake is, and probably has been historically, highly productive. The bedrock consists of shale with ironstone concretions (Lea Park Formation). Stream flow into the lake is intermittent.

Amisk Lake is thermally stratified in summer and under ice in winter (Fig. 2). Mixing in spring and fall is incomplete; consequently, concentrations of dissolved oxygen are always below saturation in the deeper waters (Fig. 2). The decomposition of organic matter leads to the development of anoxia in the hypolimnion in summer and under ice in winter, such that ~50% of the water in the north basin (mean depth 10.7 m, maximum depth 34 m) and ~75% of the water in the south basin (19.4 m, 60 m) can be completely anoxic. The depth of the ridge between the basins is 10 m. During periods of anoxia, phosphorus is released massively to the hypolimnion; mixing of the lake then introduces bioavailable inorganic phosphorus to the productive euphotic zone, which in turn promotes algal growth. Phosphorus may be the limiting nutrient for much of the year (Mitchell & Prepas 1990, Prepas 1983, Prepas & Trimbee 1988), although

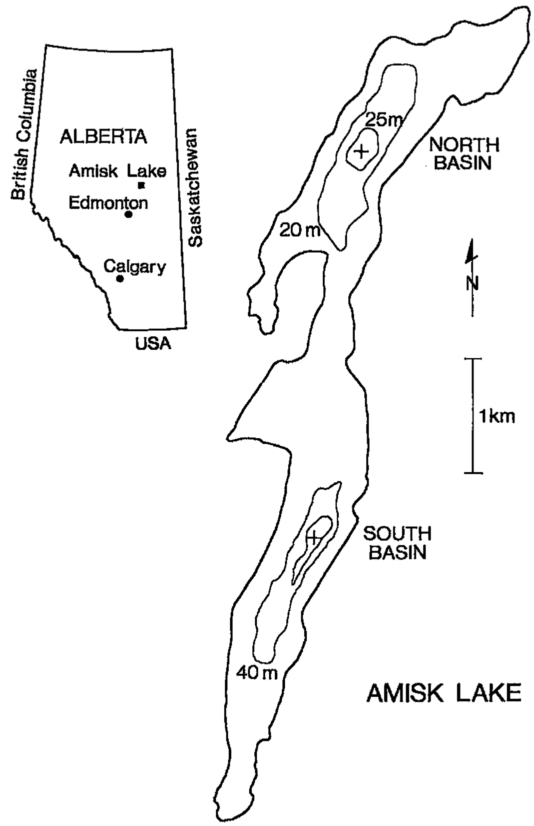

FIG. 1. Location of Amisk Lake, Alberta, and the two sampling locations. Surface area is 5 km^2.

iron also may be limiting on occasion. Since 1988, the shallower north basin has been treated with oxygen to increase concentrations of dissolved oxygen and to improve the fish populations.

The most bioavailable form of phosphorus in aquatic systems is dissolved inorganic orthophosphate ion (Sonzogni *et al.* 1982, Williams *et al.* 1980). The phosphate ion is strongly adsorbed onto the hydrated oxides of iron and, to a lesser extent, the hydrated oxides of manganese (Mortimer 1941, Bortleson & Lee 1974, Williams *et al.* 1976, Manning *et al.* 1991). Little is known of the iron–phosphate interactions in Amisk Lake and many other recreationally and economically important prairie lakes. The treatment of such lakes with iron salts and with lime has been proposed as a method of reducing the availability of phosphorus and the level of eutrophication. However, such remedial action is best justifiable if eutrophication is cultural, *i.e.*, of colonial development. Historical records of lake productivity are very limited.

The purpose of this work is to generate insights that could justify or otherwise disprove the validity of remedial plans for Amisk Lake and other important prairie lakes. This is done here by relating the main forms of iron and of phosphorus in the bottom sediments and in the suspended particulates to the availability of phosphorus.

EXPERIMENTAL DETAILS

Sediment cores were collected in June 1985 at a depth of 50 m in the South Basin and a depth of 35 m in the North Basin (Fig. 1). The cores were extruded and sectioned immediately on retrieval; the sections were packed in ice and frozen within 1 hr of collection. The dark grey sediments were freeze-dried and then stored at 4°C. Suspended particulates were collected, from 1 m beneath the surface and from the anoxic hypolimnion of the deep South Basin, by the centrifuging of 4000 L of water, through ice, in March 1991. The green (surface) and dark green (hypolimnion) particulates were frozen immediately and freeze-dried later. The hypolimnetic waters smelled of H_2S and reacted strongly with lead acetate.

Lead-210 geochronology of a sediment core from Amisk Lake (Turner & Delorme 1989) yielded current rates of sedimentation of 0.30 cm yr^{-1} and 0.029 g cm^{-2} yr^{-1}; the year 1880, which probably predates early development within the drainage basin, is placed at the 14-cm-depth sediment.

Mössbauer spectra were recorded at room temperature on a 512-channel linear acceleration spectrometer. The spectra were resolved on a mainframe computer

TABLE 1. MÖSSBAUER PARAMETERS FOR FERRIC IRON (THREE DOUBLET FITS)

	South basin				North basin			
Depth cm	HW(2d)	IS	QS	HW mm s^{-1}	HW (2d)	IS	QS	HW
0-1	0.55	0.37	0.72	0.57	0.53	0.37	0.80	0.60
1-2	0.53	0.37	0.74	0.58	0.44	0.38	0.74	0.60
2-3	0.53	0.37	0.73	0.57	0.39	0.40	0.75	0.61
3-4					0.40	0.38	0.74	0.59
4-5	0.52	0.38	0.75	0.58	0.37	0.41	0.75	0.54
5-6					0.37	0.42	0.78	0.55
6-7	0.52	0.37	0.76	0.56	0.35	0.43	0.73	0.55
7-8		0.38	0.76	0.56	0.33	0.45	0.65	0.61
10-11	0.47	0.39	0.73	0.58				
12-13	0.44	0.38	0.76	0.57	0.31	constrained		0.60
14-15					0.35	0.41	0.64	0.65
15-16	0.38	0.40	0.78	0.53	0.34	0.43	0.66	0.53
16-17	0.38	0.40	0.74	0.57	0.31	constrained		0.50
17-18	0.41	0.39	0.78	0.58	0.32	constrained		
19-20	0.42	0.39	0.79	0.52	0.30	constrained		
20-21	0.46	0.38	0.80	0.55	0.31	constrained		
21-22					0.30	constrained		

IS represents isomer shift, QS quadrupole splitting, HW halfwidth. Corresponding parameters of ferrous iron are 1.14 ± 0.02 mm s^{-1}, 2.63 ± 0.04 mm s^{-1}, 0.40 ± 0.03 mm s^{-1}. 2d represents the halfwidth of the inner doublet in a two doublet fit. Constraints were invoked because of low concentrations of ferric iron.

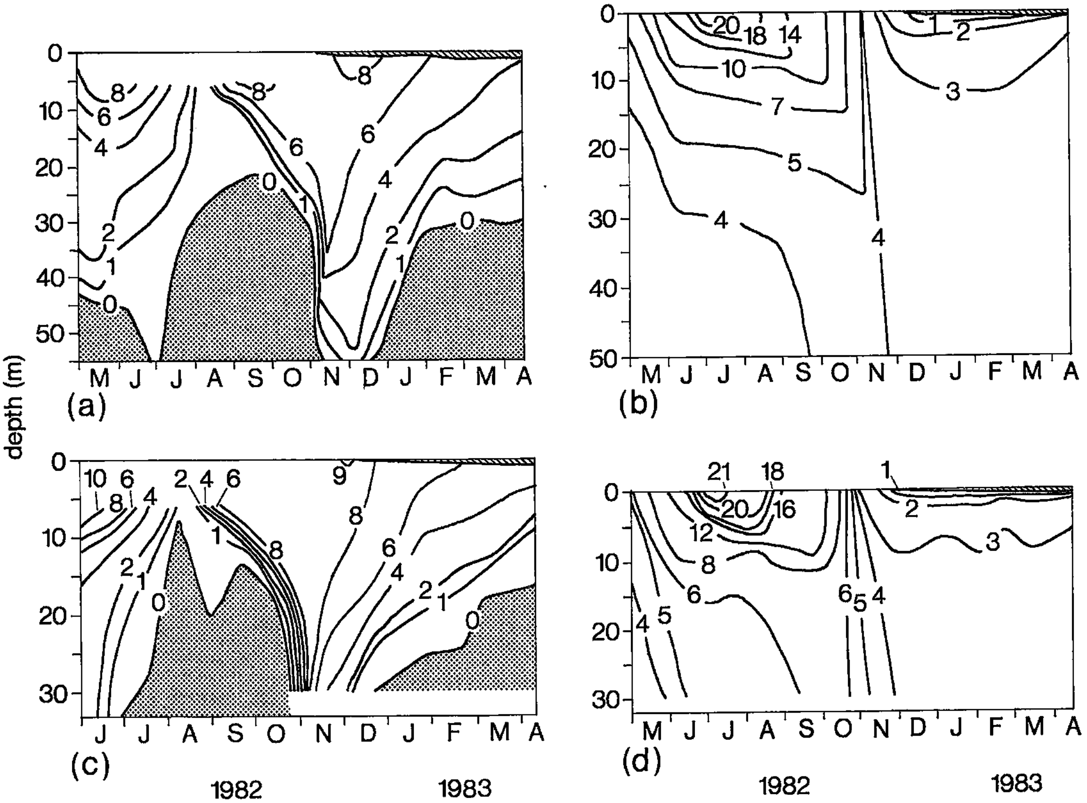

FIG. 2. Plots depicting (a) the concentration (mg L^{-1}) of dissolved oxygen and (b) the temperature (°C) in the South Basin as functions of depth and time. (c) and (d) are the corresponding oxygen and temperature profiles for the North Basin. Dotted areas indicate anoxic water, and hatched areas, ice cover.

using the programs of Stone (1967) and assuming pure Lorentzian line shapes and equal areas and equal halfwidths for absorptions within a given doublet. Values of chi-squared and the visual examination of the computed fits were used as criteria of goodness of fit. The spectrometer was calibrated against iron foil.

Visual examination of all spectra suggests the presence of two quadrupole doublets (Figs. 3, 4), *i.e.*, an outer doublet attributed to ferrous iron and an inner doublet consistent with ferric iron or pyrite or both. However, as measured for the sediments of other highly eutrophic and strongly stratified lakes (Manning *et al.* 1979, 1988), the halfwidth of the inner doublet decreases significantly and steadily with increasingly deeper sections of core, *e.g.*, from 0.53 mm s^{-1} for the 0–1 cm section of North Basin core to 0.32 mm s^{-1} for the 15–16 cm section (Table 1). Moreover, the measured values (mm s^{-1}) of isomer shift, quadrupole splitting and halfwidth change from, respectively, 0.35, 0.68 and 0.53 for the top cm of sediment to 0.31, 0.61 and 0.30 for the 19–20 cm section, *i.e.*, from values indicative of ferric iron to values clearly indicative of pyrite (Coey *et al.* 1974, Morice et al. 1969). Such trends in the sediments of other productive lakes have been attributed (Manning *et al.* 1979, 1988) to a $Fe^{3+} \rightarrow FeS_2$ reaction in strongly reducing sediments.

Consequently, a third doublet, that of pyrite, was introduced into the fitting scheme, with peak positions and halfwidths constrained to values measured for >95%-pure natural crystals of pyrite (values equivalent to an isomer shift of 0.31, a quadrupole splitting of 0.60, and a halfwidth of 0.30 mm s^{-1}). In deeper sections of sediments, some or all of these constraints were relaxed, *i.e.*, as pyrite becomes the dominant form of iron. The three-doublet fits yielded significantly lower values of chi-squared, *e.g.*, 526 against the 915 for two-doublet fits of the 5–6 cm section, improved visual fits, and a consistent basis for the resolution of all spectra. Replicate analyses of two sections of core indicated a reproducibility in pyrite concentrations of ±5% of total iron. Pyrite becomes the dominant phase in North Basin sediments

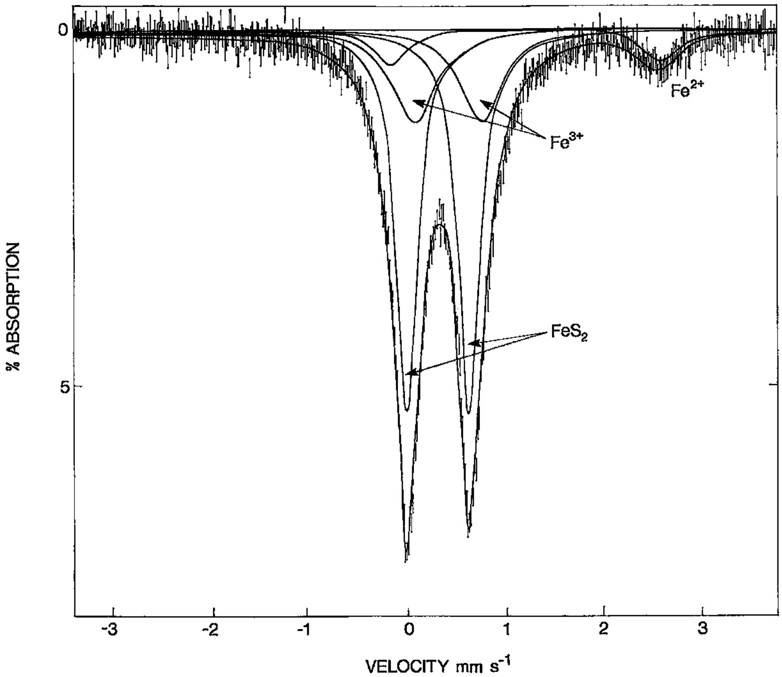

FIG. 3. Representative room-temperature Mössbauer spectrum of Amisk Lake sediment, in this case the 16- to 17-cm section of North Basin core. Chi-squared is 521 for 498 degrees of freedom.

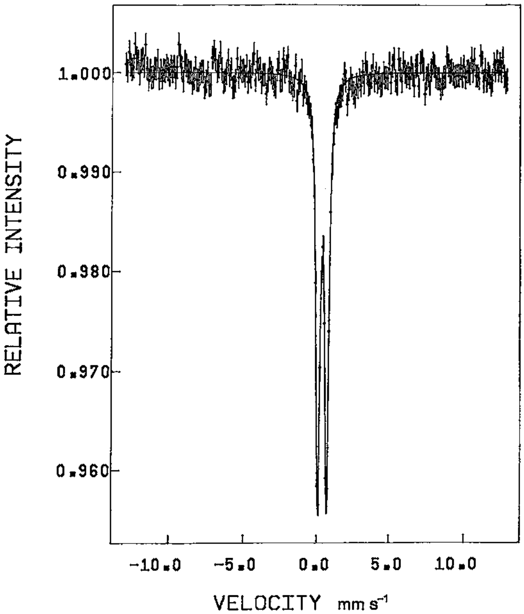

FIG. 4. Mössbauer spectrum taken at 4 K of 19–20 cm section of North Basin sediment. This spectrum and that of the 0–2 cm section (at 4 K) show the absence of magnetic forms of poorly crystalline hydrated ferric oxides.

(Table 2). The distributions of iron between ferrous, ferric and pyrite in the suspended particulates are similar to those of the top cm of bottom sediment (Table 2).

Optical microscopy confirmed the presence of abundant opaque framboids consistent with the presence of pyrite, particularly in deeper sections of core. Semiquantitative X-ray-diffraction patterns confirmed the greater abundance of pyrite in the deeper sections. Furthermore, approximately equal amounts of 0–1 cm and 1–2 cm sections of the North Basin core were combined, and 1-g aliquots were doped with, respectively, 0, 3, 4, 5, 6, and 7 mg of ground >95%-pure crystals of natural pyrite. Room-temperature Mössbauer spectra yielded concentrations of pyrite of 17.5, 21.4, 25.8, 22.0, 24.9, and 24.6% of total iron, respectively; the six points are well correlated ($r = 0.84$; at 5% level of significance, $r = 0.81$). The Mössbauer method is sensitive to small changes in pyrite concentration of approximately ±5% of total iron.

In order to differentiate between ferric ion in poorly crystalline hydrated oxides and ferric ions in structural positions in clay minerals, the spectra of two sections of North Basin sediment (1–2 cm and 19–20 cm) and of the 1-m-depth sample of suspended particulates were recorded at 4 K and over a wider range of veloci-

TABLE 2. CONCENTRATIONS OF IRON, PHOSPHORUS, CARBON AND SULFUR IN AMISK LAKE SEDIMENTS

	North basin							South basin							
Section	Fe^{2+}	Fe^{3+}	Fe(S$_2$)	NAIP	Org C	S$_T$	(Fe)S$_2$	Fe^{2+}	Fe^{3+}	Fe(S$_2$)	NAIP	Tot P	Org C	S$_T$	(Fe)S$_2$
cm							weight percent								
0-1	0.2	1.3	0.2	0.061		0.9	0.3	0.1	1.5	0.1	0.079	0.18		1.7	0.1
1-2	0.2	1.0	0.6				0.7	0.2	1.5	0.1	0.059	0.16	16.8	1.3	0.2
2-3	0.2	0.7	0.9	0.070			1.0	0.2	1.4	0.2	0.040	0.19	16.7	1.2	0.2
3-4	0.1	0.8	0.7	0.028	19.4	2.1	0.9				0.044	0.14	14.9	1.5	
4-5	0.1	0.6	1.0		19.5	2.2	1.1	0.2	1.3	0.3	0.037	0.12	15.2	2.1	0.3
5-6	0.1	0.6	1.0	0.042			1.2				0.086	0.17	15.9	2.0	
6-7	0.1	0.5	1.1		18.4	2.3	1.3	0.1	1.4	0.2	0.064	0.17	15.0	2.2	0.3
7-8	0.2	0.4	1.2	0.041			1.4	0.2	1.2	0.3	0.072	0.17	16.4	2.4	0.4
10-11				0.031	19.6	1.9		0.2	1.1	0.5	0.036	0.15	15.0	2.0	0.6
12-13	0.1	0.3	1.3	0.030	19.6	1.9	1.5	0.1	1.0	0.6	0.044	0.11	15.2	2.5	0.7
15-16	0.2	0.4	1.2		17.6	2.2	1.4	0.2	0.8	0.8	0.034	0.12	15.2	1.9	0.9
16-17	0.1	0.3	1.3				1.5	0.2	0.7	0.9	0.041	0.09	16.6	2.2	1.0
17-18					19.3	2.5		0.1	0.8	0.8	0.058	0.11	14.9	2.0	0.9
19-20	0.1	0.2	1.4	0.037		2.4	1.6	0.2	0.8	0.8	0.052	0.10	15.3	2.4	0.9
20-21	0.1	0.2	1.4		23.7	2.8	1.6	0.1	1.1	0.5	0.043	0.09	16.8	2.9	0.6
21-22	0.1	0.2	1.4				1.6						15.4	3.1	

Concentration of total iron in bottom sediment is 1.73 ± 0.20 wt %. Concentration of sulfur in pyrite, (Fe)S$_2$, is calculated from 1.73 x (% of total iron in pyrite) x (64/56). Fe(S$_2$) is the concentration of iron in pyrite. The 19- to 20-cm section of North Basin core, after treatment with 0.2 M HCl, yielded 4% Fe^{2+}, 13% Fe^{3+} and 83% Fe(S$_2$) of total iron, values little changed from those of the untreated sample. Concentrations of Mn are 0.01 wt % in the North Basin and 0.025 wt % in the South Basin. Concentrations of inorganic carbon are ~1 wt %.

Suspended particulates: The relative concentrations of Fe^{2+} (4% of total iron), Fe^{3+} (85%) and FeS$_2$ (10%) in the suspended particulates are similar to those in the top cm of bottom sediment. Concentrations of NAIP in the particulates are 0.31 wt % at 1 m depth and 0.28 wt % at the bottom. Total iron concentrations in the particulates are 0.7 wt %, and total particulate concentration is 1 mg L^{-1}.

ties (Murad 1988, Murad & Johnston 1987, Murad & Schwertmann 1980, Coey & Readman 1973). The 4 K spectra of the sections (Fig. 4) consist of a doublet, sharply defined in the 19–20 cm spectrum, with values (mm s^{-1}) of isomer shift, quadrupole splitting and halfwidth of, respectively, 0.35 ± 0.02, 0.70 ± 0.03 and 0.55 ± 0.05 for the 1-2 cm section, and 0.40 ± 0.01, 0.62 ± 0.01 and 0.35 ± 0.01 for the 19–20 cm section. No six-line magnetic pattern was developed, indicating that poorly crystalline hydrated ferric oxides are present in very low concentration (<5% of total iron). It is unlikely that all the ferric oxide particles are sufficiently small (<<10 nm) so as not to magnetically order at 4 K (Gangas *et al.* 1973): firstly, such small particles of relatively high surface-area would be unstable in strongly reducing sediments, and, secondly, oxides in the sediments of other lakes, including a nearby lake in Alberta, are known to magnetically order (Coey *et al.* 1974, Manning *et al.* 1991). The doublets of pyrite and ferric iron are unresolved at 4 K, although the significantly smaller halfwidth of the doublet for the 19–20 cm section is consistent with the greater ratio of pyrite to ferric iron, as defined by room-temperature measurements. No crystalline compound of ferric iron, *e.g.*, strengite, was detected in X-ray-diffraction patterns; consequently most of the ferric iron in the sediments seems to be located in the structure of clay minerals. The 4 K spectra of the suspended particulates were found to be less well resolved, owing to the lower iron content, and indicated that <20% of total iron is magnetically ordered.

The room-temperature spectra of the 1–2 cm and 19–20 cm sections of North Basin sediment remained essentially unchanged after washing the samples with dilute hydrochloric acid. Consequently, the ferrous iron peak at ~2.5 mm s^{-1} (Fig. 3) cannot be assigned to poorly crystalline or amorphous Fe–S compounds (Hilton *et al.* 1986).

Concentrations of total iron were determined by acid dissolution followed by atomic absorption spectrometry (Desjardins 1978); replicate analyses indicate that the precision is ±10%. Concentrations (wt%) of iron within the individual fractions, Fe^{2+}, Fe^{3+} and FeS$_2$, were then calculated from the total iron values and the area ratios in the Mössbauer spectra, and are good to ±15 wt%.

Concentrations of total phosphorus, nonapatite inorganic phosphorus (NAIP, Table 2) and of apatite phosphorus (0.015 wt%) were measured by wet-chemical fractionation (Williams *et al.* 1976). Most of the phosphorus within the NAIP fraction is considered to be bonded to poorly crystalline hydrated oxides of iron and manganese (Lucotte & d'Anglejan 1985, Manning & Gracey 1991), although in strongly reducing sediments, vivianite (Manning *et al.* 1991) and poorly crystalline iron phosphates also may be present. NAIP adsorbed on hydrated ferric oxides represents the main reservoir of bioavailable phosphorus in sediments and suspended particulates (Williams *et al.* 1976). The reproducibility of NAIP determinations is good (±5%). The specificity of the extraction is not entirely proven, but is probably accurate to better than ±10% (Lucotte & d'Anglejan 1985). Water samples were collected following the approach of Prepas (1983) and analyzed for total and dissolved phosphorus by the potassium persulfate method (Menzel & Corwin 1965).

Concentrations of organic and inorganic carbon and of total sulfur were measured by Leco induction furnace (Kemp 1971). Reproducibility of analysis is ±5%.

RESULTS AND DISCUSSION

All spectra are qualitatively similar, displaying (a) a weak outer doublet with Mössbauer parameters (Table 1) characteristic of ferrous iron in octahedral coordination in the structures of clay minerals and chlorite (Coey et al. 1974), and (b) a dominant central "doublet" that is readily and consistently resolved into doublets of ferric iron and pyrite (Fig. 3). The three-doublet fits yield Mössbauer parameters for ferric iron that are consistent from section to section and also with the parameters measured for ferric iron in the sediments of other lakes (Coey *et al.* 1974) and of nearby Narrow Lake, Alberta (Manning *et al.* 1991): concentrations of pyrite in the sediments of Narrow Lake are extremely low. Whereas the ferric iron in the deep-water sediments of nearby Narrow Lake is present in the form of hydrated oxide (Manning *et al.* 1991), with a correspondingly strongly developed magnetic pattern in the 4 K Mössbauer spectrum, the 4 K spectra of two sections (1–2 cm and 19–20 cm) of Amisk Lake core indicate, by contrast, that almost all of the ferric iron is in structural positions in clay minerals and chlorite (see above): such ferric iron is considered to be less reactive toward phosphate ion (Sonzogni et al. 1982, Williams *et al.* 1976).

The main reaction involving iron in the sediments is the reaction of sulfide ion with ferric iron bound in clay minerals (Table 2; Manning *et al.* 1979, 1988, Drever 1971). The abstraction of ferrous iron from within the structure of clay minerals by sulfide ion, on increasing depths of burial, was proposed in the sediments of a lake in Ontario (Manning *et al.* 1979). This was criticized by Hilton *et al.* (1986) on grounds that the 2.7 mm s^{-1} Mössbauer spectral peak, originally assigned to Fe^{2+}, was in fact due to FeS. However, the 2.7 mm s^{-1} peak in the spectrum of the Ontario lake sediment remained unchanged in intensity on washing with 0.2 M HCl, hence the original conclusion still stands. Iron, either ferrous or ferric, is clearly extractable from within clay structures by high concentrations of sulfide ion within the sediment.

Pyrite is formed more efficiently in the shallower North Basin sediments than in the South Basin, in terms of both the rate of formation (as a function of depth) and the percent conversion of Fe^{3+} to FeS_2 (Table 2). Concentrations of total sulfur are similar in the sediments of the two basins, whereas pyrite is present in much higher concentrations in sediments from the North Basin. The reasons may be two-fold. Firstly, the bottom waters of the North Basin are better oxygenated during the periods of mixing of the lake (Fig. 2), whereas the South Basin is approaching a meromictic state. Oxygen promotes the formation of pyrite through the oxidation of sulfide ion to amorphous sulfur, which then reacts with FeS to form pyrite (Berner 1984). Secondly, temperatures of the bottom water are higher in the North Basin (Fig. 2), promoting greater microbial activity and faster rates of reaction.

Forms of inorganic phosphorus

Vivianite, $Fe_3(PO_4)_2{\cdot}9H_2O$, is a common mineral in reducing sediments (Nriagu & Dell 1974). It has sharply defined Mössbauer absorptions at ~2.7 mm s^{-1} (Gosner & Grant 1967, Nembrini *et al.* 1983) and is soluble in hydrochloric acid (Manning *et al.* 1991); hence the quantitatively similar spectrum obtained following an acid wash also eliminates vivianite as a significant mineral. The slightly lower concentrations of ferrous iron in the washed samples (Table 2) may reflect experimental error; if due to the loss of vivianite, the implied concentration of iron is 0.035 wt%, *i.e.*, 2% of 1.73 wt% of total iron. The corresponding concentration of phosphorus is less than 0.013 wt%, hence vivianite represents a minor portion of the NAIP (Table 2).

If all the ferric iron in the 19–20 cm section of the South Basin core is hosted by a hydrated oxide, then the concentration of adsorbed NAIP at 10 wt% of Fe^{3+} (Manning *et al.* 1991, Sholkovitz & Copland 1982) is 0.02 wt%, a value significantly less than the measured concentrations of NAIP (Table 2). However, the 4 K spectra argue against a significant portion of the ferric iron being in hydrated oxides. Therefore, the NAIP in the sediments of Amisk Lake is bonded elsewhere, possibly in the form of a mixed-anion NAIP – cation – carboxylate complex (Ramamoorthy & Manning 1973), in which the central cation is one or more of Fe^{2+}, Fe^{3+}, Al^{3+} or Ca^{2+}, and the carboxylate is an available group in the abundant organic matter, *e.g.*, humic material. Aluminum ions may be released on the extraction of ferric ions from the layers of octahedra in clays. Alternatively, a refractory phosphate salt may enter the lake as a product of erosion.

Consider a hypothetical 10-m-thick hypolimnion (Fig. 2) overlying 1 m^2 of bottom sediment. If the amount of NAIP released, on reduction of ferric ions, from the bottom sediments during the summer stratification is equivalent to a concentration of phosphorus in the hypolimnion of 150 $\mu g\ L^{-1}$ (Fig. 5), then that amount is 1.5 g P m^{-2}. This amount is based on the hypolimnetic concentrations of phosphorus attained by late August or September minus the epilimnetic concentration of 40 $\mu g\ L^{-1}$ (Fig. 5). It is significantly less than the total accumulated amount of hypolimnetic

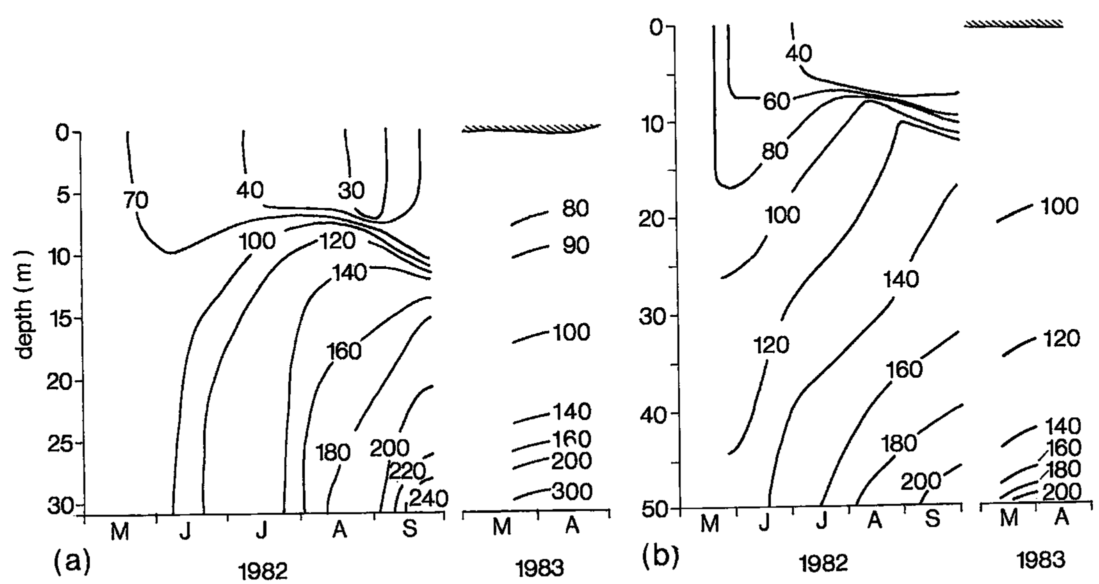

Fig. 5. Concentrations (μg L^{-1}) of total phosphorus in the North (a) and South (b) Basins as functions of depth and time. Hatched areas depict ice cover. Summer average concentrations of chlorophyll *a* are approximately ~20 μg L^{-1}; Amisk Lake is highly eutrophic. The internal recycling of phosphorus is a dominant process.

phosphorus ($\approx$4 g m^{-2} in the South Basin, $\approx$2 g m^{-2} in the North Basin); the differences allow for any year-to-year differences in release. The weight of ferric iron (in oxide) required to bind the released phosphorus is 15 g Fe^{3+} m^{-2}, based on a Fe^{3+}:P weight ratio of 10:1 for NAIP adsorbed on hydrated ferric oxide (Sholkovitz & Copland 1982, Manning *et al.* 1991). However, the top cm of sediment, which represents more than one year's sedimentation (Turner & Delorme 1989), contains ~12 g Fe^{3+} m^{-2}, almost all of which is contained in unreactive sites in clay minerals. It is therefore unlikely that sufficient hydrated ferric oxide can be precipitated at the sediment – water interface, during the brief periods of spring and fall mixing (low oxygen values, Fig. 3), to account for the phosphorus release of summer and winter (Fig. 5). This is supported by (a) the low total weight of iron in the water column in August, approximately 0.4 g m^{-2} (Table 3), and by (b) the insignificant concentrations of hydrated oxide present in the cores, at which time (June) minor amounts only of NAIP have been released (Fig. 5). Hydrated ferric oxides can play but a minor role in the cycling of phosphorus in Amisk Lake. However, this does not exclude the possibility that other compounds of iron, also susceptible to reduction and dissolution on a lowering of the redox potential, are responsible for the release of phosphorus during periods of anoxia. Sulfate reduction marks another chemically significant redox horizon in strongly reducing sediments. Sulfide ion generated under conditions of intense anoxia may well destroy mixed-anion iron-centered complexes of the type described above, forming pyrite and releasing phosphate ion. Alternatively, microbial decomposition of the organic matter (algal remains) deposited earlier in the year also could account for the release of phosphorus.

Preliminary results indicate that hypolimnetic concentrations of total phosphorus have decreased (by ~50%) since oxygen injection began (T.P. Murphy & E.E. Prepas, unpubl. work). Concentrations of total iron (<10 μg L^{-1}) and, in particular, of hydrated ferric oxide, are insufficient to account for this decrease. Lower concentrations of phosphorus may be a result of enhanced uptake by bacteria (Comeau *et al.* 1986).

TABLE 3. IRON, PHOSPHORUS (μg L^{-1}) AND OXYGEN (mg L^{-1}) CONCENTRATIONS IN NORTH BASIN OF AMISK LAKE

Depth		Iron		Phosphorus	Oxygen	Fe:P
m	dissol.	partic.	total	total	total	
0-6	0.5 (0.2)	6.5 (1.5)	7 (2)	32	9.1	0.22
6-12	0.6 (0.1	12 (1)	12 (1)	103	0.3	0.13
12-18	1.9 (0.3)	9.2 (0.2)	11 (1)	140	n.d	0.08
18-24	5.6 (0.4)	2.4 (1.6)	8 (2)	159	0.0	0.05
24-28	3.6 (0.2)	4.3 (1.3)	8 (2)	162	0.0	0.05

Numbers in brackets indicate standard errors. Iron values measured 2 August 1985, phosphorus and oxygen 12 August 1985. n.d. is not determined. Most of the phosphorus is released from the bottom sediment during anoxia and is mainly NAIP. Mössbauer studies suggest that minor amounts of particulate iron are in hydrated oxide.

Forms of carbon and sulfur

Concentrations of organic carbon and of sulfur in the bottom sediments of Amisk Lake (Table 2) greatly exceed those of the nearby unproductive Narrow Lake (Manning *et al.* 1991). The concentrations of total sulfur and of pyrite reflect the strongly reducing nature of the sediments and the activity of sulfate-reducing bacteria (Berner 1984). The concentration of sulfate ion in the water is 15 mg L^{-1}. Most of the sulfur in deeper sections of North Basin sediment is in pyrite (Table 2); pyrite contains up to ~50% of total iron in South Basin sediments.

In freshwater systems, the formation of pyrite is usually limited by the low concentrations of dissolved sulfate (Berner 1984). The high concentrations of total sulfur and pyrite produced in the sediments of Amisk Lake (Table 2) suggest that pyrite formation is limited as much by the availability of reactive iron minerals as by that of sulfate. The minor amounts of unreacted ferrous and ferric ions in North Basin sediments are possibly held in highly refractory materials. Productivity is sufficiently high and the decomposition of organic matter sufficiently rapid that sulfate may not be limiting. In this sense, conditions in Amisk Lake approach the euxinic case (Leventhal 1983).

General Discussion

Concentrations of total iron in the cores of Amisk Lake do not decrease significantly with increasing depth of burial (Table 2). Also, the trends in the concentrations of Fe^{2+}, Fe^{3+} and FeS_2 (Table 2) suggest that the conversion of ferric iron to pyrite is nearly quantitative. Consequently, almost all the iron deposited to and contained within the bottom sediments is effectively retained within the sediments, mainly as pyrite but to a lesser degree as ferrous and ferric ions in clay minerals. Moreover, during the prolonged periods of anoxia (Fig. 2), H_2S will diffuse into the hypolimnion and precipitate any ferrous ions released from the upper layers of sediments and any hydrated ferric oxides falling to the hypolimnion from the oxic epilimnion, including recent inputs from stream. The large volume of anoxic water entrained within the hypolimnion effectively supports the sediments in removing hydrated ferric oxides from the water column. Sulfide ion also may be generated within the hypolimnion during the sedimentation of organic detritus (Berner 1984, Leventhal 1983).

Iron concentrations in the water column of the North Basin, and probably through the whole lake, are extremely low relative to those of phosphorus (Table 3). In oxic water, an Fe:P molar ratio of ~2 is considered necessary for adsorption of phosphorus onto iron (as hydrated oxide) (Tessenow 1974); in Amisk Lake, the ratios range from 0.12 in the oxic zone to 0.03 in the anoxic hypolimnion. A Fe^{3+}:P mole ratio of ~5 has been calculated for the adsorption of NAIP on freshly precipitated ferric hydroxides (Manning *et al.* 1991, Sholkovitz & Copland 1982), which compares with the measured Fe^{3+}:NAIP mole ratio of ~1 for the suspended sediments in Amisk Lake (Table 2) in which, however, most of the ferric iron is relatively inert in the structures of clay minerals. Hence, it is likely that less than 5% of the inorganic phosphorus in the water column is absorbed on hydrated oxides in particulates (Tables 2, 3), confirming the insignificant role of hydrated ferric oxides in the phosphorus cycle in Amisk Lake. Phosphorus released from sediments to the anoxic hypolimnion is, in turn, transferred to the euphotic zone during spring and fall mixing, and is then available for algal growth. The low concentrations of total iron and, in particular, of hydrated iron oxides ensure that phosphate is relatively weakly adsorbed onto other substrates, *i.e.*, calcium carbonate or aluminum oxides. Thus internally recycled phosphorus (Shaw 1989) is readily bioavailable.

The 14-cm sediment horizon corresponds to deposition approximately 110 years B.P., *i.e.*, significantly earlier than the main colonial development of the watershed in approximately 1940 (Mitchell & Prepas 1990). The absence of significant concentrations of vivianite, the anoxic sulfate-reducing quality of the deeper sediments, and the levels of organic carbon are all indicative of pre-settlement conditions in which Amisk Lake was probably highly eutrophic, and naturally so. Colonial settlement in the watershed has likely intensified the level of eutrophication, although the degree of intensification is not known because of the lack of historical data.

The contrast between the iron–phosphorus relationships in Amisk Lake and in nearby Narrow Lake is remarkable. Narrow Lake is a deep clear unproductive lake overlying sediments with the phosphorus content (1–2 wt% NAIP) of low-grade fertilizer (Manning *et al.* 1991). Ferrous ions in iron-rich groundwater percolate into the oxic water column and are rapidly precipitated as hydrated ferric oxides: phosphorus is thus removed from the water column before it can stimulate algal growth. However, in Amisk Lake, the pyrite and ferric profiles in the sediments (Table 2) and the 4 K spectra (Fig. 4) are consistent with the conversion of clay-bound ferric iron to pyrite, and indicate that minor amounts of hydrated ferric oxides reach the sediments. The relatively low concentrations of pyrite in the top cm of sediment and in the suspended particulates (Table 3) indicate that small amounts only of ferric oxides can have reacted to form pyrite in the hypolimnion and in the months (*i.e.*, top cm of sediment) following sedimentation to the bottom (Turner & Delorme 1989). Consequently, relatively small concentrations of ferric oxides are introduced to the lake either from exogenous sources or from the bottom sediments. Moreover, it can be argued that many highly eutrophic lakes are deficient in phosphate-binding oxides. Thus, on the basis of a concentration of suspended particulates of 1 mg L^{-1}, for an average lake, and an iron concentration (within the particulates) of 1.0 wt%, the concentration of iron in the water column is 10 μg L^{-1}, in lakes that may have concentrations of phosphorus of 20–100 μg L^{-1}. Organically enriched sediments and anoxic hypolimnia further accentuate the iron deficiency by preferentially removing labile oxides as poorly crystalline compounds of Fe–S and pyrite.

The initial treatments with iron salts could stimulate algal growth, bearing in mind the very low concentrations of available iron. Additions of iron to markedly reduce algal productivity would of necessity need to be extremely large. Natural trophic control in Narrow Lake has been effected by many years of heavy inflow of iron in groundwater, as a consequence of which the sediments are not massive sinks of decomposing organic matter. Iron treatment should have the aim of maintaining a semipermanent and a sufficient concentration of redox-sensitive mobile iron, *i.e.*, hydrated oxides, in the water column so as to reduce the availability of phosphorus. Surface sediments of higher redox potential would reduce the binding of iron as pyrite, leading to the greater return of iron to the water as ferrous iron. Additions of iron would need to be repeated for several years in order to build up a few centimeters of sediment of higher redox potential. Based on an added concentration of iron ten times that of phosphorus (say 100 mg P m^{-3}, Fig. 4) and a lake volume of 8×10^7 m^3, the required annual addition of iron is 80 tonnes, equivalent to 400 tonnes of ferrous sulfate heptahydrate. Additions of such magnitude overwhelm current levels of natural iron in the water, less than 1 tonne, based on an iron concentration of ~9 μg L^{-1} (Table 2).

Consequently, any remedial treatment of Amisk Lake with iron salts should be balanced between (a) the need for additional insights into the way the lake would respond to massive additions of iron, in order to develop a strategy to forestall any deterioration in water quality on further economic development of the watershed, and (b) the desirability, from a scientific aspect, of keeping the lake in its unusual iron-deficient state. Greater inputs of nutrients, in the absence of any remedial action, could lead progressively to an intensification in eutrophication, to lower levels of oxygen, to major fish kills in winter, and hence to a significant impact on the local economy. Remedial options may then depend on some assessment of precolonial eutrophication.

The contrast between Amisk Lake and Narrow Lake can be used to highlight both the diversity of lakes on the sedimentary plains of western Canada and the immense challenges for management of those systems. Both lakes lie in glacial meltwater channels in central Alberta, some 60 km apart. The drainage basins of both lakes are basically undisturbed, and the soils are orthic grey luvisols. Yet the geochemistry of the bottom sediments is radically different, with Narrow Lake sediments containing high concentrations of ferric oxides and Amisk Lake sediments containing relatively low concentrations. Narrow Lake has relatively low algal biomass (average chlorophyll *a* for seven years: 2.4 μg L^{-1}) and good water-quality, whereas Amisk Lake has high algal biomass and is clearly eutrophic (average summer chlorophyll *a*: 16 μg L^{-1}) (Mitchell & Prepas 1990, Bradford *et al.* 1990).

ACKNOWLEDGEMENTS

The authors thank M.N. Charlton, C. Frampton, K.J. Gracey and J.F.H. Shaw and members of the Technical Operations Division for assistance. The low-temperature spectra were recorded and resolved with the assistance of (the late) Dr. T. Birchall. The referees are thanked for their many useful comments.

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Received February 10, 1993, revised manuscript accepted September 21, 1993.