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PYRITE AND VIVIANITE INTERVALS IN THE BOTTOM SEDIMENTS OF EUTROPHIC BAPTISTE LAKE, ALBERTA, CANADA

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ABSTRACT

The highly eutrophic status of Baptiste Lake, Alberta, may be related to altered groundwater flow resulting from land-clearing activities since colonial settlement approximately 80 yr B.P. Sections from the top 42 cm of sediment cores from Baptiste Lake, which represent 150 yr B.P. to the present, were analyzed for forms and concentrations of iron and phosphorus. The 30–42 cm interval (90–150 yr B.P.) is marked by intensive formation of vivianite; concentrations of potentially bioavailable orthophosphate ion in some sections exceed 1 wt%. This probably reflects a period when inflowing groundwater contained high concentrations of iron and phosphorus, which precipitated at the sediment surface under oxic conditions that likely prevailed at the time. In contrast, the top 25 cm (80 yr B.P. to the present) show sedimentary formation of pyrite consistent with anoxic conditions at the sediment–water interface, the deposition of organically enriched sediments, and severe eutrophication. The waters of Baptiste Lake have become more eutrophic since colonial settlement.

Keywords : pyrite, vivianite, lake sediments, phosphorus, groundwater, trophic level, Baptiste Lake, Alberta.

SOMMAIRE

Le statut fortement eutrophique du lac Baptiste, en Alberta, pourrait être la conséquence d'un réseau modifié de flux d'eau souterraine lié au défrichement des terres suite à la colonisation, il y a environ quatre-vingt ans. Les échantillons prélevés des 42 cm de carottes de la partie supérieure de la section sédimentaire au lac Baptiste, intervalle représentant cent-cinquante ans de sédimentation, ont été analysés afin de connaître la spéciation et les concentrations du fer et du phosphore. L'intervalle de 30 à 42 cm (90–150 ans avant aujoud'hui) se distingue par la formation massive de vivianite; les concentrations des ions orthophosphate potentiellement biodisponibles dans certains échantillons dépassent 1% par poids. Cet enrichissement témoignerait d'une période où les nappes d'eau souterraines qui nourissaient le lac avaient des teneurs élevées de fer et de phosphore, qui ont précipité à la surface du sédiment sous conditions oxyques préconisées à cette période. En revanche, sur les 25 cm au haut de la colonne stratigraphique (80 ans jusqu'à présent), il y a eu formation sédimentaire de pyrite, ce qui implique des conditions anoxyques à l'interface sédiment–eau, la déposition de sédiments enrichis en matière organique, et une eutrophication sévère. Les eaux du lac Baptiste sont devenues plus fortement eutrophiques depuis l'ère coloniale.

(Traduit par la Rédaction)

Mots-clés : pyrite, vivianite, sédiments lacustres, phosphore, eau souterraine, niveau trophique, lac Baptiste, Alberta.

INTRODUCTION

Baptiste Lake, Alberta, is a naturally eutrophic lake (Hickman *et al.* 1990, Mitchell & Prepas 1990) 10 km^2 in surface area, situated 165 km northwest of Edmonton, Alberta. The lake lies in a glacial meltwater channel. The underlying bedrock is marine shale of the La Biche Formation. Clayey glacial till is the dominant surficial deposit. The watershed, 310 km^2 in area, is 58% forest, 16% agricultural land, 25% of lakes, bogs and marshes, and 1% cottage shoreline development (Mitchell & Prepas 1990). The watershed was basically undisturbed prior to the first large influx of settlers in 1909 to 1914.

Baptiste Lake has two basins, the south basin being the deeper, joined by a relatively shallow neck (Fig. 1). Both basins are thermally stratified in summer and in

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winter under ice cover. However, mixing is incomplete in spring and autumn in the south basin (Fig. 2), but is incomplete in the north basin in the spring only. The hypolimnia are anoxic for much of the year, at which time phosphorus is massively released from the bottom sediments (Fig. 2). This release stimulates a blue-green algal bloom on overturn. The main contributors to water inflow are: streams 67%, precipitation 18%, and groundwater 12% (Crowe & Schwarz 1981, Shaw & Prepas 1989). The pattern of groundwater flow is unusual in that flow into the lake bottom increases with distance from shore (Shaw & Prepas 1989). This is consistent with an offshore hydrological connection between the underlying aquifer and the bottom sediments.

Prior to 1000 years B.P., Baptiste Lake was probably meromictic (Hickman *et al.* 1990). The vertical distributions of pollen and pyrite spherules in the sediment suggest that the lake has become more eutrophic with time and that the intensity of anaerobic conditions in the bottom waters has been variable (Hickman *et al.* 1990). Pyrite is formed in reducing sediments intermittently exposed to oxygen (Berner 1984). Human disturbance in the watershed has increased since the early 1900s.

We have collected sediment cores from the surface of the bottom sediments to a depth of 42 cm, which represents approximately 150 years of deposition (Turner 1995). We determine the main forms of phosphorus and iron in the top 42 centimeters of bottom sediment and relate them to the bioavailability of phosphorus and trophic status of the lake. Our main aim is to use the sediment cores to track changes in the trophic level of the lake since before colonial settlement.

EXPERIMENTAL DETAILS

Gravity cores of bottom sediment were collected from the deeper south basin in May 1991 and from both basins in February 1992. The dark grey silty clay cores were sectioned into 1-cm slices down to a depth of 30 cm and into 2-cm slices thereafter. One core from the south basin was collected and sectioned for ^{210}Pb chronology (Turner 1995) using the method of Appleby & Oldfield (1978). The method is based on the assumption of a variable rate of sedimentation. Discontinuities in sediment porosity (as a function of sediment depth) indicated a variable rate of sedimentation. All sections

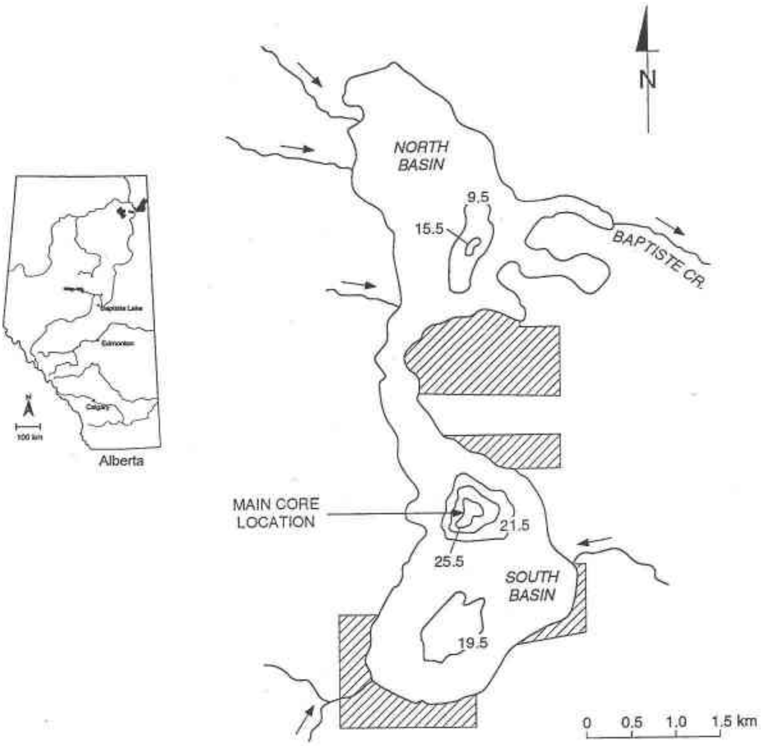

FIG. 1. Diagram depicting the deep hole and main sampling location in south basin of Baptiste Lake. Hatched areas represent various developments, *e.g.*, cottages and campgrounds. Contour intervals are in meters.

were frozen immediately on retrieval and freeze-dried within ten days.

Room-temperature Mössbauer spectra were recorded on a 512-channel spectrometer and analyzed using the programs of Stone (1967). Values of chi-squared and the visual examination of the spectra were used as criteria of goodness of fit. The Mössbauer spectra of two sections, 2–4 cm and 34–36 cm, also were recorded at 4 K to quantify poorly crystallized magnetically ordered oxides of iron (Murad 1988).

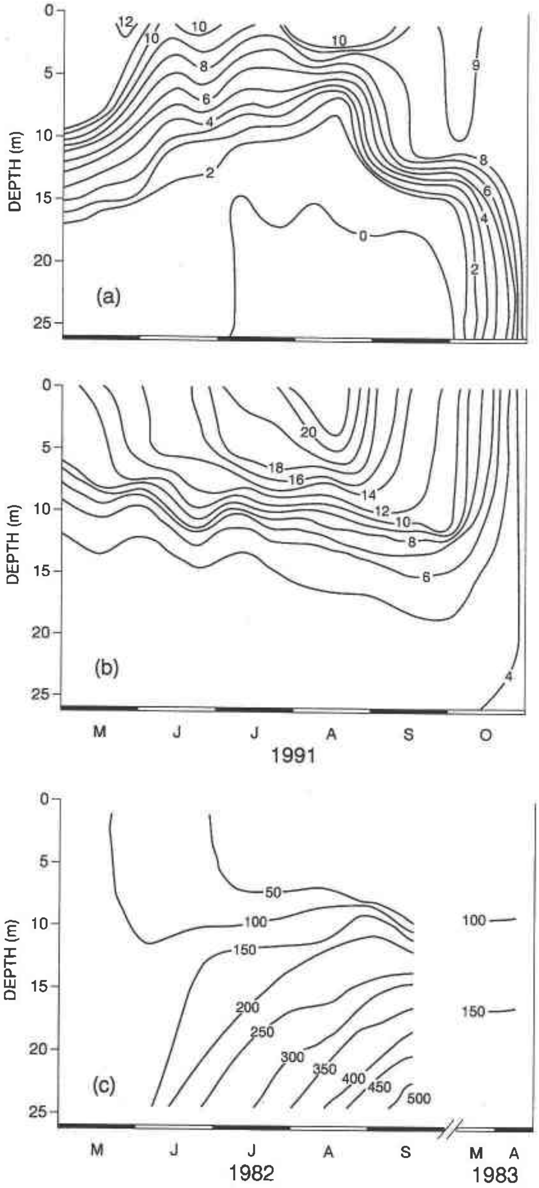

FIG. 2. Isopleths depicting (a) concentrations of dissolved oxygen (mg L^{-1}), (b) temperature °C, and (c) concentrations of total phosphorus (mg L^{-1}) in the south basin of Baptiste Lake as functions of depth and time. Summer average epilimnetic concentrations of phosphorus and chlorophyll **a** exceed 40 and 20 μg L^{-1}, respectively.

Concentrations of total iron, Al, Mn, and Ca in the dried sediments were measured by, sequentially, digestion in aqua regia, evaporation to dryness, dissolution of the residue in dilute HCl, and atomic absorption spectrometry using suitable standards and controls. Concentrations of Fe^{2+}, Fe^{3+}, and FeS_2 were then determined from area ratios in the Mössbauer spectra and total iron values, assuming equal recoil-free fractions for all forms. Total concentration of metals are reproducible to ±5% and are good to ±10%.

Concentrations of nonapatite inorganic phosphorus (NAIP), the principal pool of bioavailable phosphorus in sediments (Williams *et al.* 1980), insoluble apatite phosphorus, and organically bound phosphorus were measured by wet-chemical extraction (Williams *et al.* 1976). Values are reproducible to ±5% and are good to ±10%. Water samples were collected and analyzed for total phosphorus and dissolved phosphorus following methods described earlier (Menzel & Corwin 1965, Prepas 1983).

Concentrations of organic carbon and total sulfur (S_T) were determined with a Leco induction furnace (Kemp 1971); values are reproducible to ±3% and are good to ±5%. Concentrations are given as weight percent of dry sediment.

RESULTS

Spectral resolution

Visual examination of the higher-energy absorption in the room-temperature Mössbauer spectra, as a function of depth, indicates that two types of spectrum are present. Thus, the envelope attributed to ferrous iron is more intense and has an additional sharply defined shoulder in spectra of sections of core deeper than 30 cm (Fig. 3). A second core from the south basin, collected in February 1992, displayed quantitatively similar spectral features. The main iron compounds entering the lake are clay minerals and hydrated ferric oxides in surface waters and ferrous ions in solution in groundwater. Hence, the two types of spectra reflect different diagenetic processes occurring over different periods within the sediment. Redox potentials within the sediments are strongly dependent on the rate of breakdown of organic matter and, hence, on algal productivity in the lake. The Mössbauer spectra were resolved by invoking two different schemes. For upper sections of the sediment column, which show two visually obvious doublets, three doublets were invoked marking ferrous ions in structural sites in clay minerals, ferric ions in oxides and clay

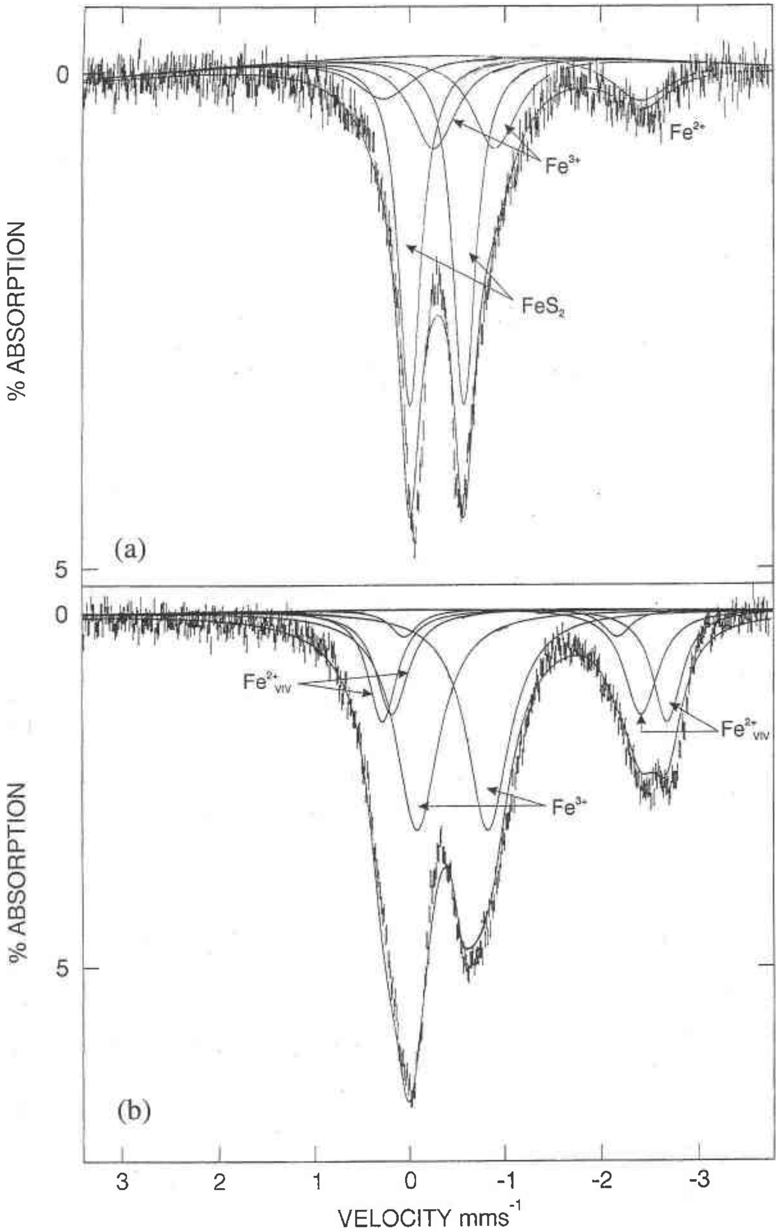

FIG. 3. Room-temperature Mössbauer spectra of (a) 2 to 4 cm section of sediment core, and (b) 34 to 36 cm section. The spectra show, respectively, the development of pyrite and vivianite signatures.

minerals, and Fe^{2+} ions in pyrite, FeS_2 (Manning *et al.* 1979, 1994). The absorptions of ferric ions and pyrite are superimposed and are not resolved by eye in room-temperature spectra (Manning *et al.* 1979). In all computations, the peak positions and half-widths of the pyrite doublet were constrained at values determined for >95%-pure crystals of pyrite, *i.e.*, at values corresponding to an isomer shift of 0.30 mm s^{-1}, a quadrupole splitting of 0.60 mm s^{-1}, and a half-width of 0.30 mm s^{-1} (Morice *et al.* 1969). Optical microscopy and semiquantitative X-ray diffraction showed that opaque framboids are particularly abundant in the 8–20 cm sections of core. Electron microscopy confirmed the FeS_2 composition of the framboids. The presence of pyrite was further confirmed by the narrowing, as a function of depth of section, of the composite "ferric" doublet in a two-doublet fit (one ferrous and one ferric doublet) (Manning *et al.* 1979). Thus the half-widths of 0.58 ± 0.02 mm s^{-1} measured for the 0–1 and 1–2 cm sections are more typical of ferric ions in oxides and clays, whereas the value of 0.37 ± 0.02 mm s^{-1} measured for the 14–15 cm section is more indicative of pyrite (Manning *et al.* 1979). Most of the sulfur in the top 25 cm of core is clearly in pyrite (Table 1).

Sections 3–4 cm and 9–10 cm showed little change in the Mössbauer spectrum after an acid wash, hence poorly crystalline FeS compounds are relatively minor phases. This is consistent with their low concentrations in the strongly reducing sediments of other prairie lakes (Manning *et al.* 1994).

The additional presence of vivianite in sections of south basin core deeper than 30 cm is indicated by the sharply defined bifurcate absorption at 2.9 mm s^{-1}, *i.e.*, at an energy corresponding to the $Fe^{2+}{}_{I}$ and $Fe^{2+}{}_{II}$ absorptions in vivianite (Manning *et al.* 1991, Nembrini *et al.* 1983). Vivianite, $Fe_3(PO_4)_2{\cdot}8H_2O$, is a major sink for inorganic phosphorus in moderately reducing sediments in which iron and inorganic phosphorus are highly mobile and in which the sulfide ion is not produced in high concentration (Manning *et al.* 1991). Vivianite was confirmed by X-ray diffraction, and also by noting the considerably reduced ferrous absorption on washing the 34–36 and 36–38 cm sections in dilute HCl, in which vivianite is soluble. The concentration of Fe^{2+} (clay) in washed samples is consistent with that in the top 20 cm of core (Table 1). Hence, most of the ferrous iron absorption in the deeper sections of south basin core is due to vivianite. The $Fe^{2+}{}_{I}$ and $Fe^{2+}{}_{II}$ higher-energy absorptions were clearly resolved in spectra of sediment retrieved from Narrow Lake (Manning *et al.* 1991), a mesotrophic lake located in a glacial meltwater channel in close proximity to Baptiste Lake. The spectra of the 34–36 and 36–38 cm sections of Baptiste Lake sediment were successfully resolved using four doublets, one ferric iron, two vivianite ($Fe^{2+}{}_{I}$ and $Fe^{2+}{}_{II}$) and one clay (Fe^{2+}). The remaining spectra were then resolved by constraining all ferrous iron doublets (peak positions and widths). This was deemed necessary because the $Fe^{2+}{}_{I}$, $Fe^{2+}{}_{II}$, and Fe^{2+} (clay) absorptions are superimposed and because their low-energy peaks lie beneath the dominant envelope which is due to ferric iron. The degree of oxidation of the vivianite is not known, hence the ferric iron envelope is a composite of ions bound in clay, hydrated oxide and vivianite. Vivianite peaks are poorly developed in spectra of sediments from the north basin.

TABLE 1. ELEMENTAL CONCENTRATIONS* IN SECTIONS OF A SEDIMENT CORE, BAPTISTE LAKE , ALBERTA

Depth	Fe_T	Fe^{2+}	Fe^{3+}	$Fe(S_2)$	P_{Viv}	NAIP	Ca	S_T	P_T	Mn	BP
0–1	2.8	0.4	2.2	0.2		0.061	5.8	0.39	0.16	0.31	2
1–2	2.8	0.48	1.7	0.64		0.086	6.1	0.58	0.13		4
3–4	2.8	0.31	1.7	0.74		0.05		1.01	0.16		9
4–5	2.8	0.34	1.6	0.84		0.051	5.5	0.99	0.13	0.34	10
7–8	2.8	0.48	1.2	1.18		0.055	7.6	1.47	0.14	0.49	17
9–10	2.8	0.36	1	1.4		0.049		1.76	0.17		23
12–13	2.8	0.39	0.8	1.48		0.06			0.16		30
14–15	2.8	0.34	1.1	1.34		0.032		1.22	0.17	0.37	37
19–20	3.95	0.38	2.1	1.48		0.046	2.3	1.79	0.12		55
24–25	3.62	0.33	2.1	1.23		0.056		1.71	0.14		76
Depth	Fe_T	Fe^{2+}	Fe^{3+}	$Fe^{2+}{}_{Viv}$	P_{Viv}	NAIP	Ca	S_T	P_T	Mn	BP
28–30	5.13	2.12	3	1.7	0.63	0.74	1	0.42	0.85	0.77	90
30–32	4.31	1.16	3.2	0.8	0.3	0.44			0.57		99
32–34	1.81	0.69	1.1	0.3	0.11	0.22	2.6	0.38	0.29	0.17	112
34–36	4.97	2.29	2.7	1.90**	0.7	1.2	1.2		1.4	1.28	127
36–38	5.58	2.51	3.1	2.20**	0.81	1.24	1	0.65	1.33	1.38	142
38–40	4.85	2.18	2.7	1.8	0.67	0.76	1	0.48	0.85	0.97	157
40–42	3.02	1.24	1.8	0.8	0.3	0.19	1.4	0.36	0.27	0.52	170

* Weight% of dry sediments. Total iron concentrations for 0 to 15 cm depth are 0.10 wt%. Concentrations of apatite-bound phosphorus along the length of core are 0.04±0.01 wt%. Concentrations of organically bound phosphorus are 0.06±0.03% and show no obvious trend with depth of burial. Concentrations of organic C are 20.2±1.5 wt% for 0–25 cm depth, and 14.9±1.3 wt% for the 30–42 cm interval.
** Measured by HCl extraction; concentrations of Fe^{2+} in residue are 0.4 and 0.3 wt% for the 34–36 and 36–38 cm section, respectively. P_{VIV} is equal to Fe_{VIV} divided by 2.7. In the 34–36 cm and 36–38 cm sections, 80% of NAIP is extracted by HCl. Vivianite was not detected in the upper 20 cm of core. Concentrations of Al show no significant trend with depth, averaging 2.0±0.5 wt%. Depth is quoted in cm. BP: date in years before present.

The 4 K spectra show that for the 2–4 cm and 34–36 cm sections of Baptiste Lake sediments, magnetically ordered ions contain, respectively, 64% and 68% of total spectral absorption. In the 2–4 cm section, the magnetic behavior is derived from ferric iron in oxides; the sharpness of the pyrite absorption is accentuated. Ferrous ions in vivianite also order magnetically at 4 K (Gonser & Grant 1967); hence the broad unresolved bands in the 4 K spectra of the 34–36 cm section undoubtedly arise from ferric ions in both oxides and vivianite. Most of the ferrous iron in the 34–36 cm section is in vivianite (Fig. 3), amounting to approximately 30% of the total iron (Table 1).

Mössbauer spectral assignments

The spectra of all sections in the 0–25 cm depth interval are satisfactorily resolved on the basis of the Fe^{2+}–Fe^{3+}–FeS_2 scheme in which the ferrous iron is in clay (Fig. 3). Measured values of isomer shift, quadrupole splitting and half-width are, respectively, 1.13 mm s^{-1}, 2.60 mm s^{-1}, and 0.42 mm s^{-1} for ferrous iron, and 0.40 mm s^{-1}, 0.70 mm s^{-1}, and 0.55 mm s^{-1} for ferric iron; all values are good to ±0.03 mm s^{-1}. The corresponding parameters for pyrite are constrained. The measured parameters are consistent with the presence of ferrous ions in structural sites in clay minerals and with ferric ions in similar sites and also in hydrated oxides (Coey *et al.* 1974, Manning *et al.* 1991). These consistent resolutions confirm (Table 1) the conversion of ferric iron into pyrite with time, *i.e.*, on burial, a trend observed in the reducing sediments of other lakes (Manning *et al.* 1979, 1994). Sediments laid down in approximately 1920 (Turner 1995), now buried to depth of 25 cm (Table 1), became sufficiently enriched in organic matter so as to promote the later production of sulfide ion and pyrite; lower redox potentials reflect increasing algal productivity within the lake consequent upon settlement. The high concentrations of pyrite reflect the currently highly eutrophic condition of Baptiste Lake.

The resolution of the Mössbauer spectra of the deeper sediments yielded hyperfine parameters for ferric iron that are similar to those measured for the shallower sections. Measured concentrations of pyrite are minor at less than 5% of total iron. Few framboids were observed under the optical microscope, hence the computer-derived content of pyrite may be spurious. The sediments laid down prior to approximately 1920, *i.e.*, in the depth interval 30–40 cm (Turner 1995), are enriched in total iron, ferrous iron (strongly), ferric iron, manganese and NAIP, when measured against concentrations of apatite, relative to their concentrations in the 0–25 cm section of core (Table 1). In contrast, concentrations of organic carbon are lower than in the later sediments (Table 1). Elevated concentrations of iron, manganese and inorganic phosphorus are consistent with sediment horizons formed under conditions of high redox potential (Manning *et al.* 1991, Nembrini *et al.* 1983); in contrast, thin bands of sediment containing >1 wt% NAIP underlie oligotrophic Lake Ontario and mesotrophic Narrow Lake. The latter lake is in the same meltwater channel as Baptiste Lake, but has a smaller drainage ratio and has experienced less disturbance in the watershed. Whereas most of the iron in the Fe–P horizon in Lake Ontario sediments is present as poorly crystallized hydrated ferric oxide (Manning *et al.* 1983), in Narrow Lake sediments, of higher organic content, the Fe^{3+}–phosphate compound precipitated initially is rapidly converted into vivianite (Manning *et al.* 1991). Vivianite is formed under mildly reducing conditions and under high concentrations of available iron and phosphate ions (Nriagu & Dell 1974). The watersheds of Baptiste and Narrow lakes drain similar terrain. In addition, groundwater flow into the offshore sediments represents an important contribution to the total inflow (12% and 37%, respectively, for Baptiste and Narrow lakes; Shaw & Prepas 1989, Shaw *et al.* 1990). The deeper sediments, at 30–42 cm, with a nutrient composition of low-grade fertilizer, probably mark a period in the history of Baptiste Lake when trophic conditions were similar to those currently in mesotrophic Narrow Lake.

Forms of phosphorus

Concentrations of NAIP over the top 25 cm of north basin sediment are relatively low (Table 1) and comparable to concentrations in sediments of other eutrophic prairie lakes (Manning *et al.* 1994). The sediments in the 30–42 cm depth range are massive sinks for NAIP (Table 1), and their Mössbauer spectra correspondingly show clear evidence for vivianite (Fig. 3); in support, most of this NAIP is released on washing with 0.2 M HCl (Table 1). Moreover, these deeper sections show no enrichment in the inert elements Al and apatite-P (Table 1), elements derived largely from erosional inputs. The elevated concentrations of organically bound phosphorus in the 32–34 cm and 34–36 cm sections (Table 1) may not be real. Concentrations of organic phosphorus are measured as the difference between concentrations of total P and NAIP + apatite-P (Williams *et al.* 1976). For these two sections, the concentrations of organic P are subject to the great error inherent in the measuring of small differences between two large values (Table 1).

Soluble reactive phosphorus is released massively to the hypolimnion during summer and winter anoxia (Fig. 2). The sediments show no visual indication of a brown oxidized surface layer of hydrated ferric oxide, nor are concentrations of ferric iron significantly elevated over the top centimeter (Table 1): phosphorus release is probably due to the breakdown of freshly deposited algal remains rather than to the reduction of oxide–phosphate compounds.

Core chronology

The ^{210}Pb profile confirms that sedimentation has been continuous and undisturbed over the top 42 cm of core, or over approximately 150 years of deposition (Table 1). Rates of sedimentation are 0.63 cm yr^{-1} and 200 g m^{-2} yr^{-1} (Turner 1995).

DISCUSSION

The contrasting forms and behavior of iron, phosphorus, sulfur, and carbon compounds in the 0–20 and 30–42 cm sections of sediment reflect different redox regimes following deposition over the past 150 years (Table 1). This further reflects periods of different dynamics of phosphorus and, possibly, different trophic levels in the lake. The sulfate-reducing horizon (0–25 cm) is consistent with highly anoxic sediment, a consequence of oxygen depletion in the bottom waters and richly organic sediments. Baptiste Lake is currently highly eutrophic, and limited agriculture in the watershed has likely contributed to that condition (Cooke & Prepas 1998).

The high concentrations of iron, Mn, NAIP, and vivianite in the 30–42 cm sections are probably the result of processes similar to those now occurring in the bottom sediments of mesotrophic Narrow Lake (Manning *et al.* 1991). Both lakes lie within the same geological formation, and both receive measurable inflow of groundwater. Groundwater is an important source of inflow to Narrow Lake. Groundwater inflow has been suggested both as a mechanism for enhancing P recycling from bottom sediments to the euphotic zone, and as a factor controlling major-ion chemistry in prairie lakes (Shaw *et al.* 1990). Whereas groundwater at Narrow Lake averages a higher portion of total annual inflow compared to Baptiste Lake (37 *versus* 12%, respectively), groundwater input into Baptiste Lake fluctuates and has been estimated to be as high as 22% of total water inflow (Trew *et al.* 1987). In Narrow Lake, percolation of iron-rich groundwaters through the bottom sediments leads to the massive coprecipitation of hydrated ferric oxide and NAIP before the phosphate ion can become bioavailable (Manning *et al.* 1991). Burial in the reducing sediments leads to the reduction of ferric oxides and the formation of vivianite. It is probable that a similar process took place in Baptiste Lake prior to the turn of the century, *i.e.*, high concentrations of ferrous and phosphate ions in groundwaters percolating upward through the offshore sediments were precipitated at the sediment–water interface. Moreover, since redox potentials within the sediments were not sufficiently low so as to generate sulfide ion, it is likely that less organic matter was deposited in the sediments (Table 1) and that the bottom water was better oxygenated. Current quality of water may be inferior to that which existed for a period of at least 70 years prior to approximately 1920. The change in water quality may be related to a change in groundwater, or the pattern of groundwater flow, which in turn may arise from land-clearing activities on settlement.

The high concentrations of NAIP in the deeper sections of core, *e.g.*, the 1.2 wt% measured for the 34–36 and 36–38 cm sections (Table 1), are largely accounted for by the precipitation of vivianite. However, the use of the concentration of ferrous iron leads to an underestimation of the vivianite concentration because of the partial oxidation (Nembrini *et al.* 1983) of structural ferrous iron to ferric on exposure of samples to air. Hence, more NAIP is contained within the vivianite structure than is indicated in Table 1. Unfortunately, the broad bands in the 4 K Mössbauer spectra are too broad to enable resolution of vivianite and ferric oxide components. Nevertheless, vivianite accounts for the bulk of the NAIP in the deeper sections of sediment.

To raise the concentration of NAIP over a 10-m-thick hypolimnion by 200 μg L^{-1} is equivalent to the release of 2 g P m^{-2} of sediment, which is the total amount of NAIP contained in the top 3 cm of sediment. This much NAIP would require the reduction of approximately 20 g Fe^{3+} in hydrated oxide (Manning *et al.* 1994), based on the classical model for the anoxic release of adsorbed NAIP (Mortimer 1941). It is unlikely that this much hydrated ferric oxide can exist in the sediments, bearing in mind that the bottom waters are anoxic for much of the year and that sulfide formation is well entrenched beneath the top centimeter of sediment.

How rapidly is this massive pool of vivianite-NAIP released to the porewaters and hence to the lake? The mesotrophic status of Narrow Lake suggests that the vivianite is only slowly eroded. Hypolimnetic total phosphorus (TP) release rates are much lower in Narrow Lake (summer mean 1.4 ± 0.3 mg m^{-2} d^{-1}) than in eutrophic Baptiste and Amisk lakes (11.0 ± 2.0 and 7.7 ± 0.3 mg m^{-2} d^{-1}, respectively; Prepas & Burke 1997). Vivianite lies in deeper sediment in Baptiste Lake than in Narrow Lake. Phosphorus is released in massive quantities to the hypolimnion of Amisk Lake, in which the sediments are devoid of vivianite (Manning *et al.* 1994).

Whereas inorganic phosphorus is released from the sediments in summer (Fig. 2), iron is almost completely removed from the water column and deposited in the sediments (Table 2). These trends highlight the disassociation of iron and NAIP under strongly reducing conditions, due in part to the precipitation of iron as poorly crystalline sulfides. Much of this iron is retained within the sediments as pyrite. Highly eutrophic lakes that are strongly stratified over much of the year are therefore liable to become depleted in iron.

Concentrations of extractable iron in the epilimnion of Baptiste Lake in May (30 μg L^{-1}, Table 2), prior to stratification and the release of sediment phosphorus, are a relatively small proportion of total iron. Over the summer, most of the total iron is removed from the water column (Table 2), such that the concentration of total iron is lower than that of inorganic phosphate ion (Fig. 2). The removal of iron arises from the settling out of particulate matter and the consequent precipitation of poorly crystalline iron sulfide under anoxic conditions. In the epilimnion in both summer and winter in Baptiste Lake, there is insufficient extractable (available) iron to bind but a small fraction of the NAIP. Con-

TABLE 2. CONCENTRATIONS (mg L^{-1}) OF TOTAL IRON AS A FUNCTION OF WATER DEPTH IN BAPTISTE LAKE

Date	Depth (m)							
	1	7	11	15	17	21	23	25
7 May	0.32	0.37	0.38	0.34	0.36	0.35	0.35	0.35
4 June	0.29		0.34	0.31	0.38	0.31	0.31	0.35
30 June	0.32	0.17	0.42	0.71	0.17	0.20	0.19	0.13
29 July	0.06	0.10	0.04	0.06	0.011	0.06	0.08	0.01
26 Aug	0.07	0.09	0.08	0.10	0.10	0.12	0.10	0.12
21 Oct	0.60							

Concentrations of extractable iron (0.1M HCl) were 0.03 mg L^{-1} or lower in the water column in the summer of 1992.

centrations of total iron reach 300 to 500 μg L^{-1} during spring and fall overturns, and drop as low as 40 μg L^{-1} throughout the summer. As ferric ions in poorly crystalline hydrated oxides bind approximately 10% by weight of phosphate ion (Manning *et al.* 1983), Baptiste Lake may be considered to be deficient in iron. Fe concentrations in groundwater-fed wells of the region range from <40 to >15 μg L^{-1}, hence disturbance in the watershed may have influenced the flow pattern of iron-rich groundwater. These calculations, which estimate the amount of Fe necessary for the reduction of the NAIP in Baptiste Lake, may explain the highly eutrophic condition of this lake.

This work serves to highlight the fragility of the unique mesotrophy of nearby Narrow Lake (Manning *et al.* 1991). Interference with the pattern of flow of iron-rich groundwater through watershed disturbance would likely render Narrow Lake eutrophic on account of nutrient runoff from prairie soil.

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