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INTENSIVE FORMATION OF VIVIANITE IN THE BOTTOM SEDIMENTS OF MESOTROPHIC NARROW LAKE, ALBERTA

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ABSTRACT

Narrow Lake, Alberta, is unusual among prairie lakes in that the water is clear, and nutrient concentrations and algal productivity are relatively low. However, the bottom sediments of this mesotrophic lake contain extremely high concentrations of nonapatite inorganic phosphorus (~ 1.5 wt.%) in the form of vivianite and adsorbed on hydrated ferric oxides. Ferrous and manganese ions in groundwater percolating upward through the bottom sediments are precipitated in oxygenated deeper water, effectively controlling phosphorus concentrations in the overlying water. The main sink for phosphorus switches from the oxide to vivianite with increasing depth of burial in the sediments. Mössbauer spectral data suggest that the freshly precipitated hydrated oxide is similar to ferrihydrite. Thus in this lake, high concentrations of phosphorus are effectively bound in the deep-water sediments and are not available to planktonic algae.

Keywords: vivianite, ferrihydrite, phosphorus, sediments, mesotrophy, lake, Alberta.

SOMMAIRE

Le lac Narrow, en Alberta, est anomal parmi les lacs des prairies: l'eau y est claire, et la concentration des éléments nutritifs et la production d'algues sont relativement faibles. Par contre, les sédiments profonds de ce lac mésotrophe contiennent des concentrations élevées (~ 1.5% par poids) de phosphore inorganique non lié à l'apatite, présent sous forme de vivianite et adsorbé sur des oxydes ferriques hydratés. Les ions de Fe^{2+} et de Mn des eaux sous-terraines, lixiviés des sédiments du fond, forment un précipité dans la couche d'eau oxygénée profonde, ce qui exerce un contrôle sur les teneurs en phosphore dans les couches d'eau supérieures. La vivianite devient donc le site principal du phosphore, de préférence à l'oxyde, avec une augmentation de la profondeur d'enfouissement des sédiments. D'après les spectres Mössbauer, l'oxyde hydraté nouvellement précipité ressemblerait à la ferrihydrite. Les teneurs élevées en phosphore dans ce lac seraient donc piégées dans les sédiments profonds et non disponibles aux algues planctoniques.

(Traduit par la Rédaction)

Mots-clés: vivianite, ferrihydrite, phosphore, sédiments, mésotrophie, lac, Alberta.

INTRODUCTION

Narrow Lake (54°37′N, 114°37′W) is a small (~ 1 km^2 surface area) deep (mean depth ~ 20 m) clear lake located in glacial till 140 km north of Edmonton, Alberta (Fig. 1). With a Secchi depth exceeding 5 m and low summer concentrations of total phosphorus (~ 12 μg L^{-1}) and chlorophyll *a* (~ 3 μg L^{-1}), the lake is classed as mesotrophic. This high trophic character is remarkable in that most freshwater prairie lakes are naturally eutrophic (Allan & Kenney 1978, Barica 1974, Prepas & Trew 1983). Phosphorus is the limiting nutrient in Narrow Lake (Prepas 1983, Prepas & Trimbee 1988), and groundwater flow through the bottom sediments is likely the largest source of phosphorus to the lake (Shaw *et al.* 1989).

The aims of the work are to determine (a) the forms of nonapatite inorganic phosphorus, the main source of bioavailable phosphorus (Williams *et al.* 1980), in the bottom sediments and (b) the roles of these sediment compounds in controlling the trophic character of the lake. Other nearby lakes (*e.g.*, Amisk and Baptiste Lakes), also with undeveloped and forested shorelines, are highly eutrophic; algal blooms are massive, and the bottom sediments sulfidic.

EXPERIMENTAL

Gravity cores of bottom sediments were collected in June 1985 from beneath 20 m of water in the shallow North Basin and from beneath 35 m of water in the deep South Basin. Both basins were strongly stratified at the time of collection, with bottom temperatures of 5°C in the South Basin and 6°C in the North Basin (Fig. 2). Concentrations of dissolved oxygen were depleted in both basins (~ 2 mg L^{-1} in

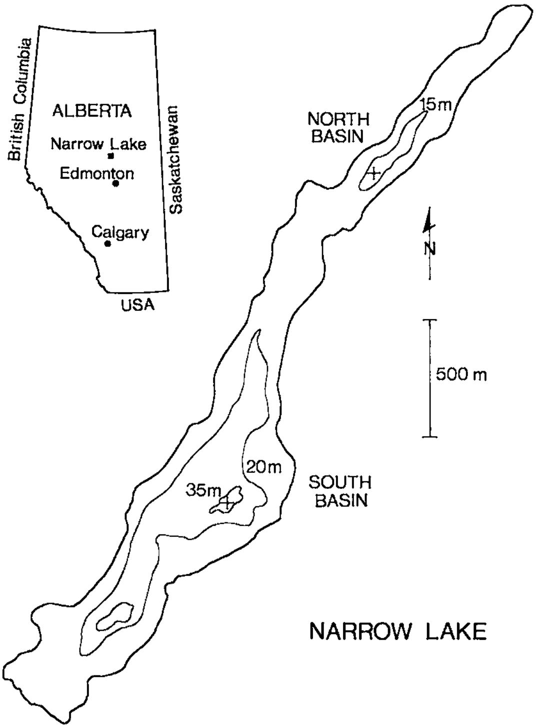

FIG. 1. Location of Narrow Lake, Alberta, and the two sampling locations.

the bottom waters of the South Basin) (Fig. 2). The cores were extruded and sectioned immediately into 1-cm slices from 0 to 22 cm depth, frozen, and freeze-dried on return to the laboratory. All sections were grey in color.

Room-temperature Mössbauer spectra were recorded on a 512-channel spectrometer and computed on a mainframe computer using the programs of Stone (1967). Lorentzian line-shapes were assumed, and the areas and half-widths of peaks within a quadrupole doublet were constrained to be equal. Visual examination and values of chi-squared were used as criteria of goodness of fit. Three-doublet and four-doublet fitting schemes were invoked. The three-doublet scheme was based on one strong central ferric iron doublet and on two ferrous iron doublets, clearly marked by their high-energy peaks at ~2.6 and 2.9 mm s^{-1} (Fig. 3). The lower-energy partner of each of the two ferrous doublets is located beneath the central ferric absorption at ~0 mm s^{-1} velocity (Fig. 3). The progressive and parallel increases in the strengths of the spectral signals due to the two ferrous iron absorptions, which occur with increasing depth of burial in the sediment, strongly suggest that the two doublets mark ferrous ions in two different sites in one compound. Sharply defined X-ray-diffraction patterns confirmed the presence of vivianite in the deeper South Basin sediments. Moreover, optical microscopy revealed an abundance of very pale blue crystals in the South Basin sediments, the color and morphology of which are indicative of weakly oxidized vivianite (Faye *et al.* 1968). The weak color indicates a low concentration of ferric ions in vivianite; the correspondingly weak absorptions of the ferric ions are not considered important to, nor actually resolvable in, the resolution of the Mössbauer spectra. The North Basin sediments, in contrast, gave neither X-ray diffraction nor optical microscopic evidence for significant amounts of vivianite.

In order to obtain convergence in the computer resolution of the spectra of the 0- to 1-cm and 1- to 2-cm sections of South Basin sediments, the peak positions and peak half-widths of the Fe^{2+}_{I} and Fe^{2+}_{II} vivianite doublets were constrained at previously published values (Nembrini *et al.* 1983); the half-width of the Fe^{2+}_{I} doublet was constrained in three other spectral resolutions (2 to 3 cm, 3 to 4 cm, and 4 to 5 cm). Such constraints are justified because of the low concentrations of vivianite in these sections and also because of potential interference from the presence of much smaller amounts of Fe^{2+} ions in clay minerals (Manning *et al.* 1988, Coey *et al.* 1974).

An additional (fourth) doublet, with parameters constrained to those of pyrite (isomer shift: 0.31 mm s^{-1}, quadrupole splitting: 0.60 mm s^{-1}, and half-width: 0.30 mm s^{-1}) was introduced into the second scheme (Manning *et al.* 1988); a few opaque pyrite framboids were observed on examination of the sediment under an optical microscope. Pyrite is clearly a minor phase (Table 1), in contrast to the highly pyritic sediments of hypereutrophic Figure Eight Lake, Alberta (Manning *et al.* 1988) and of nearby eutrophic Amisk Lake (abundant framboids seen by optical microscopy). All computations converged successfully; results for the four-doublet scheme are presented here (Table 1).

Mössbauer spectra recorded at 4 K display a well-developed magnetic six-line pattern, with a measured field gradient (435 - 448 kOe) consistent with ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$ (Murad & Schwertmann 1980).

Concentrations of total iron and total manganese were measured by bomb digestion and atomic absorption spectrometry (Agemian & Chau 1975). Concentrations of nonapatite inorganic phosphorus (NAIP) were measured following the wet-chemical methods of Williams *et al.* (1976); apatite-P is considered too insoluble to be readily available. Most of the organically bound phosphorus is in esters and phospholipids and is also considered relatively unavailable (Williams *et al.* 1980). Concentrations of carbon and sulfur were measured using a Leco

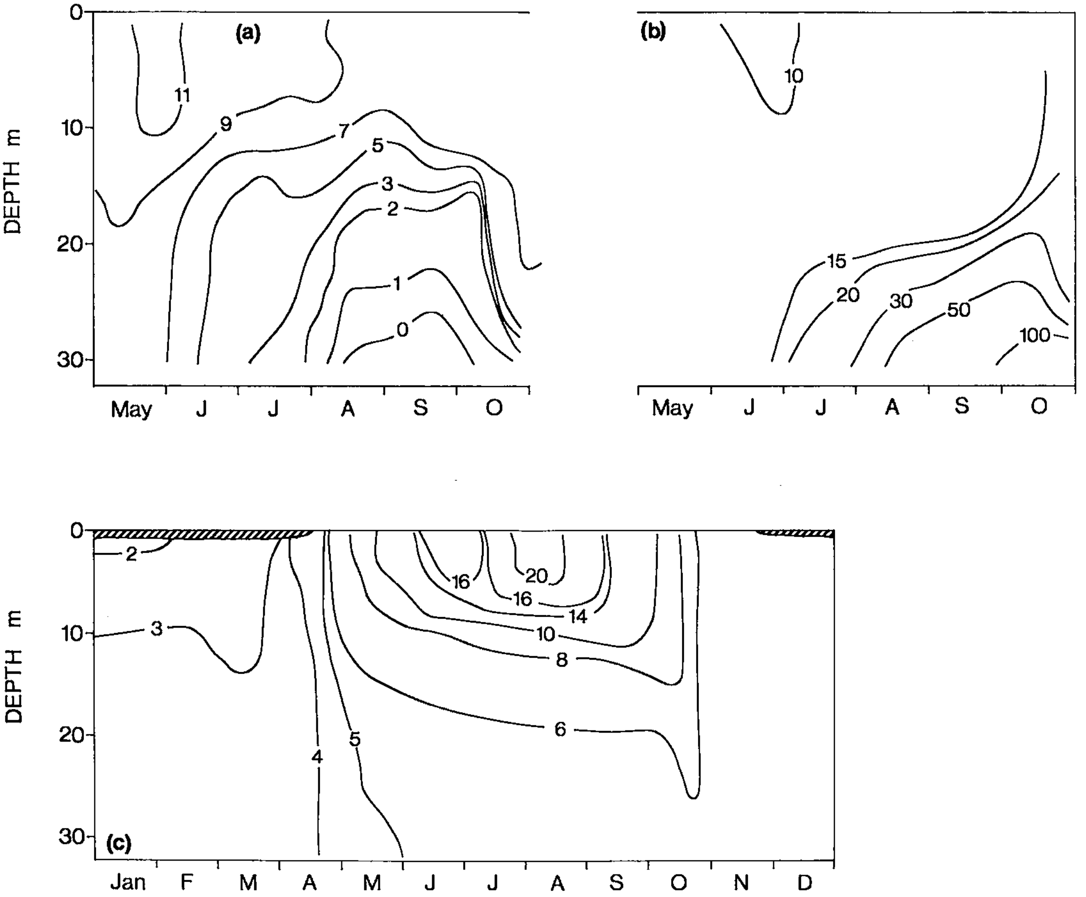

FIG. 2. Plots depicting (a) concentrations of dissolved oxygen (mg L^{-1}), (b) concentrations of total phosphorus (μg L^{-1}), and (c) temperature (°C) as functions of time in the deep South Basin of Narrow Lake, 1984. Hatched area represents ice cover. Oxygen is less severely depleted in the hypolimnetic waters of the North Basin, and phosphorus release is much lower.

induction furnace (Kemp 1971). All concentrations are presented as weight percent of dry sediment.

RESULTS AND DISCUSSION

Mössbauer spectral assignments

All spectra of South Basin sediments are dominated by a relatively broad central doublet (Fig. 3), which contains the significant absorptions of (a) ferric ions in hydrated ferric oxides, the major contributor, (b) the lower-energy components of the two ferrous ion doublets in vivianite, and (c) the weak doublets of pyrite. Calculated values of isomer shift (IS), relative to iron foil, quadrupole splitting (QS), and half-width (HW) are: for Fe^{3+} 0.41 ± 0.02 mm s^{-1}, 0.80 ± 0.03 mm s^{-1}, and 0.54 ± 0.03 mm s^{-1}; for Fe_{II}^{2+} 1.20 ± 0.02 mm s^{-1}, 3.01 ± 0.02 mm s^{-1}, and 0.32 ± 0.02 mm s^{-1}; and for Fe_{I}^{2+} 1.11 ± 0.02 mm s^{-1}, 2.56 ± 0.03 mm s^{-1}, and 0.40 ± 0.03 mm s^{-1}, respectively. The ferrous ion values are in good agreement with those published (Coey *et al.* 1974, Nembrini *et al.* 1983, Gonser & Grant 1967) for the respective ions in vivianite. Approximately 50% of total sulfur is in pyrite (Table 1).

The spectra of the shallow North Basin sediments are well fitted (Fig. 4) on the basis of one ferric iron doublet and, in marked contrast to the South Basin muds, one ferrous doublet. Measured Mössbauer parameters of IS, QS, and HW are 1.13, 2.60 and 0.43 mm s^{-1} for Fe^{2+}, and 0.36, 0.67, and 0.62 mm s^{-1} for Fe^{3+}, respectively; all values are good to ±0.02 mm s^{-1}. All values agree well with those measured for Figure Eight Lake sediments (Manning *et al.* 1988). The introduction of a pyrite doublet into

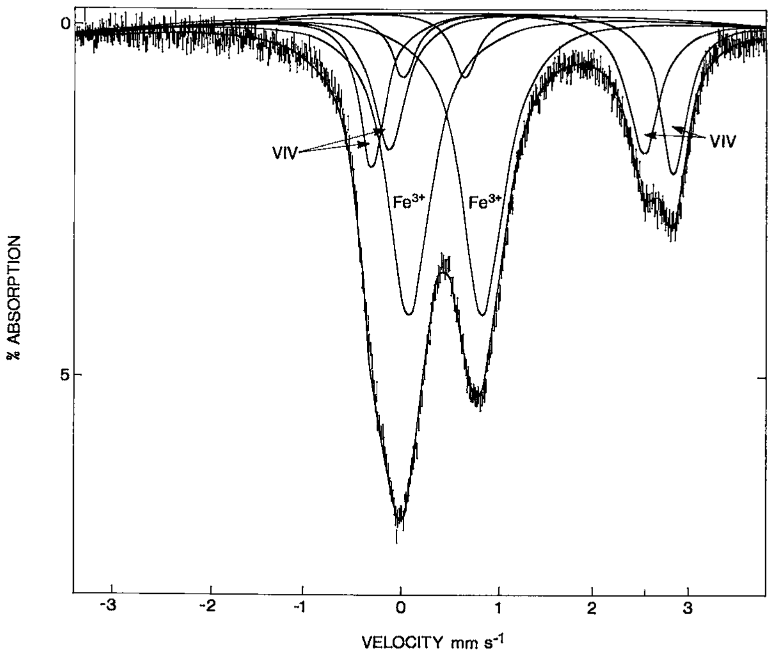

FIG. 3. Room-temperature Mössbauer spectrum of 17- to 18-cm section of sediment collected from the deep South Basin of Narrow Lake. VIV represents the vivianite absorptions, beneath which lie the weaker unresolved absorptions of ferrous ions in clay minerals and chlorite. The weak pyrite doublet is unlabeled. Chi-squared is 695 for 489 degrees of freedom.

TABLE 1. CONCENTRATIONS OF IRON, MANGANESE, ALUMINUM, C AND S IN NARROW LAKE SEDIMENTS

Section cm	Fe_T	Fe^{3+}	$Fe(S_2)$	Fe^{2+}_{II}	Fe^{2+}_{I}	Mn_T	Al_T	NAIP	S_T	Org C	$NAIP_{calc}$
	weight percent										
				Deep (South) Basin							
0-1	11.3*	9.7	0.5	0.5	0.4						
1-2	11.3	10.2	0.3	0.3	0.5	1.9	1.05	1.29	0.66	15.5	1.19
2-3	11.3	9.6	0.3	0.8	0.6			1.54	0.57	11.5	1.40
3-4	11.3	8.6	0.3	1.1	1.3	1.9	0.99				
4-5	11.3	8.2	0.3	1.3	1.5	2.1	0.99	1.45	0.64	15.5	1.54
5-6	9.3	8.2	0	0.5	0.6				0.65		
7-8	9.3	6.4	0.2	1.2	1.5	1.8	0.93	1.75	0.81	14.4	1.31
9-10	9.3	5.5	0.5	1.6	1.6	1.4	1.19	1.50	0.93	15.8	1.44
12-13	7.5	4.7	0.3	1.2	1.3				0.79	13.0	
14-15	7.5	4.2	0.3	1.3	1.7	0.9	1.26	1.50			1.14
17-18	7.5	4.4	0.4	1.3	1.4	0.8	1.27		0.81	12.2	
19-20	7.5	4.3	0.4	1.3	1.6	1.1	1.71	1.72		10.7	1.15
21-22	10.9	8.0	0.2	1.3	1.3	1.2	0.97	1.46	0.56	13.0	1.52
				Shallow (North) Basin							
0-1	2.02	1.66	0	0.36 (clay)		0.14	2.61	0.048	0.42	18.8	na
4-5	2.04	1.67	0	0.36 (clay)		0.06	3.22	0.031	0.78	18.3	na
10-11	2.00	1.61	0.02	0.36 (clay)		0.04	3.32	0.029	0.64	18.5	na
18-19	2.05	1.68	0	0.37 (clay)		0.04	3.29	0.035	0.49	16.0	na

* Total iron (Fe_T) concentrations in sections 1 to 2 cm, 2 to 4 cm, and 4 to 5 cm are 11.0, 12.0, and 10.9 wt. %: for simplicity, all sections in the 0-5 cm depth are given an average Fe_T value. Similarly, Fe_T values for sections from 5 to 10 cm and from 12 to 20 cm are averages of at least two individually analyzed sections. Concentrations of apatite-P are ~0.02 wt. % P in both basins. na is not applicable.

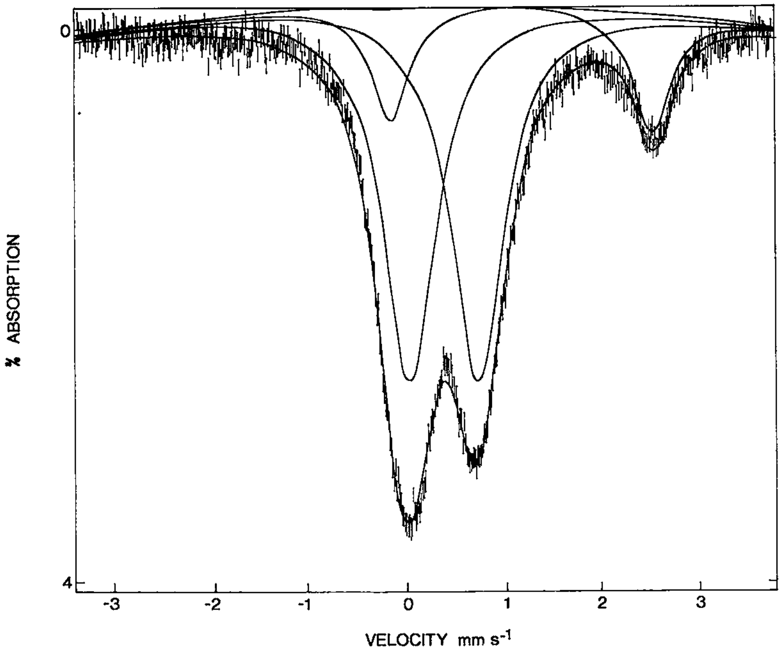

FIG. 4. Room-temperature Mössbauer spectrum of 4- to 5-cm section of sediment collected from the shallow North Basin. Chi-squared is 610 for 494 degrees of freedom.

the fitting scheme yielded insignificant amounts of FeS_2; neither could the computer detect significant absorption at energies corresponding to Fe^{2+}_{II} (vivianite). The spectra of the North Basin sediments took considerably longer to accumulate compared with the South Basin, consistent with considerably lower concentrations of total iron in the North Basin sediments (Table 1). Hence, the relative weakness of the ferrous-clay absorption (Fig. 3) in the spectra of the South Basin sediments arises from the massive precipitation of ferric hydroxide in the deeper water and of vivianite within the sediment (Fig. 5). The Al concentrations (Table 1) confirm the greater proportion of clay in the North Basin sediments.

The Mössbauer parameters for ferric iron measured in the South Basin and North Basin are significantly different, particularly with respect to quadrupole splitting (see text above). The relatively large QS value (0.8 mm s^{-1}) for the South Basin sediments is indicative of the precipitation of an oxide similar in structure and composition to ferrihydrite (Murad & Schwertmann 1980). Ferrihydrite is formed when percolating groundwaters containing ferrous ions and organic matter meet an oxidizing horizon (Coey & Readman 1973, Schwertmann & Fischer 1973, Tipping *et al.* 1989). These observations are consistent with the precipitation of ferrihydrite in the oxygenated deep water of the South Basin; in contrast, the QS values of ferric ions in the North Basin sediments are indicative of oxides and clays deposited in the lake as products of erosion. The lack of a well-developed X-ray-diffraction pattern indicates that the hydrated ferric oxide is poorly crystallized.

Forms of manganese

Concentrations of total manganese (Table 1) in the (deep) South Basin sediments greatly exceed those in the (shallow) North Basin, but are comparable to the elevated concentrations measured in the 0.1-cm-thick active subsurface layers in Lake Ontario sediments (Manning *et al.* 1983). The Mn values clearly exceed those measured in the ~1-cm-thick brown oxidized surface layers of Lake Ontario sediments (~1%, Manning *et al.* 1984). In both Lake Ontario situations, porewater Fe^{2+}, Mn^{2+}, and phosphate ions are precipitated at strong redox boundaries. The enhanced Mn:clay ratios and the strong redox processes leading to the precipitation of ferric iron suggest that most of the Mn, in sediments of the South Basin, is present as hydrated Mn^{4+} oxide (Stumm & Morgan 1981). The minor amounts of manganese present in the sediments of the North Basin of Narrow Lake are incorporated in clay minerals and other products of erosion.

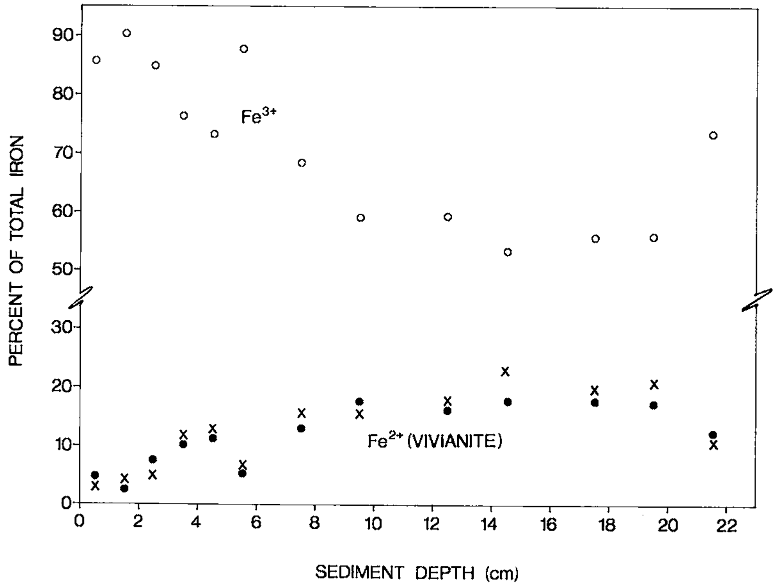

FIG. 5. Plots showing the distribution of iron between vivianite (Fe^{2+}) and hydrated ferric oxide (Fe^{3+}) as a function of sediment depth (*i.e.*, time). Approximately 5% of total iron is in pyrite. Filled circles mark points for Fe_I^{2+}, crosses for Fe_{II}^{2+}.

Forms of inorganic phosphorus

Concentrations of apatite-P in the deep and shallow basin sediments are comparable (~0.02% P), suggesting that the apatite is derived from shoreline erosion. Apatite is highly insoluble, and the phosphorus is unavailable (Williams *et al.* 1980). Concentrations of NAIP in the South Basin sediments are extremely high and greatly exceed NAIP values measured in bottom sediments from the North Basin (Table 1), from other prairie lakes (Allan & Williams 1978), and from all but special situations in the Great Lakes (Williams *et al.* 1976, Manning *et al.* 1984), *e.g.*, the ferric-iron-rich subsurface layers in some areas of Lake Ontario (~1% NAIP; Manning *et al.* 1983). The hydrated ferric oxides actively precipitating in these layers in Lake Ontario sediments adsorb ~10% NAIP by weight of Fe; these oxides are probably ferrihydrite.

The total amount of NAIP contained within the vivianite crystals and adsorbed on the hydrated ferric oxides cannot be accurately calculated, mainly because the precise compositions of the vivianite and the oxide are not known. Nevertheless, it is easily shown that most of the NAIP measured is associated with vivianite and ferric oxides. The ideal Fe_{II}:Fe_I ratio in vivianite, $Fe_3^{2+}(PO_4)_2{\cdot}8H_2O$, is 2:1 (Gonser & Grant 1967); hence the measured ~1:1 Fe_{II}^{2+}:Fe_I^{2+} ratio (Table 1) indicates that (i) either Fe^{3+} or Mn^{2+} ions are substituting preferentially into Fe_{II} sites on partial oxidation, or (ii) a significant proportion of the Fe_I^{2+} ions measured actually mark ferrous ions in clay minerals or chlorite (or both), or (iii) a combination of (i) and (ii). Weak development of color in the vivianite crystals suggests that, as a first approximation, ferric ion substitution is minor; weak color implies weak $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer processes (Faye *et al.* 1968). With regard to (ii), the concentration of ~0.36 wt.% Fe^{2+} (clay) in the shallow North Basin sediments (Table 1), when transcribed to the deeper sections of the South Basin sediments, indicates that a significant proportion of the Fe_I^{2+} absorption is due to Fe^{2+}(clay); the Mössbauer parameters for Fe_I^{2+} and Fe^{2+} (clay) are very similar (see text above). Assuming that the Fe_{II}^{2+} ion is the main occupant ion of the Fe_{II} site and that $[Fe_I^{2+}]$ is equal to $0.5[Fe_{II}^{2+}]$, then $[NAIP]_{calc}$ is equal to $0.1[Fe^{3+}] + 0.37 \times 1.5\ [Fe_{II}^{2+}]$, where brackets represent concentrations, and 0.37 is the weight ratio of P:Fe in vivianite. Reasonable agreement is obtained between measured and calculated values of NAIP (Table 1). The substitution of Mn^{2+} ions into the Fe_{II} site would yield higher values of NAIP in vivianite.

Clearly, there is sufficient ferric oxide and vivianite in the bottom sediments to account for most of the NAIP. Moreover, the data (Table 1, Fig. 5) show that on reduction of ferric iron, with increasing depth of burial, the main sink of NAIP switches from adsorption on ferric oxides to incorporation into vivianite. The NAIP-binding capacity of Mn^{4+} ions is ignored in these calculations, but in Lake Ontario sediments, Mn^{4+} oxides are less efficient binders of NAIP than are ferric oxides (Manning *et al.* 1983).

The coexistence of significant concentrations of vivianite and hydrated ferric oxides in the sediments of the South Basin is inconsistent with thermodynamic principles (Nriagu & Dell 1974). Vivianite forms under strongly reducing conditions, under which ferric ions are unstable. In South Basin sediments, concentrations of ferric iron decrease with time (Fig. 5), but the rate of reduction is clearly slow. The persistence of ferric ion is, therefore, a function of the kinetics of the reduction reaction. The reduction of ferric iron may be hindered by its chemical form, in which the central cation is bonded to phosphate ions, organic anions (*e.g.*, humate and fulvate), and to clay surfaces (Stumm & Morgan 1981). Furthermore, temperatures of the bottom waters remain low year-round (Fig. 2), further inhibiting microbial activity. Ferric iron is persistent in the reducing sediments of the Great Lakes (Manning *et al.* 1984) and in the sulfidic sediments of a prairie lake (Manning et al. 1988).

The redox potential at the sediment–water interface changes from positive to negative between spring and autumn (Fig. 2). For most of the year, ferrous ions diffusing from the sediments into the overlying water are oxidized, and may weakly crystallize to form ferrihydrite. During the brief period of bottom anoxia in September (Fig. 2), redox conditions at the surface of the sediments favor the formation of vivianite, provided sulfide ions do not cause precipitation of most of the labile iron as FeS compounds. However, the gradual increase in concentrations of vivianite with increasing depth of burial (Fig. 5), and at the expense of ferric iron, indicates that most of the vivianite is formed within the sediments.

General discussion

The contrast between the deep-water sediments, which have a phosphorus content equivalent to that of low-grade fertilizer, and the water column, with the phosphorus concentrations of a mesotrophic lake, makes Narrow Lake most unusual. The remarkable P-binding capacity of the sediments undoubtedly arises from the high concentrations of ferric oxide precipitated in the deeper water. These ferric (and manganese) oxides are deposited to the sediments, having removed phosphate ions from solution before the growth of algae can be stimulated. Low concentrations of available phosphorus are followed by limited algal growth and, consequently, by a low rate of metabolism of dead organic matter in the bottom sediments. Further, weak generation of sulfide in the sediments prevents massive reduction of ferric iron and the consequent formation of FeS_2 and phosphorus release. Vivianite generally occurs in anoxic low-sulfide sediments (Berner 1981) and in sediments underlying eutrophic lakes (Cornwell 1987). The lower concentrations of organic carbon in the deeper South Basin sediments (Table 1) suggest that much of the carbon is terrigenous: organic matter generated within the lake would be deposited in greater amounts in the deeper basin.

Calculated ratios of Fe^{3+}:Fe^{2+} (clay) in the near-surface sediments of the South Basin (~25) greatly exceed those of the North Basin (~4, Table 1) and of Figure Eight Lake, Alberta (~2.5, Manning *et al.* 1988). Erosional inputs from stream flow and surface run-off would lead to similar Fe^{3+}:Fe^{2+} (clay) ratios for all Narrow Lake sediments. Because vivianite formation controls the concentration of soluble phosphate in sediment porewaters generally (Nriagu 1972, Nriagu & Dell 1974, Emerson & Widmer 1978, Tessenow 1974) and because groundwater flow is an important source of phosphorus to Narrow Lake, then the low concentrations of phosphorus in the overlying water also can be attributed to iron–phosphate precipitation reactions in the sediments. Groundwaters in the glacial till around Narrow Lake and in tills located up to 100 km away contain a high concentration of dissolved iron (R.D. Shaw and A.S. Crowe, pers. comm.), indicating that the groundwater is probably anoxic (Stumm & Morgan 1981). Ferrous ions also are released to the porewaters through the reduction of hydrated ferric oxides within the sediment. High activities of ferrous ion and reducing conditions favor the formation of vivianite. Hence, the trophic character of the lake is controlled internally. The groundwater flow system in the vicinity of Narrow Lake must not be disturbed by human activity: an interruption in the input of iron could lead to greater productivity in the water, a higher input of organic matter to the sediments from the overlying water, and the generation of sulfide ion. Massive release of phosphorus to the water could then occur.

The summer release of soluble reactive phosphorus to the hypolimnion (Fig. 2) can arise from the flushing out of porewaters by groundwater flow, in the absence of an oxidized surface-layer of sediment, or by reduction of hydrated ferric oxides in the surface sediments. Most of the total phosphorus in the deep water is soluble reactive phosphorus. The precipitation of ferric oxides in oxygenated water probably generates particles of different sizes and crystallinities, each with different susceptibility to reduction. Based on a groundwater (porewater) P loading rate of 43 mg m^{-2} yr^{-1} (Shaw *et al.* 1990) and a 10-m-thick hypolimnion (Fig. 2), the calculated maximum concentrations of soluble reactive phosphorus in the overlying water would be 4 μg P L^{-1}: the measured values of 20 to 100 μg P L^{-1} (Fig. 2) indicate that reduction and dissolution of hydrated ferric oxides in the surficial sediments are the major source of summer release of phosphorus. The top cm of sediment in the deep basin contains ~10 g P m^{-2}, which, if completely released to a 10-m-thick hypolimnion, would yield ~1000 μg P L^{-1}.

A layer of subsurface sediment underlying Lago Maggiore contains ~3% Fe and ~0.3% P and abundant concretions of vivianite (Nembrini *et al.* 1983), probably formed through the reduction of a layer of ferric hydroxide. Vivianite is formed continuously and in considerably higher concentrations in Narrow Lake sediments. These studies suggest that the available phosphate concentrations in eutrophic lakes could be reduced through the addition of ferrous or ferric ions. The binding capacity of freshly precipitated hydrated ferric hydroxide for NAIP is ~10% of the weight of Fe, which suggests an ideal iron:phosphorus input to the lake of 10:1. On deposition of this initial load of ferric oxide to the sulfide-producing sediments and mixing-in to a depth of ~1 cm through bioturbation, much of the ferric iron would be reduced and converted to FeS_2. Phosphorus would then be released, particularly to a warm hypolimnion. The iron treatment would need to be repeated over several years so as to raise the redox potentials in the sediments sufficiently to minimize production of sulfide and promote formation of vivianite. Spent pickle liquor, a by-product of the steel industry, could be a suitable source of iron.

Phosphorus concentrations in relatively deep prairie lakes such as Narrow Lake differ greatly, encompassing the relatively unproductive Narrow Lake to the hypereutrophic Baptiste Lake. Baptiste Lake is located 10 km north of Narrow Lake and in the same glacial meltwater channel as Narrow Lake. Most of these deep prairie lakes have relatively low inputs of external phosphorus, and the more productive lakes have high internal loads of phosphorus from sediments extending from the shallower regions to the deepest part of the lake (Shaw 1989). The variability in concentration of phosphorus in surface water in these deep prairie lakes is directly related to the phosphorus binding capacity of the bottom sediments. The deep sediments in Narrow Lake provide an extreme example of a lake in which simultaneous loadings of phophorus and iron protect the lake from increased phosphorus loadings to the surface waters.

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