



TD 226 N87 No. 90-05 c. 1 INTENSIVE VIVIANITE FORMATION IN THE BOTTOM SEDIMENTS OF MESOTROPHIC NARROW LAKE, ALBERTA

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NWRI Contribution No. 90-05

## INTENSIVE VIVIANITE FORMATION IN THE BOTTOM SEDIMENTS OF

MESOTROPHIC NARROW LAKE, ALBERTA

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### MANAGEMENT PERSPECTIVE

Narrow Lake is a small, deep, clear lake of significant recreational value, located 140 km north of Edmonton, Alberta. Low phosphate and chlorophyll levels are indicative of a mesotrophic lake, in marked contrast to the highly eutrophic character of most prairie lakes. Remarkably, the bottom sediments have the phosphorus content of low-grade fertilizer. Iron-rich groundwaters seeping into deeper water cause precipitation of phosphorus and deposition to the sediments, rendering the phosphorus unavailable for algal growth. This natural control of trophic level by iron suggests that steel mill pickle liquor waste could find application in lake restoration.

### PERSPECTIVE DE GESTION

Le lac Narrow est un petit lac profond, à eau claire et de valeur récréative significative, qui est situé à 140 km au nord d'Edmonton, en Alberta. Les niveaux peu élevés de phosphate et de chlorophylle sont plus caractéristiques d'un lac mésotrophe, condition qui s'oppose aux eaux fortement eutrophes de la plupart des lacs de prairie. De façon tout aussi remarquable, les dépôts de fond ont une composition semblable à celle d'engrais à faible teneur en phosphate. Les eaux souterraines, riches en fer, se mélangent aux eaux profondes et provoquent la précipitation du phosphore et son accumulation dans les sédiments, rendant le phosphore non disponible pour la croissance des algues. Ce contrôle naturel des niveaux trophiques par le fer suggère que les solutions de dérochage qui sont rejetées par les aciéries pourraient être utilisées dans la restauration des lacs.

#### 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 percent) 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 sedi-Mossbauer spectral data suggest that the freshlyments. precipitated hydrated oxide is similar to ferrihydrite. Thus in this lake, high sediment phosphorus is effectively bound in the deep-water sediments and is not available to planktonic algae.

**KEYWORDS:** Vivianite, ferrihydrite, phosphorus, sediments, mesotrophy, lake.

ABRÉGÉ

Le lac Narrow, situé en Alberta, se distingue parmi les lacs de prairie par la clarté de son eau, par de basses concentrations en sels nutritifs et par une croissance d'algués relativement faible. Malgré tout, les sédiments de ce lac mésotrophe contiennent des concentrations extrêmement élevées de phosphate inorganique autre que l'apatite (environ 1,5 % en poids), notamment sous forme de vivianité et adsorbé aux hydroxydes ferriques. Les ions ferreux et de manganèse des eaux souterraines, qui filtrent à travers les sédiments, sont précipités par les eaux profondes oxygénées, ce qui a pour effet de limiter la concentration de phosphore dans les eaux superficielles. L'accumulation de phosphore progresse de la forme oxydée à la forme vivianite à mesure que l'on avance en profondeur dans les sédiments. Les données de spectres Mössbauer suggèrent que les oxydes hydratés, nouvellement précipités, sont voisins de l'hydrate ferrique. **I**1 apparaît donc que le phosphore des sédiments de ce lac est effectivement lié en eau profonde et qu'il n'est pas disponible pour les algues planctoniques.

MOTS CLÉS : Vivianite, hydrate ferrique, phosphore, sédiments, mésotrophie, lac.

## INTRODUCTION

Most prairie lakes are naturally eutrophic, reflecting the fertility of local soils (Allan & Kenney 1974, Barica 1974, Prepas & Trew 1983). Stratification in summer and, often, under ice in winter leads to hypolimnion anoxia and intense sulfide production in the bottom sediments (Manning et al. 1988). Oxygen starvation in winter causes severe fish kills (Barica & Mathias 1979). Small lakes are extremely important to the prairie way of life, for recreational and agricultural usage, and also as wildlife refuges.

Narrow (54°37'N, 114°37'W) Lake is a small (1 km<sup>2</sup> surface area) deep clear lake located in glacial till -140 km north of Edmonton, Alberta (Fig. 1). The shoreline is undeveloped and the watershed is almost completely Narrow is a headwater lake, water entering by forested. precipitation, groundwater, and, intermittently, by stream. With a Secchi depth exceeding 5 m and low summer concentrations of total phosphorus (-12  $\mu$ g L<sup>-1</sup>) and chlorophyll <u>a</u> ( 3  $\mu$ g L<sup>-1</sup>), the lake is classed as mesotrophic. Concentrations of total nitrogen in summer, -600  $\mu$ g L<sup>-1</sup>, and a series of boassays (Prepas 1983, Prepas & Trimbee 1988), suggest that phosphorus is the limiting nutrient. The water column becomes thermally stratified soon after ice-out and remains so throughout the summer (Fig. 2).

Narrow Lake was only partially saturated with dissolved oxygen when it stratified in the spring months of nine years from 1980 through 1989 (Fig. 2). By August, concentrations of dissolved oxygen usually decline to ~1 mg  $0_2$  L<sup>-1</sup> over the deeper sediments.

Groundwater percolating through the phosphorusrich bottom sediments is likely the largest source of phosphorus to the lake water (Shaw et al. 1989): groundwater, therefore, promotes the recycling of phosphorus from sediment to the surface water. Release of soluble reactive phosphorus from the bottom sediments is particularly heavy during severe oxygen depletion in late summer (Fig. 2). Although true anoxia does not develop in the hypolimnetic waters, except for a brief period in September, the surficial sediments probably become anoxic. 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 role 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

Bottom sediment gravity cores 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, with bottom temperatures of 5°C in the South Basin and 6°C in the North Basin. Dissolved oxygen concentrations were depleted in both basins (~2 mg L<sup>-1</sup>in the bottom waters of the South Basin). The cores were extruded and sectioned immediately into 1 cm slices from 0 to 22 cm depth, frozen and freezedried on return to the laboratory. All sections were grey in colour.

Room temperature Mossbauer 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 threedoublet 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<sup>-1</sup> (Fig. 3). The lower-energy partner of each of the two ferrous doublets is located beneath the central ferric absorption at

-0 mm s<sup>-1</sup> velocity (Fig. 3). The progressive and parallel increases in the spectral signal strengths of the two ferrous 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 colour and morphology of which were indicative of weakly-oxidized vivianite (Faye et al. 1968). The weak colour indicates a low concentration of ferric ions in vivianite and their correspondingly weak absorptions are not considered important to, nor actually resolvable in, the resolution of the Mossbauer 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 O- to-1-cm and 1- to-2-cm sections of South Basin sediments, the peak positions and peak half-widths of the  $\mbox{Fe}^{2+}_{\ I}$  and  $\mbox{Fe}^{2+}_{\ II}$  vivianite doublets were constrained at previously published values (Nembrini et al. 1983); the half-width of the  $\text{Fe}_{I}^{2+}$  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 vivianite concentrations 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<sup>-1</sup>, quadrupole splitting = 0.60 mm s<sup>-1</sup> and half-width = 0.30 mm s<sup>-1</sup>) 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, PGM). All computations converged successfully and results for the four-doublet scheme are presented here (Table 1).

Mossbauer spectra recorded at 4K, displayed a well-developed magnetic six-line pattern, with a measured field gradient 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 induction furnace (Kemp 1971). All concentrations are presented as weight percent of dry sediment.

#### **RESULTS AND DISCUSSION**

## Mossbauer Spectral Assignments

All South Basin sediment spectra 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<sup>3+</sup> 0.41  $\pm$  0.02 mm s<sup>-1</sup>, 0.80  $\pm$  0.03 mm s<sup>-1</sup>, and 0.54  $\pm$  0.03 mm s<sup>-1</sup>; for Fe<sup>2+</sup><sub>II</sub> 1.20  $\pm$ 0.02 mm s<sup>-1</sup>, 3.01  $\pm$  0.02 mm s<sup>-1</sup>, and 0.32  $\pm$  0.02 mm s<sup>-1</sup>; and for Fe<sup>2+</sup><sub>I</sub> 1.11  $\pm$  0.02 mm s<sup>-1</sup>, 2.56  $\pm$  0.03 mm s<sup>-1</sup>, and 0.40  $\pm$ 0.03 mm s<sup>-1</sup>, respectively. The ferrous ion values are in good agreement with those published (Coey et al. 1974, Nembrini et al. 1983, Gosner & 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 Mossbauer parameters of IS, QS, and HW, are 1.13, 2.60 and 0.43 mm s<sup>-1</sup> for  $Fe^{2+}$  and 0.36, 0.67, and 0.62 mm s<sup>-1</sup> for  $Fe^{3+}$ , respectively; all values are good to  $\pm 0.02$  mm s<sup>-1</sup>. All values agree well with those measured for Figure Eight Lake sediments (Manning et al. The introduction of a pyrite doublet into the 1988). fitting scheme yielded insignificant amounts of FeS<sub>2</sub>; neither could the computer detect significant absorption at energies corresponding to Fe<sup>2+</sup><sub>II</sub> (vivianite). The spectra of the North Basin sediments took considerably longer to accumulate compared with the South Basin, consistent with considerably lower total iron concentrations of the North Basin sediments (Table 1). Hence, the relative weakness of the ferrous-clay absorption (Fig. 4) in the South Basin sediment spectra arises from the massive precipitation of ferric hydroxide in the deeper water and of vivianite within the The Al concentrations (Table 1) confirm the sediment. greater proportion of clay in the North Basin sediments.

The Mossbauer 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 erosion products. 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 the Lake Ontario situations, porewater  $Fe^{2+}$ ,  $Mn^{2+}$ , and phosphate ions are precipitated at strong redox boundaries. The form of the manganese is 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 erosion products.

## 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-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 FeII:FeI ratio in vivianite,  $Fe_3^{2+}(PO_4)_2 \cdot 8 H_2O_7$ is 2:1 (Gosner & 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<sub>II</sub> sites on partial oxidation, or (ii) a significant proportion of the  $\mathrm{Fe}_{\mathrm{I}}^{2+}$  ions measured actually mark ferrous ions in clay minerals and/or chlorite, or (iii) a combination of (i) and (ii). Weak colour development in the vivianite crystals suggests that, as a first approximation, ferric ion substitution is minor; weak colour implies weak Fe<sup>2+</sup>+Fe<sup>3+</sup> charge-transfer processes (Fage et al. 1968). With regard to (ii), the concentration of ~0.36 wt percent  $Fe^{2+}(clay)$  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  $\mbox{Fe}_{1}^{2+}$  absorption is due to Fe<sup>2+</sup>(clay); the Mossbauer parameters for Fe $_{
m I}^{2+}$  and Fe<sup>2+</sup> (clay) are very similar (see text above). Assuming that  ${\sf Fe}_{II}^{2+}$  ion is the main occupant ion of the  ${\sf Fe}_{II}$  site and that  $[Fe_{I}^{2+}] = 0.5[Fe_{II}^{2+}]$ , then  $[NAIP]_{calc} = 0.1[Fe^{3+}] + 0.37 x$ 1.5[Fe $_{I\,I}^{2+}$ ], 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 FeII 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) 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).

# General Discussion

The contrast between the deep-water sediments, which have a phosphorus content equivalent to that of lowgrade fertilizer, and the water column, with the phoshorus concentrations of an 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 sulfide generation in the sediments prevents massive reduction of ferric iron and the consequent formation of  $FeS_2$  and phosphorus release. Vivianite generally occurs in anoxic lowsulfide 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 terriginous.

Calculated ratios of  $Fe^{3+}$ :  $Fe^{2+}$  (clay) in the nearsurface 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<sup>3+</sup>:Fe<sup>2+</sup> (clay) ratios for all Narrow Lake sediments. Because vivianite formation controls the concentration of soluble phosphate in sediment porewaters generally (Nriagu 1972, Nriagu & Dell 1973, Emerson & Widmer 1978, Tessenow 1974) and because groundwater flow is an important source of phosphorus to Narrow Lake, then the low phosphorus concentrations in the overlying water can also 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, personal communication), indicating that the groundwater is probably

anoxic (Stumm & Morgan 1981). Ferrous ions are also released to the porewaters through the reduction of hydrated ferric oxides within the sediment. High ferrous ion activities and reducing conditions favour 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 phosphorus release 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 over the sediments 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<sup>-2</sup> yr<sup>-1</sup> (Shaw et al. 1989) 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<sup>-1</sup>: the measured values of 20 to 100 µg P L<sup>-1</sup> (Fig. 2) indicate that reduction and dissolution of hydrated ferric oxides in the surficial sediments is the major source of summer phosphorus release. The top cm of sediment in the deep basin contains ~10 g P m<sup>-2</sup>, which if completely released to a 10-m-thick hypolimnion, would yield ~1000  $\mu$ g P L<sup>-1</sup>.

A layer of subsurface sediment underlying Lago Maggiore contains -3% Fe and -0.3% P and abundant concentrations 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 freshlyprecipitated hydrated ferric hydroxide for NAIP is ~10% of the weight of Fe, suggesting 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 mixingin to a depth of ~1 cm through bioturbation, much of the ferric iron would be reduced and converted to FeS<sub>2</sub>. 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 sulfide production and promote vivianite formation. 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 external phosphorus inputs, and the more productive lakes have high internal phosphorus loads from sediments extending from the shallower regions to the deepest part of the lake (Shaw 1989). The variability in surface water phosphorus concentration 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 phosphorus and iron protect the lake from increased phosphorus loadings to the surface waters.

## ACKNOWLEDGEMENTS

We thank M.N. Charlton, A.S. Crowe, T. Mayer, J.F.H. Shaw, and R.D. Shaw for much assistance.

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## CAPTIONS FOR FIGURES

- FIG. 1. Diagram showing the two sampling locations in Narrow Lake, Alberta.
- FIG. 2. Plots depicting (a) concentrations of dissolved oxygen (mg L<sup>-1</sup>), (b) concentrations of total phosphorus ( $\mu$ g L<sup>-1</sup>), 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.
- FIG. 3. Room temperature Mossbauer 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 unlabelled. Chi-squared is 695 for 489 degrees of freedom.
- FIG. 4. Room temperature Mossbauer spectrum of 4 to 5 cm section of sediment collected from the shallow North Basin. Chi-squared is 610 for 494 degrees of freedom.

FIG. 5. Plots showing the distribution of iron between vivianite (Fe<sup>2+</sup>) and hydrated ferric oxide (Fe<sup>3+</sup>) as a function of sediment depth (i.e., time). Approximately 5% of total iron is in pyrite.

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NAIP <sub>calc</sub>				1.19	1.40		1.54		1.31	1.44		1.14		1.15	1.52		Ŭġ	'nà	na	na	to 5 cm	cm depth	rom 5 to	analyzed	na is		
0.rg C				15.5	11.5		15.5		14.4	15.8	13.0		12.2	10.7	13.0		18.8	18.3	18.5	16.0	and 4	he 0-5	tions f	idually-	Dastns.		
ት		sin				0 .66	0.57		0.64	0.65	0.81	0.93	0.79		0.81		0.56		0.42	0.78	0.64	0.49	:0 4 CI	is in t	or sec	indiv	n Doth
NALP				1.29	1.54		1.45		1.75	1.50		1.50		1.72	1.46		0.048	0.031	0.029	0.035	cm. 2 t	section	ilues f	ist two	ся Р 1		
A۱ <sub>T</sub>	cent			1.05		0.99	0.99		0.93	1.19		1.26	1.27	1.71	76.0	asin	2.61	3.22	3.32	3.29	to 2 0	, all	Fer va	at lea	M 20°C		
MnT	it per	) Bas		1.9		1.9	2.1		1.8	1.4		0.9	0.8	1.1	1.2	th)	0.14	0.06	0.04	0.04	ns 1	icity	rly,	م	ہ ۲		
Fe <sup>2+</sup>	weigh	(South	0.4	0.5	0 • 0	1.3	1.5	0*0	1.5	1.6	1.3	1.7	1.4	1.6	1.3	W (Nor	~	~	_	~	sectio	simpl	Simila	erage:	e-P P		
Fe <sup>2+</sup> I I		Deep	0.5	0.3	0.8	1.1	1.3	0.5	1.2	1.6	1.2	1.3	1.3	1.3	1.3	Shallo	0.36 (clay	0.36 (clay	0.36 (clay	0.37 (clay	ations in	wt%: for	value.	cm are av	or aparil		
e( S <sub>2</sub> )			0.5	0.3	0°3	0.3	0.3	0	0.2	0.5	0.3	0.3	0.4	0.4	0.2		0	0	0.02	0	oncentr	d 10.9	ige Fer	to 20	rations		
Fe <sup>3+F</sup>			9.7	10.2	9°0	8.6	8.2	8 <b>.</b> 2	6.4	ۍ م	4.7	4 .2	4 °4	4 .3	8.0		1.66	1.67	1.61	1.68	Fer) C	.0, an	avera	om 12	oncent		
Fe <sub>T</sub>			11.3*	11.3	11.3	11.3	11.3	<b>6</b> .9	9°3	6	7.5	7.5	7.5	7.5	10.9		2.02	2.04	2 <b>.</b> 00	2.05	iron (	.0, 12	ven an	and fr	ns. u plicabl		
Sect ion	Ē		0-1	1-2	2-3	3-4	4-5	5-6	7-8	9-10	12-13	14-15	17-18	19-20	21-22		0-1	4-5	10-11	18-19	* Total	are 11	are gi	10 cm	section not api		



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FIGURE 4

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V 22 Ó eX 20 Ó × - @ 0 ×e <u>9</u> SEDIMENT DEPTH (cm) Ó × 4 Fe<sup>2+</sup> (VIVIANITE) Ó ×ø <u>ല</u> 9 0 θ× Ô 0 × Fe<sup>3+</sup> G Ò ×ø 0 × 4 0 ×e 0 × 2 Q ×e Ò ø× 0 20-90-2 60-50þ 80go 6

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PERCENT OF TOTAL IRON





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