The Lacustrine Carbon Cycle as Illuminated by the Waters and Sediments of Two Hydrologically Distinct Headwater Lakes in North-Central Minnesota, U.S.A.

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THE LACUSTRINE CARBON CYCLE AS ILLUMINATED BY THE WATERS AND SEDIMENTS OF TWO HYDROLOGICALLY DISTINCT HEADWATER LAKES IN NORTH-CENTRAL MINNESOTA, U.S.A.

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ABSTRACT: The accumulation rates of $CaCO_3$ and organic carbon (OC) in lake sediments are delicately balanced between production in the epilimnion and destruction in the hypolimnion. The cycling of these two forms of carbon makes a "carbon pump" that greatly affects the biogeochemical cycles of other elements. To further understand these biogeochemical dynamics, the lakes, streams, and wetlands of the Shingobee River headwater area of north-central Minnesota have been subjected to intensive hydrologic and biogeochemical studies. Williams Lake, situated close to the highest point in the regional flow system, is hydrologically closed, with no surface inlet or outlet, and ground water and precipitation as the only sources of water. Shingobee Lake, situated at the lowest point in the regional flow system, has the Shingobee River as an inlet and outlet. The surface waters of both lakes are over-saturated, and the bottom waters undersaturated, with respect to $CaCO_3$ during the summer. The small amount of $CaCO_3$ that is precipitated in the epilimnion of Williams Lake during the summer is dissolved in the undersaturated hypolimnion and sediments with the result that no $CaCO_3$ is incorporated into the profundal surface sediments. Because of the high phytoplankton productivity of Shingobee Lake, sufficient $CaCO_3$ is produced in the epilimnion that large amounts survive the corrosive hypolimnion and sediments, and an average of 46 wt. % accumulates in surface sediments.

Another consequence of higher phytoplankton productivity in Shingobee Lake is that the hypolimnion becomes oxygen deficient within a month after overturn in both the spring and fall. Because of reducing conditions that develop in the hypolimnion of Shingobee Lake, high concentrations of dissolved Fe and Mn accumulate there during summer stratification. Precipitation of Fe and Mn oxyhydroxides during periods of fall and spring overturn results in high concentrations of Fe and Mn in surface sediments. In Williams Lake, high concentrations of Fe and Mn do not build up in the hypolimnion.

The concentration of $CaCO_3$ is about 80 wt. % in lower Holocene sediments of both lakes. The lower Holocene sediments in both lakes also contain high concentrations of Fe and Mn, and the lower Holocene sediments of Shingobee are laminated. The waters of both lakes had identical values of $\delta^{13}C$ and $\delta^{18}O$ during the early Holocene, but the waters of Williams Lake "evolved" during the early Holocene, increasing about 10‰ in both $\delta^{13}C$ and $\delta^{18}O$. Deposits of lacustrine marl occur as much as seven meters above the present elevation of Williams Lake, the highest of the two lakes. Taken together, these observations suggest that the lakes were once connected to form a larger lake called Lake Willobee with a hypolimnion that was anoxic, at least seasonally.

INTRODUCTION

The carbon cycle in lakes can have profound effects on the biogeochemical cycles of other elements, particularly those of Fe, Mn, Ca, P, and Si. By carbon cycle we refer to the lacustrine "carbon pump" as described by Dean (1999) in which carbon is fixed by photosynthesis in the epilimnion, thus removing CO_2, increasing the pH, and O_2. Respiration of this fixed carbon in the hypolimnion consumes O_2, produces CO_2, and lowers the pH. The concept of the carbon pump is well known in the ocean (e.g., Broecker and Peng 1982). The isotopic manifestations of the lacustrine

carbon pump were described by McKenzie (1982, 1985) and Hollander and McKenzie (1991). This carbon pump also recycles P and, if the carbon-fixing organisms are diatoms, Si. In hardwater lakes, the increased pH in the epilimnion can trigger precipitation of $CaCO_3$. However, the lower pH of the hypolimnion can result in the dissolution of some, and perhaps all, of the $CaCO_3$ produced in the epilimnion. If oxygen depletion in the hypolimnion is severe enough to produce seasonal anoxia, there is a profound effect on the cycles of redox-sensitive elements such as Fe and Mn, causing the dissolved forms (Fe^{2+} and Mn^{2+}) to accumulate in the hypolimnion. When the O_2-depleted hypolimnion mixes with the O_2-rich epilimnion, these two elements may precipitate as oxyhydroxides and (or) other phases. All of these processes have been well documented in Elk Lake in north-western Minnesota (Fig. 1; Dean and Megard 1993; Megard et al. 1993; Nuhfer et al. 1993; Dean 1999).

Iron-rich springs are common in the headwaters region of the Shingobee River about 40 km southeast of Elk Lake, as indicated by orange ferric-hydroxide deposits. The lakes, streams, and wetlands of the Shingobee River headwater area have been the subjects of intensive hydrologic and biogeochemical studies by researchers in the U. S. Geological Survey (USGS) and several universities for more than 15 years (Winter 1997). Collectively known as the Interdisciplinary Research Initiative (IRI), these studies have provided a wealth of information about the lakes and their watersheds, including an extensive database on the chemistry of surface and ground waters. Most studies have focused on two of these lakes, Williams and Shingobee (Fig. 1). Williams Lake has no surface-water inflow. Ground-water inflow varied from 58% to 76% of the total water input over a 12-year period, and the rest of the water is supplied by precipitation (LaBaugh et al. 1995). Shingobee Lake has the Shingobee River as an inlet and outlet, and it is estimated that about 30% of the water enters as ground water (T.C. Winter personal communication). Because the concentrations of major dissolved ions in the lake are similar to those in the Shingobee River and ground water in the region (Table 1), it is likely that local ground water may exert a considerable influence on the chemical characteristics of the Shingobee River and, therefore, of Shingobee Lake (LaBaugh, 1997a). The chemical characteristics of Williams Lake are a product of simple mixing of ground water and precipitation (LaBaugh et al. 1995). As a result of these differing hydrologic conditions, Williams Lake has a considerably longer water residence time (ca. 3 years) than Shingobee Lake (ca. 6 months; Winter and Rosenberry 1997).

The IRI study provides a unique opportunity to test the carbon pump in two very different lakes utilizing the extensive background of hydrologic, limnologic, chemical, and biogeochemical data. Some preliminary results from analyses of surface sediments and longer sediment cores have been presented elsewhere (Schwalb et al. 1995; Dean and Bradbury 1997). In this paper we use some of the IRI data (mostly published in Winter 1997) to examine the properties and processes in the water column as they might relate to the characteristics of sediment particles raining from the water column, as well as how they might modify that sediment rain during deposition and subsequently during diagenesis. A major focus of the IRI study is on the carbon cycles of these two lakes. Consequently, we will emphasize how these processes and products of the water column affect the carbon cycle and the biogeochemical cycles of other elements as recorded in the sediments.
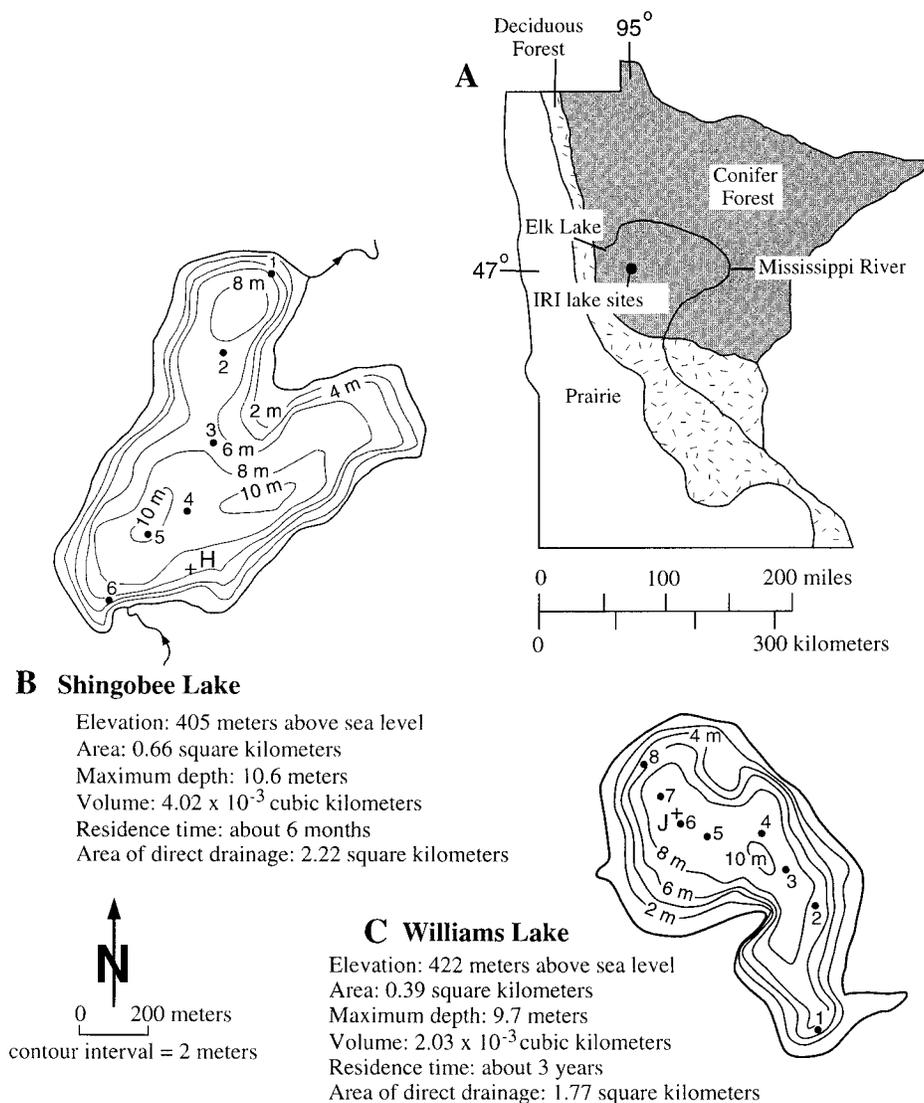
B Shingobee Lake

Elevation: 405 meters above sea level
Area: 0.66 square kilometers
Maximum depth: 10.6 meters
Volume: 4.02×10^{-3} cubic kilometers
Residence time: about 6 months
Area of direct drainage: 2.22 square kilometers

C Williams Lake

Elevation: 422 meters above sea level
Area: 0.39 square kilometers
Maximum depth: 9.7 meters
Volume: 2.03×10^{-3} cubic kilometers
Residence time: about 3 years
Area of direct drainage: 1.77 square kilometers

0   200 meters
contour interval = 2 meters

FIG. 1.—Maps showing **A)** Elk Lake and the USGS Interdisciplinary Research Initiative (IRI) lake sites relative to the present vegetation zones of Minnesota; **B)** locations of surface-sediment samples (1–6) and long core SL-H relative to the bathymetry of Shingobee Lake; **C)** locations of surface-sediment samples (1–8) and long core WL-J relative to the bathymetry of Williams Lake.

SEDIMENT SOURCES

As a result of differences in hydrology and nutrient supply to Williams and Shingobee Lakes, the average concentration of total phosphorus is about twice as high in Shingobee Lake as in Williams Lake (LaBaugh 1997a), and the mean phytoplankton standing stock, as measured by chlorophyll-a, is about three times higher in Shingobee Lake than in Williams Lake (Table 2; Cloern et al. 1997). Because of the higher productivity of Shingobee Lake, and because Williams Lake is fed mainly by ground water, Shingobee Lake has a greater abundance of particles (seston) suspended in the water column. In addition to the greater production of organic par-

ticles, or particulate organic matter (POM), in Shingobee Lake, there are two sources of inorganic particles not found in Williams Lake, namely detrital material brought in by the Shingobee River and precipitated calcium carbonate ($CaCO_3$). It is the abundance and composition of the seston that ultimately determines the composition of the sediments on the lake bottom. Some $CaCO_3$ precipitates in Williams Lake, but most of it forms on the leaves of rooted aquatic vegetation in the littoral zone (McConnaughey et al. 1997). The hypolimnion of Williams Lake is undersaturated with $CaCO_3$ most of the year, so that any $CaCO_3$ precipitated in the open water, or transported from the littoral zone, is dissolved in the undersaturated hypolimnion.

TABLE 1.—*Chemical compositions of Shingobee River, Shingobee Lake, Williams Lake, and ground waters.*

Lake	Specific Conductance (μS)	Concentration in milliequivalents per liter							μg/l	
		Ca	Mg	Na	K	Cl	SO₄	Alkalinity	Fe	Mn
Williams[1]	145	1.25	0.62	0.060	0.023	0.011	0.043	1.89	9.0	4.5
Shingobee[1]	341	2.40	1.32	0.239	0.040	0.033	0.82	3.90	11.0	57.0
Shingobee R.[1] above lake	364	2.47	1.24	0.180	0.040	0.028	0.104	3.84	66.6	58.6
Shingobee R.[1] below lake	360	2.40	1.40	0.258	0.046	0.035	0.069	3.99	58.6	55.6
Ground Water[1] into Williams	416	3.24	1.23	0.113	0.030	0.047	0.187	4.40	9.0	13.5

[1] Data on water chemistry are from LaBaugh (1997a).

TABLE 2.—*Mean seston abundance, composition, and sediment accumulation rates over the deepest parts (10 m) of Williams and Shingobee lakes*[1].

	Williams Lake	Shingobee Lake
Mean Standing Stock[2]:		
Total seston	23,800	32,148
Particulate carbon (PC)[3]	3,795	5,712
Particulate nitrogen (PN)	403	901
Chlorophyll-a	27	72
Seston composition:		
Phytoplankton fraction of PC[3]	36%	63%
Nonphytoplankton fraction of PC[3]	64%	27%
atomic PC : PN ratio	11	7.4
Sediment accumulation rate[4]:		
Total seston	350	757
Abiotic seston	180	531
PC	85	113
PN	9.5	10.6
Chlorophyll-a	0.5	0.7

[1] Data from Cloern et al. (1997). Measurements were made four times (in April, August, October, 1989, and February, 199). Water samples were collected every meter and filtered as described by Cloern et al. (1997).

[2] Standing stocks are in milligrams per square meter, and were calculated using seasonally weighted measurements from depths between 0 and 8 meters.

[3] Assumes that PC is mostly organic carbon, which is an underestimate if inorganic carbon comprises a significant fraction of PC, as it does in Shingobee Lake as precipitated CaCO₃.

[4] Sediment accumulation rates are in grams per square meter per year, and were determined by paired sediment traps deployed at eight meters for 5–7 days.

Data in Table 2 show that although the abundance and accumulation rates of total particulate carbon (PC) are higher in Shingobee Lake than in Williams Lake, PC is not a significantly larger proportion of the total seston. PC constitutes 18 wt. % and 15 wt. % of total seston abundance and accumulation rate, respectively, in Shingobee Lake, and 16 wt. % and 24 wt. %, respectively, in Williams Lake. The proportion of particulate organic carbon (POC) in Shingobee Lake is much less than that of total PC because the seston in Shingobee Lake contains a significant amount of particulate inorganic carbon (PIC) as precipitated $CaCO_3$, but POC and PIC were not measured separately by Cloern et al. (1997). Although the higher organic productivity of Shingobee Lake is not well expressed in PC abundance and sedimentation rate, it is expressed in the phytoplankton fraction of PC (Table 2), which is calculated as [50 x (chlor-a/PC)] (Cloern et al. 1992).

In summary, the sediment-particle rain (seston) in Shingobee Lake, relative to that in Williams Lake, should contain a higher amount of detrital clastic (aluminosilicate) material brought in by the Shingobee River, a higher amount of organic matter, and a higher amount of precipitated $CaCO_3$ as a product of the higher algal productivity (discussed below). These differences should be reflected in the composition of the sediments in the two lakes.

SURFACE SEDIMENTS

Field and Analytical Methods

Surface sediments were collected in 1995 using an Ekman box corer along transects in both lakes (Fig. 1); only the top 2 cm of sediment were analyzed. Concentrations of total carbon (TC) and inorganic carbon (IC) were determined by coulometric titration of CO_2 following extraction from the sediment by combustion at 950° C and acid volatilization, respectively (Engleman et al. 1985). Weight percent IC was converted to weight percent $CaCO_3$ by dividing by 0.12, the weight fraction of carbon in $CaCO_3$. Organic carbon (OC) was determined by difference between TC and IC. Data on loss on ignition (LOI) of sediments from Minnesota lakes presented by Dean (1974) indicated that the amount of organic matter (OM), as measured by LOI at 550° C, usually is about twice the OC content. Confirmation of this 2-to-1 relation for organic matter in lake sediments will be demonstrated below for both lakes.

Semiquantitative estimates of mineral contents of powdered bulk samples were determined by standard X-ray diffraction techniques (e.g., Moore and

Reynolds 1989). The sample was packed into an aluminum holder and scanned from 15° to 50° 2Θ at 2° 2Θ/min using Ni-filtered, Cu–Kα radiation at 45 kV and 30 mA.

Splits of powdered samples of sediment were analyzed for major, minor, and trace elements in a multi-acid digest by inductively coupled, argon-plasma emission spectrometry (ICP; Lichte et al. 1987). USGS rock standards were included with the sediment samples, and 10% of the samples were duplicated. Precision, determined by analyzing rock standards and duplicate samples over the past 8 years, is better than 10% at a concentration of 10 times the limit of detection. Results for Al, Fe, Mn, S, and P will be discussed in this paper: Fe, Mn, S, and P because they relate to the carbon pump, and Al as representative of the nonreactive aluminosilicate fraction of the sediments. The amount of inorganic, noncarbonate material was calculated as the difference between 100 wt. % and the sum of the weight percentages of OM and $CaCO_3$. This value is often referred to as the ''detrital–clastic'' fraction, although in the sediments of many lakes this fraction also includes siliceous remains of diatoms and any authigenic minerals (other than $CaCO_3$). The concentrations of Fe, Mn, and P in the sediments of both lakes were recalculated on a carbonate- and organic-free (cof) basis in order to compare sediment concentrations between lakes without the effects of $CaCO_3$ and OM dilution. We realize that the cof fraction does contain biogenic silica as diatom debris. The diatom measurements reported in Dean and Bradbury (1997) include relative counts, but total biogenic silica was not measured. In general, diatoms are a major component of the plankton community in Williams Lake but only a minor component in Shingobee Lake (LaBaugh 1997b).

Results

The concentrations (in weight percent) of OC, $CaCO_3$, Fe, Mn, and P in the surface sediments along the two transects are shown in Figures 2 and 3, and average concentrations of OC, OM, IC, $CaCO_3$, Al, Fe, Mn, and P are given in Table 3. The sediment samples from Williams Lake are virtually carbonate free, although small amounts of $CaCO_3$ (up to 0.7 wt. %) occur in sediments at the north end of the lake (Fig. 2). Sediment samples from Shingobee Lake, on the other hand, are carbonate rich with up to 73 wt. % $CaCO_3$ (Table 3; Fig. 3), decreasing from north to south. The OC contents of sediments in Williams Lake (17–30 wt. %) are about three times higher than those of Shingobee Lake sediments (4–14 wt. %). Concentrations of Fe, Mn, and P in Williams Lake sediments are highest in the central part of the lake. Concentrations of Fe and Mn in Shingobee Lake sediments, like those of $CaCO_3$, decrease from north to south and are considerably higher than those in Williams Lake. For sediments from both lakes, the Al concentration is highly correlated with the ''detrital–clastic'' fraction as defined above, and can be taken as a measure of the amount of aluminosilicate material in the sediments.

LONG CORES

Field and Analytical Methods

The longer sediment cores were collected from the ice surface in the deep basin of Williams Lake (core J, 8 m water depth, Fig. 1C) and from the sublittoral zone on the south end of Shingobee Lake (core H, 6 m water depth, Fig. 1B) with a modified Livingstone piston corer (Wright 1967). Weight percentages of OM and total carbonate, calculated as $CaCO_3$, were determined by LOI at 550° and 1000° C, respectively, at the Limnological Research Center, University of Minnesota, on samples collected every 10 cm. Abundances of TC, IC, and OC were determined by coulometry, as described above, on samples of bulk sediment collected every 20 cm.

Stable-carbon isotope ratios in organic matter were determined using standard techniques (see Dean et al. 1986, and references therein). Acidified samples were combusted under oxygen pressure in an induction furnace. The resulting CO_2 was dehydrated and purified in a high-vacuum, gas-
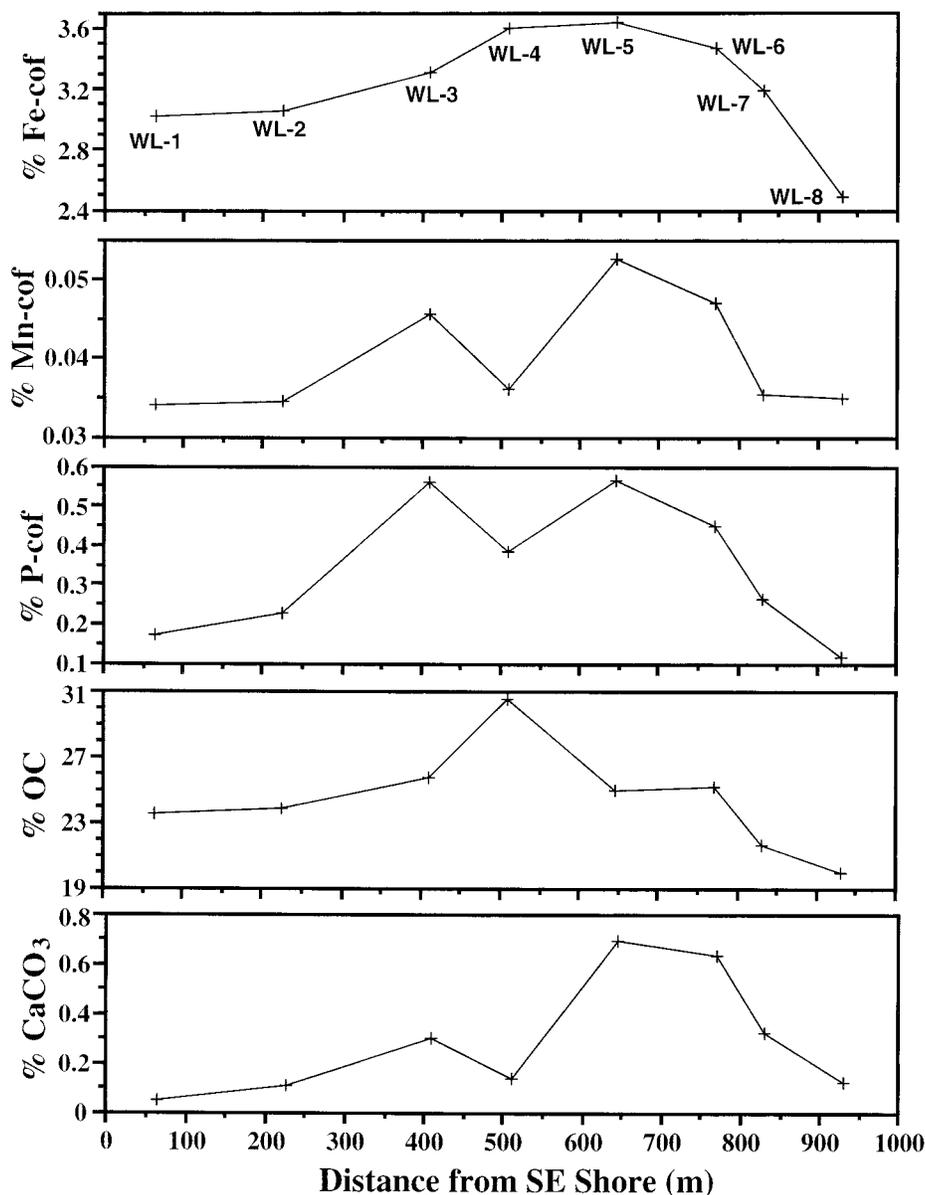
FIG. 2.—Transect of percentages of $CaCO_3$, organic carbon (OC), phosphorus (P), manganese (Mn), and iron (Fe) in 8 samples of surface sediments from Williams Lake relative to distance from the southeastern shore (see Fig. 1 for location of transect). Concentrations of P, Mn, and Fe are calculated on a carbonate- and organic-free basis (cof).

transfer system, and isotope ratios were determined using an isotope-ratio mass spectrometer. Results are reported in the standard per mil (‰) δ notation relative to the Vienna Pee Dee Belemnite (VPDB) marine-carbonate standard.

Chronologies

The chronologies for the two cores used for this study, expressed as radiocarbon years before present (yr B.P.), are based on five accelerator mass spectrometry (AMS) radiocarbon dates from the Williams Lake core and pollen zonation from both cores (Locke 1995; Locke and Schwalb 1997). The linearity of the curve of age versus depth (Fig. 4), and the fact that bulk-sediment dates agree well with wood dates (Fig. 5), suggest that the reservoir effect in Williams Lake is not very large. The radiocarbon ages have not been calibrated to account for variations in ^{14}C production in the atmosphere so that the dates at this site can be compared with the uncalibrated radiocarbon dates for other published sites. The overall sedimentation rate based on the radiocarbon dates is 0.067 cm/yr.

The pollen zonation defined for Williams and Shingobee Lakes (Figs. 5, 6) resembles those of Whitlock et al. (1993) for Elk Lake, located approximately 40 km northwest of Shingobee Lake, and McAndrews (1966) for Bog D and Martin Pond near Elk Lake, where the zones have been dated by radiocarbon and, for Elk Lake, by varve chronology (Anderson et al. 1993). Five local pollen assemblage zones were identified in the cores from Williams and Shingobee Lakes (Figs. 5 and 6; Locke 1995; Schwalb et al. 1995; Locke and Schwalb 1997) that divide the Holocene into five periods: The spruce period (>10,000–9800 yr B.P.), the jack/red pine period (9800–7700 yr B.P.), the prairie period (7700–4000 yr B.P.), the hardwood period (4000–3200 yr B.P.), and the white pine period (3200 yr B.P. to present).

The boundary between the jack/red pine zone and the prairie zone is dated at 7680 ± 90 yr B.P. from a piece of wood in core J from Williams Lake (Locke 1995; Locke and Schwalb 1997). The dates of the other boundaries were estimated from dates on bulk carbonate and wood from nearby Bog D (McAndrews 1966), Portage Lake (McAndrews et al. 1973), and Elk Lake (Whitlock et al. 1993; Anderson et al. 1993). The dates of the pollen zone boundaries in Williams Lake agree well with the radiocarbon age model (Fig. 4), and we assume that we can apply the same dates to the pollen zones boundaries in the Shingobee Lake H core (Fig. 6).
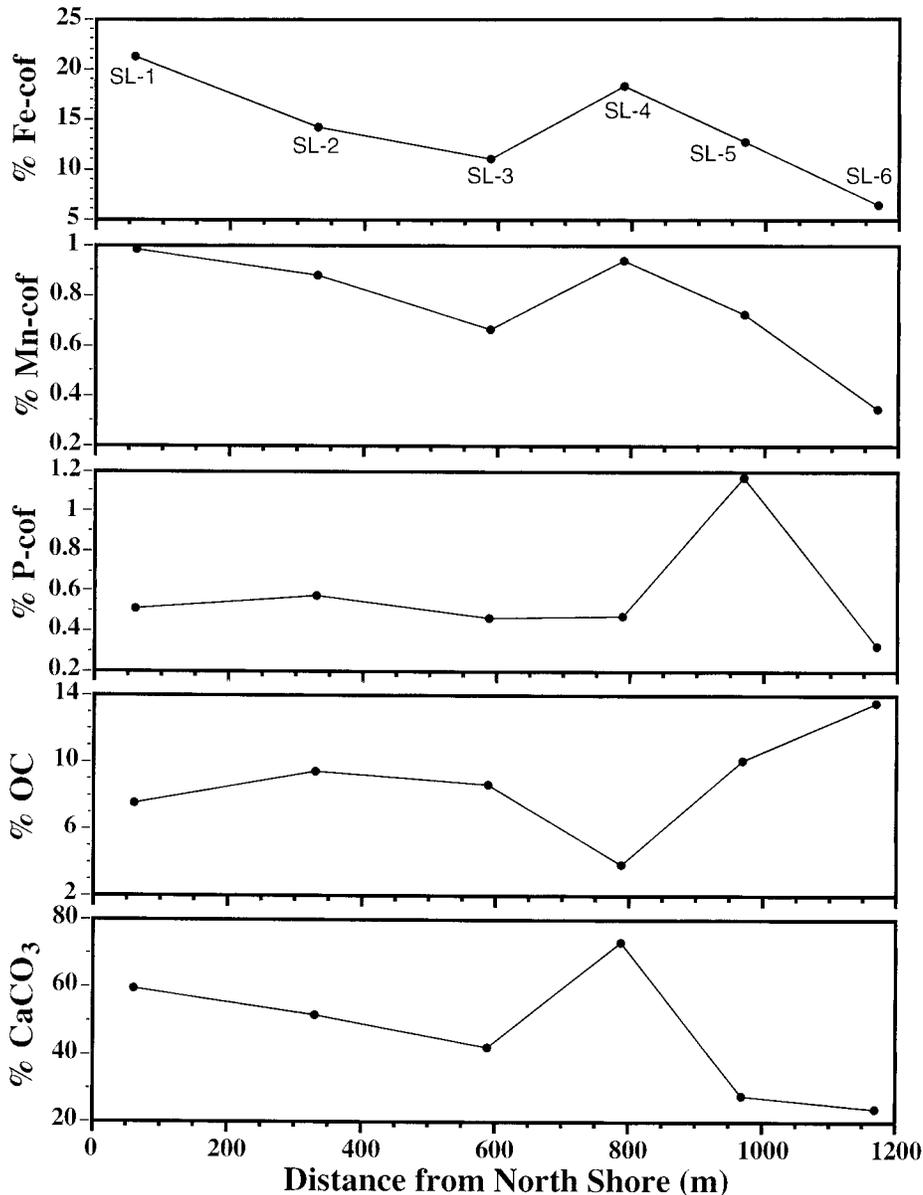
FIG. 3.—Transect of percentages of CaCO₃, organic carbon (OC), phosphorus (P), manganese (Mn), and iron (Fe) in 6 samples of surface sediments from Shingobee Lake relative to distance from the north shore (see Fig. 1 for location of transect). Concentrations of P, Mn, and Fe are calculated on a carbonate- and organic-free basis (cof).

Carbon Concentrations

Figures 5 and 6 show that the two methods of determining the amount of CaCO₃ (calculated from LOI and IC) agree quite well and that the 2-to-1 relation between percent OM and percent OC holds for the sediments in both lakes. Lower Holocene sediments in both Williams and Shingobee Lakes contain about 80 wt. % CaCO₃ (Figs. 5, 6). The CaCO₃ content of sediments in Shingobee Lake remained at about that level with some fluctuations to values as low as 60 wt. % throughout the Holocene. The CaCO₃ content of sediments in Williams Lake, on the other hand, decreased markedly throughout the jack/red pine zone to about 40 wt. % at the base of the prairie zone. It then fluctuated for about 1000 years, decreased gradually with little fluctuation throughout the prairie zone as the OC content slowly began to increase, and finally dropped to zero at the top of the prairie zone. This transition at the top of the prairie zone was accompanied by fluctuation in concentrations of both CaCO₃ and OC, as shown by the high-resolution (2-cm sampling interval) insets between 380 and 320 centimeters below lake floor (cmblf) in Figure 5. The fluctuations in wt. % CaCO₃ result in

dark-light banding, which apparently is a common feature of the prairie–forest transition in lake sediments in west-central Minnesota (H.E. Wright personal communication) and is informally referred to as "raccoon-tail banding."

Carbon Isotope Results

Values of $\delta^{13}C$ of bulk CaCO₃ (Fig. 7; Schwalb and Dean 2002) and in benthic ostracode shells (Schwalb et al. 1995, Schwalb and Dean 2002) increase dramatically in sediments of both lakes between the beginning of the jack/red pine zone and the middle of the prairie zone. The increases in $\delta^{13}C$ values in CaCO₃ are paralleled by increases in $\delta^{13}C$ values of OC of about the same magnitude as those in CaCO₃ in both lakes, but the increase is about 10‰ in Williams Lake CaCO₃ and OC and only about 4‰ in Shingobee Lake (Fig. 6). The increases in $\delta^{13}C$ values in both CaCO₃ and OC in both lakes suggests that the total carbon reservoirs may have been influenced by the same factor or factors. Values of $\delta^{13}C$ in bulk carbonate and OC in Shingobee sediments both decrease throughout the white pine

TABLE 3.—*Composition of surface sediments from Williams and Shingobee lakes.*

Variable	Williams Lake	Shingobee Lake
wt. % OC[1]	24.6	8.8
wt. % OM[2]	49.2	17.6
wt. % IC[1]	0.03	5.50
wt. % $CaCO_3$[1]	0.23	46.2
wt. % Al	3.1	1.4
wt. % Fe	1.6	4.6
wt. % Mn	0.02	0.25
wt. % P	0.16	0.23
bulk-sediment MAR[3]	60	385
OC MAR	15	34
OM MAR	29	68
IC MAR	—	21
$CaCO_3$ MAR	—	178
Fe MAR	0.96	18
Mn MAR	0.012	0.96
P MAR	0.096	0.89
wt. % Al-cof[4]	6.3	5.4
wt. % Fe-cof	3.1	14.0
wt. % Mn-cof	0.04	0.76
wt. % P-cof	0.31	0.59
wt. % Fe-detrital[5]	1.24	0.56
wt. % Mn-detrital	0.020	0.009
wt. % P-detrital	0.027	0.012
wt. % Fe-excess[5]	0.36	4.0
wt. % Mn-excess	0.0	0.24
wt. % P-excess	0.13	0.22

[1] Data from Dean and Bradbury (1997).
[2] wt. %OM = wt. %OC × 2
[3] MAR = mass accumulation rate (in g m^{-2} yr^{-1})
[4] cof = carbonate- and organic-free
[5] the detrital concentration is relative to the concentration in upper continental crust, and the excess concentration is the difference between the total and detrital concentrations (see text for methods of calculation).

zone (Fig. 7), whereas those in OC in Williams sediments remain constant. $CaCO_3$ disappears from the sediments of Williams Lake at a depth of about 320 cmblf (Fig. 5).

DISCUSSION

Carbon Isotopes, Hydrology, and Productivity

Values of $\delta^{13}C$ increase upward in lower Holocene sediments in Williams Lake by about 10‰ in both $CaCO_3$ and OM, and in Shingobee Lake by about 4‰ in both $CaCO_3$ and OM (Fig. 7). Similar increases in values of $\delta^{13}C$ in marl and organic matter over the same time interval also were observed in sediments deposited during the forest–prairie transition in Pickerel Lake, South Dakota (Dean and Schwalb 2000), and in Elk Lake, about 40 km northwest of Williams and Shingobee Lakes (Dean et al. 2002). The usual explanations for increases in values of $\delta^{13}C$ in authigenic lacustrine carbonates and OM with time are increased lake productivity or a change from ^{13}C-depleted C_3 vegetation (e.g., pine forest) to ^{13}C-enriched C_4 vegetation (e.g., prairie grasses) in the drainage basin. The most commonly cited model for ^{13}C enrichment by increased productivity is the cultural eutrophication of Lake Greifen, Switzerland (McKenzie 1982, 1985; Hollander and McKenzie 1991). As a result of increased productivity (eutrophication) of Lake Greifen during the 20th century and burial of ^{13}C-depleted OM, the entire carbon reservoir of the lake became progressively enriched in ^{13}C, as did algal organic matter and precipitated $CaCO_3$. C_3 and C_4 plants have very different $\delta^{13}C$ values averaging about -27 and -12‰, respectively, as a result of their different photosynthetic pathways (O'Leary 1988; Cerling and Quade 1993). A change from forest to prairie might deliver more ^{13}C-enriched organic matter and dissolved inorganic carbon (DIC) to the lake (Cerling and Quade 1993). Lacustrine algae (C_3) tend to have $\delta^{13}C$ values ranging from the high negative 20s to the low negative 30s (Dean and Stuiver 1993).

In Williams Lake, an increase in water residence time would also produce a ^{13}C-enriched carbon reservoir as more exchange of carbon between surface water and atmosphere ($\delta^{13}C = -7$‰) occurred over time (Kendall et al. 1997). The equilibrium fractionation between CO_2 and DIC is about
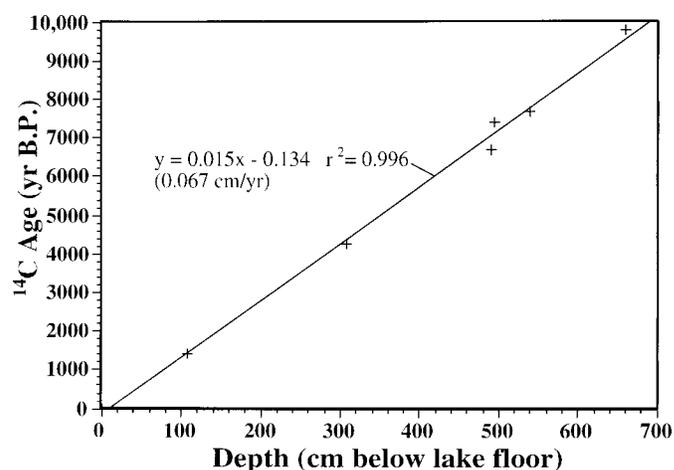

FIG. 4.—Radiocarbon age model for the Williams Lake J core (see Fig. 6 for stratigraphic locations and type of materials analyzed, wood and organic carbon, for each sample).

$+8$‰ (Arthur et al. 1983), so DIC formed in equilibrium with atmospheric CO_2 would have a value of about $+1$‰. This is a likely explanation for some of the progressive enrichment in carbonate and organic matter in Williams Lake sediments during the early Holocene (Fig. 7), and the strong carbon- and oxygen-isotope covariance reported by Schwalb et al. (1995) and Schwalb and Dean (2002).

Measurements of $\delta^{13}C$ and $\delta^{18}O$ in samples collected during a dry period in the fall on a transect along the Shingobee River and through Shingobee Lake, and one sample collected at the same time from Williams Lake, show that both $\delta^{13}C$ and $\delta^{18}O$ increase from -11‰ to -7‰, downstream along the Shingobee River transect, suggesting an evaporation trend (Kendall et al. 1997). Williams Lake, on the other hand, had values of $\delta^{13}C$ and $\delta^{18}O$ that are enriched in ^{13}C and ^{18}O by about 5‰ and 6‰, respectively, relative to the most enriched Shingobee Lake samples. The carbon isotope composition of Shingobee Lake varies by about 4‰ seasonally in response to the biological transfer of ^{13}C-depleted OC from the epilimnion to the hypolimnion, but an average value (e.g., the value of the whole lake after spring overturn) is about -11‰ (R.G. Striegl personal communication). The seasonal variation of $\delta^{13}C$ in Williams Lake with less photic-zone productivity is only about 2‰, with an average value for the $\delta^{13}C$ of DIC of about -4‰. This -4‰ value is about 7‰ more ^{13}C enriched than average Shingobee Lake DIC (R.G. Striegl personal communication), which is similar to the enrichment reported by Kendall et al. (1997).

$CaCO_3$ formed from DIC in both lakes is enriched in ^{13}C by about 3–5‰. Modern marl in Shingobee Lake has $\delta^{13}C$ values of about -6‰ (Fig. 7), and modern ostracodes have $\delta^{13}C$ values that range from -6 to -8‰ (Schwalb et al. 1995), which are all more enriched than the average DIC value of -11‰. We do not have cores of modern sediment from the littoral zone of Williams Lake, but $\delta^{13}C$ values of $CaCO_3$ precipitated on leaves of the rooted aquatic plants *Potomogeton* and *Myriophylum* have $\delta^{13}C$ values that range from $+1$ to $+4$‰, and those of the calcareous alga *Chara* range from $+1$ to $+2$‰ (T.A. McConnaughey unpublished data). Modern ostracodes from Williams Lake have $\delta^{13}C$ values that range from -1 to $+3$‰ (Fig. 7; Schwalb et al. 1995). All of these modern carbonates are more enriched in ^{13}C than the average DIC $\delta^{13}C$ value of -4‰.

It appears from both the sediment and water isotopic evidence that most of the increase in values of $\delta^{13}C$ in Williams Lake carbonates during the early Holocene was due to increased residence time of the lake and not burial of ^{13}C-depleted organic carbon. Kendall et al. (1997) reached the same conclusion for the covariant increases in values of $\delta^{13}C$ and $\delta^{18}O$ in DIC and water along their Shingobee River transect. In contrast, the increase in $\delta^{13}C$ in Shingobee Lake carbonate during the early Holocene
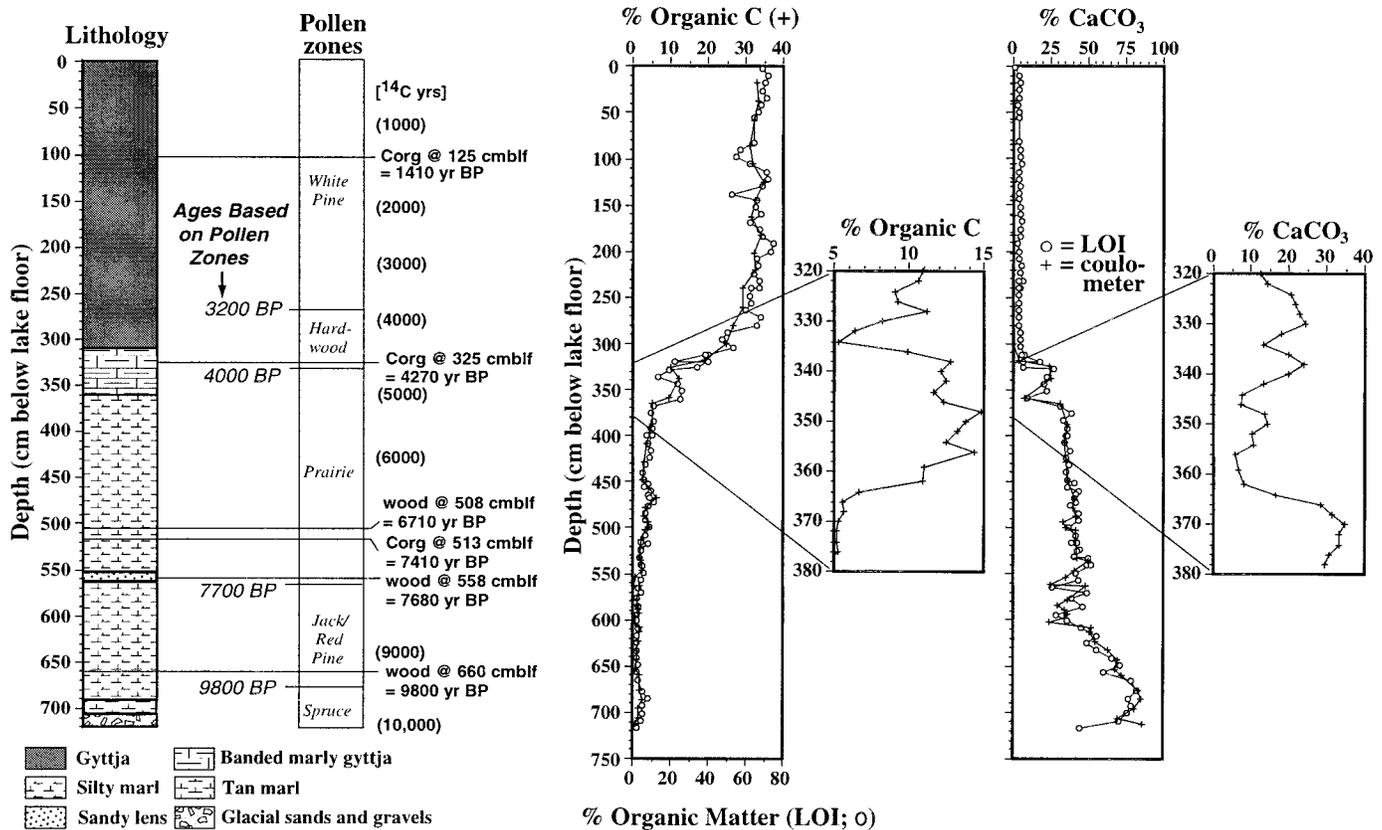
FIG. 5.—Lithology, pollen zones, radiocarbon ages, and percentages of organic carbon (OC, by coulometry), organic matter (by loss on ignition, LOI, at 550° C), and CaCO₃ calculated from percent inorganic carbon (IC) by coulometry and LOI at 1000° C for samples from the Williams Lake J core. High-resolution profiles (2-cm samples) of percent OC and CaCO₃ for the transition between CaCO₃-rich and OC-rich sediments between 380 and 320 cmblf are shown as insets.

(Fig. 7) is not matched by an increase in values of $\delta^{18}O$ (Schwalb et al. 1995; Schwalb and Dean 2002). This increase is only about 4‰, less than the 10‰ increase in Williams Lake carbonate. Today, Shingobee Lake has a much higher phytoplankton productivity than Williams Lake. The increased enrichment in ^{13}C of Shingobee Lake carbonate, matched by a similar enrichment in Shingobee Lake organic matter, but not by an enrichment of ^{18}O in Shingobee Lake carbonate, could be due to increased productivity and burial of more ^{13}C-depleted organic according to the Lake Greifen model discussed above. Alternatively, the ^{13}C enrichment could simply be due to the change in the drainage basin from the C_3-plant-dominated pine forest to a C_4-plant-dominated prairie. The fact that values of $\delta^{13}C$ decreased to early Holocene levels following reforestation during the late Holocene (Fig. 7) suggests that vegetation change in the drainage basin and not productivity was the main cause of the increase in $\delta^{13}C$ in Shingobee Lake in the mid-Holocene, and probably some of the increase of 10‰ in Williams Lake. The present average difference in $\delta^{13}C$ between Williams and Shingobee is about 7‰, and we suggest that this was about the amount of the 10‰ mid-Holocene increase in Williams Lake that was due to changing hydrology; the remaining 3‰ may represent vegetation change in the drainage basin during the early Holocene. By the middle of the prairie period (ca. 5000 yr B.P.), Williams Lake was hydrologically closed and remained that way throughout the rest of the Holocene (Schwalb and Dean 2002), which is probably why the carbon-isotope composition of that lake ($\delta^{13}C$-org; Fig. 7) did not respond to reforestation of the drainage basin as it did in Shingobee Lake.

The Carbon Redox Pump

The Water Column.—The marked differences in phytoplankton productivity and residence time in Williams and Shingobee Lakes should be

reflected most notably in the differences between the epi- and hypolimnions of the two lakes during summer stratification. For example, do the hypolimnions become anoxic, and if so, when? What are the biogeochemical consequences of this anoxia? Do they follow the Elk Lake model? The biogeochemical events during periods of summer stratification and fall overturn in Elk Lake are as follows (Dean 1999): algal photosynthesis during summer in the epilimnion consumes CO_2, produces organic matter and dissolved oxygen (DO), and increases pH, triggering calcite precipitation (Dean and Megard 1993). Some (most?) of the organic matter produced in the epilimnion decomposes in the hypolimnion, imposing a high biological oxygen demand on the hypolimnion, which becomes anoxic at some point during the summer depending upon how high that demand is.

Decomposition of organic matter also produces CO_2 and lowers the pH, causing the hypolimnion to become undersaturated with respect to calcite. Immediately after spring overturn, the iron and manganese concentrations throughout the water column in Elk Lake are $< 3 \ \mu g \ L^{-1}$. During summer stratification with an anoxic hypolimnion, concentrations of Fe and Mn increase in the hypolimnion, reaching several parts per million by late summer (Megard et al. 1993). There are marked concentration gradients of these two ions in the unmixed hypolimnion, decreasing away from the sediments, indicating that the iron and manganese are derived from dissolution of iron and manganese minerals in the sediments.

At fall overturn when iron- and manganese-rich, anoxic hypolimnetic waters of Elk Lake mix with well-oxygenated epilimnetic waters, there is precipitation of ferric hydroxide that is manifested as a bright orange floc in sediment traps and high iron concentrations in the sediment collected in the traps (Nuhfer et al. 1993). When varves in sediment cores from Elk Lake are examined under the microscope, ferric hydroxide appears as an
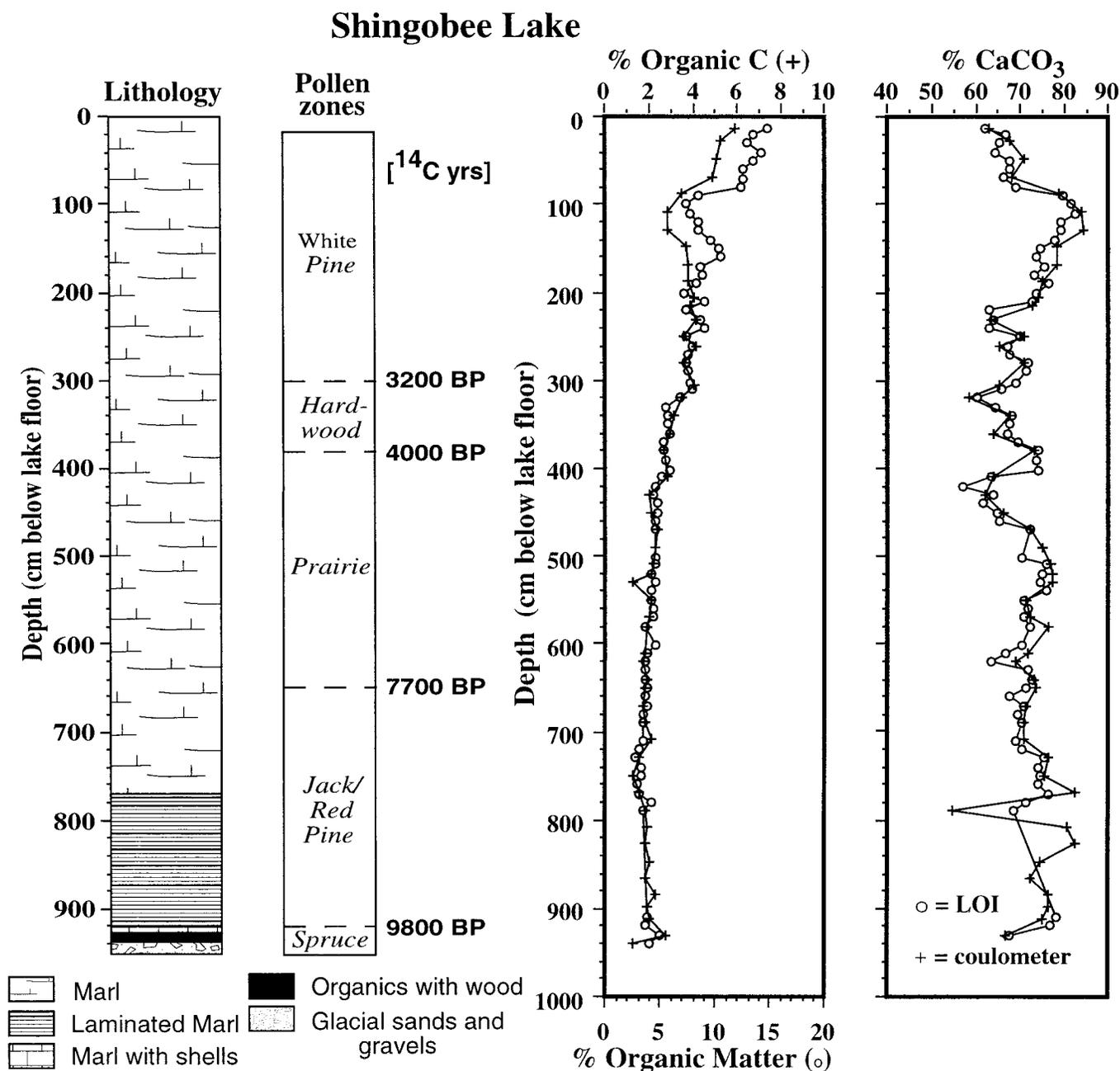
Shingobee Lake

FIG. 6.—Lithology, pollen zones, radiocarbon ages, and percentages of organic carbon (OC, by coulometry), organic matter (by loss on ignition, LOI, at 550° C), and CaCO$_3$ calculated from percent inorganic carbon (IC) by coulometry and LOI at 1000° C for samples from the Shingobee Lake H core.

orange gel-like layer overlying the white CaCO$_3$ layer deposited during late summer (Anderson 1993). The ferric hydroxide layer in varves often has a thin black band at the base, suggesting that manganese oxyhydroxides may precipitate out before the ferric hydroxide. An iron-manganese phosphate mineral also occurs in sediment traps and cores, and is tentatively identified as rockbridgeite [(Fe, Mn)Fe$_2$(PO$_4$)$_3$(OH)$_5$] on the basis of weak X-ray diffraction peaks (Nuhfer et al. 1993; Dean 1993). Manganese carbonate (rhodochrosite) also has been identified by X-ray diffraction. The iron and manganese minerals formed, as described above, under oxic conditions in the epilimnion, are unstable under anoxic conditions in the hypolimnion and sediment pore waters. Some portions of the previously formed iron and manganese minerals dissolve, releasing iron, manganese, and phosphorus to the hypolimnion. The amounts of organic matter,

CaCO$_3$, and iron and manganese minerals that are ultimately buried in the sediments, therefore, are functions of the balance between production in the epilimnion and destruction in the hypolimnion and sediments. The incorporation of Fe, Mn, OC, CaCO$_3$, Si, P, and other elements in lake sediments is, therefore, mainly dependent on the "carbon pump" and its effects on redox conditions in the lake (Dean 1999).

The hypolimnion of Williams Lake usually is well oxygenated for at least several months after spring overturn (Figs. 8A, 9A). However, the hypolimnion of Shingobee Lake is oxygen deficient ($<$ 1 ppm DO) most of the time (Figs. 8B, 9C). The effect of differences in primary productivity between the two lakes is reflected in the relative strengths of the carbon pumps in the two lakes as measured by DO. In 1997, the entire water column in Williams Lake was still well oxygenated at the end of May (Fig.
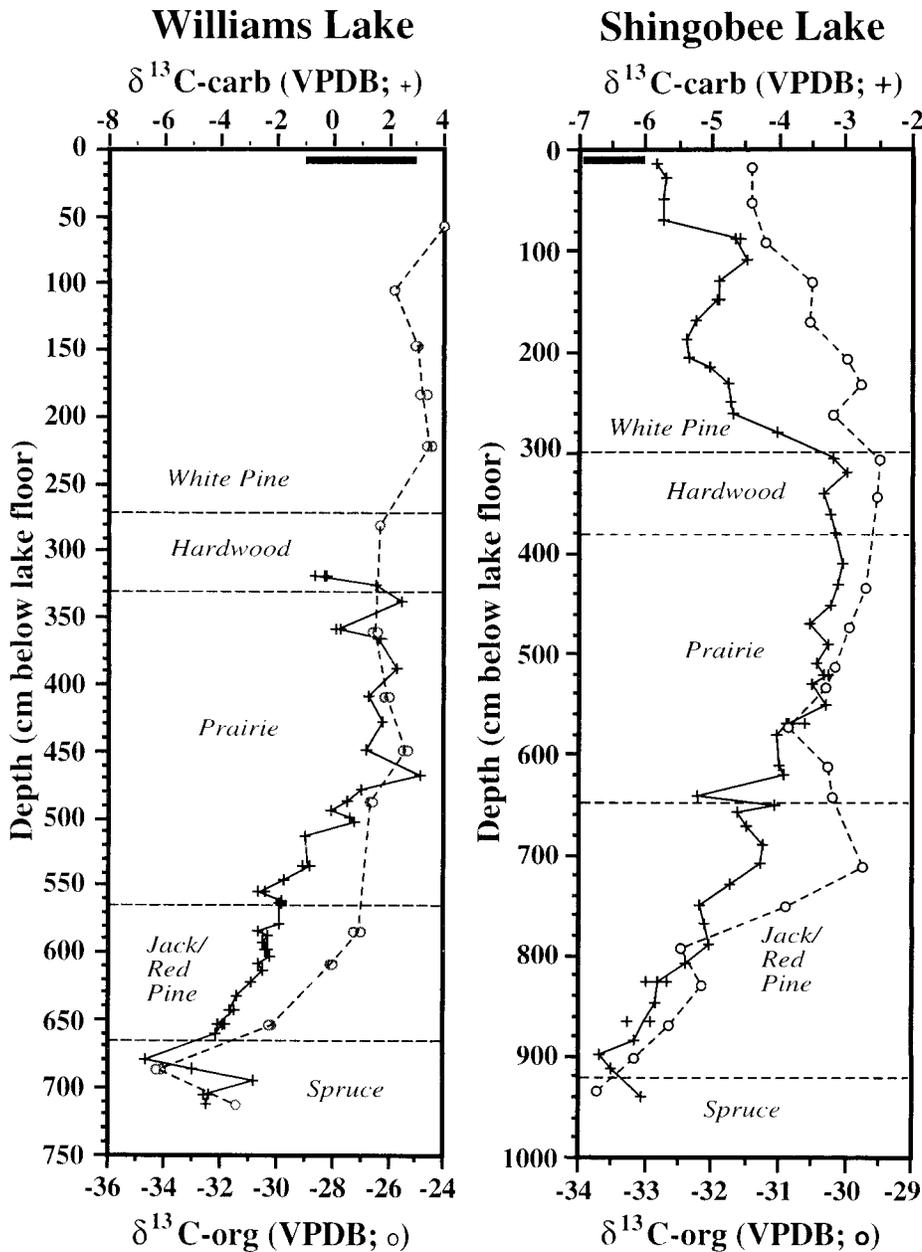
FIG. 7.—Values of $\delta^{13}C$ in bulk carbonate and organic matter in samples from the Williams Lake J core and Shingobee Lake H core. Bar at the top of each diagram represents the range of values of $\delta^{13}C$ in modern ostracode shells (Schwalb et al. 1995).

9A), but in Shingobee Lake, respiration of the higher organic matter produced in the epilimnion had nearly depleted the hypolimnion of DO by that time (Fig. 9C).

The pH of the water column in both Williams and Shingobee Lakes is about 7.0 after spring overturn (4/29/97 in Figs. 9B and D), but the pH in Shingobee rapidly stratifies in response to CO_2 production by respiration in the hypolimnion, resulting in a lower pH (Fig. 9D). Precipitation of $CaCO_3$ is controlled mainly by the concentrations of calcium, bicarbonate, and carbonate, and by pH, which controls the relative abundances of bicarbonate and carbonate. In hardwater of lakes in central Minnesota, there is a linear relation between log total dissolved cations in milliequivalents per liter (epm), and calcite saturation; calcite saturation is reached at about 0.5 log total cations (Dean and Megard 1993). Using the data on water chemistry of Williams and Shingobee Lakes in Table 1, the average log total cations are 0.29 and 0.60 for Williams and Shingobee, respectively. This simple index suggests that, on average, Williams Lake is undersatu-

rated, and Shingobee Lake is oversaturated, with respect to calcite. As another simple index, calcite saturation in central Minnesota lakes is also linearly correlated to pH, reaching saturation at a pH of about 7.73 (Dean and Megard 1993). Using this index, the epilimnion of Shingobee Lake is oversaturated, and the hypolimnion is undersaturated (Fig. 9D). The lack of $CaCO_3$ in surface profundal sediments in Williams Lake (Fig. 2), and its abundance in surface profundal sediments of Shingobee Lake (Fig. 3), together with the DO and pH profiles (Fig. 9), indicate that the carbon pumps are operating in both lakes but at a higher rate in Shingobee Lake. In spite of a hypolimnion that is severely oxygen deficient most of the time, the epilimnion of Shingobee Lake clearly produces $CaCO_3$ at a rate that is much higher than the rate at which it is dissolved in the undersaturated hypolimnion and sediments.

According to the Elk Lake model, oxygen deficiency in the hypolimnions of Williams and, especially, Shingobee Lakes should affect the redox cycling of Fe and Mn. The average concentration of Fe in the hypolimnion
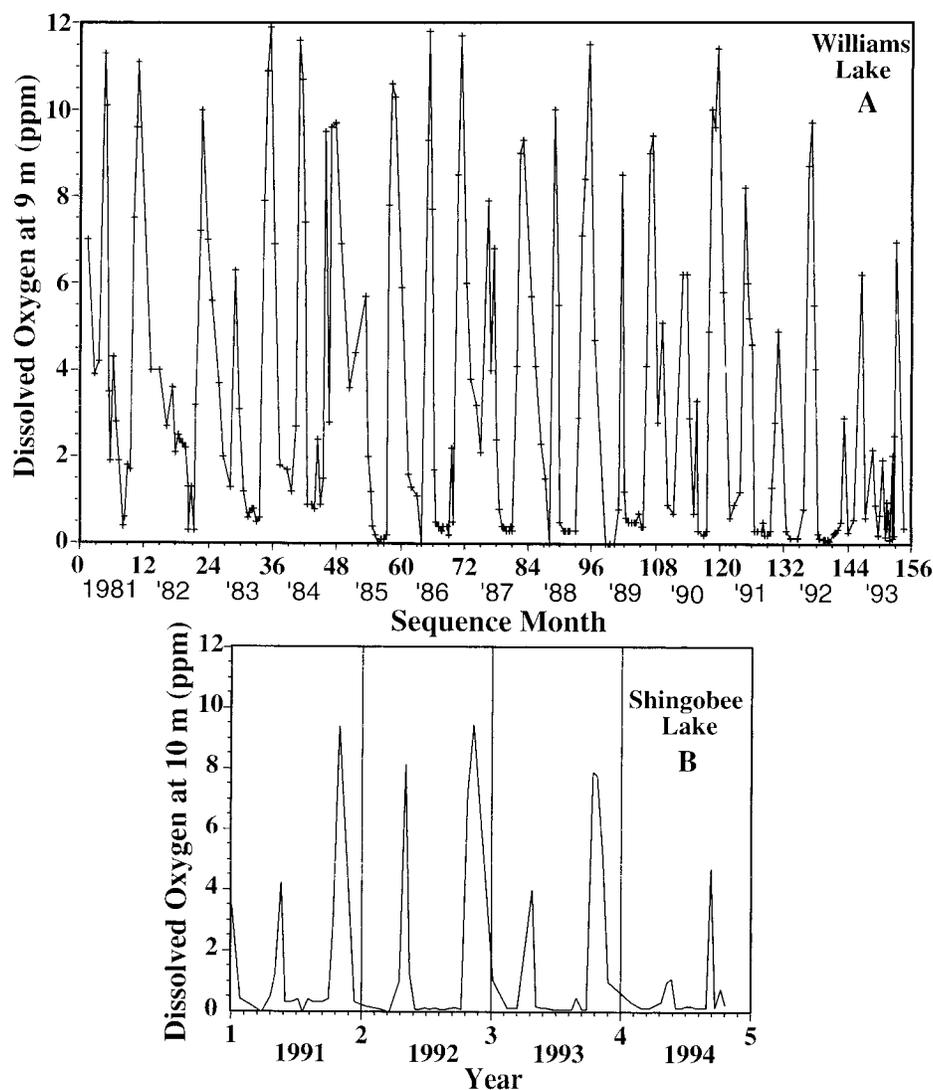
FIG. 8.—Concentration of dissolved oxygen **A)** at 9 m in Williams Lake for the period 1981 to 1993, and **B)** at 10 m in Shingobee Lake for the period 1991 to 1994.

of Williams Lake over the period from 1979 to 1993 (32 μg L^{-1}) is not substantially higher than that in the epilimnion (20 μg L^{-1}) and is not higher during summer stratification (Fig. 10A). The average concentration of Mn in the hypolimnion of Williams Lake over the period from 1979 to 1993 (45 μg L^{-1}) is higher than that in the epilimnion (6.1 μg L^{-1}), and highest values occurred during summer stratification, at least since 1988 (Fig. 10B). Accumulation of Mn in the hypolimnion of Williams Lake during the summer began in 1988, peaked in 1991, and then decreased in 1992 and 1993. Our first thought was that this might reflect a more anoxic hypolimnion. Figure 8A, however, shows that the bottom of the hypolimnion (9 m) of Williams Lake appears to have become more oxygen deficient, and in fact, anoxic, in the 1990s. Another possibility is that both less oxygen and more Mn in the hypolimnion of Williams Lake may be related to a period of drought that occurred between 1988 and 1992, when the level of Williams Lake went down as much as one meter (T.C. Winter personal communication). The hypolimnion of Williams Lake is only about 2 m thick (Fig. 9A), so if it was one meter thinner it would not take much respiration to deplete the DO. From these data we conclude that the carbon pump does not appear to have much of an effect on the Fe cycle in Williams Lake but started to affect the Mn cycle in 1988.

The Fe and Mn story is much different in Shingobee Lake. Because of the higher phytoplankton productivity in Shingobee Lake, the hypolimnion usually becomes oxygen deficient (< 1 ppm DO) within a month of overturn in both the fall and spring (Figs. 8B, 9C). Both dissolved Fe (Fig. 10C) and Mn (Fig. 10D) accumulate in the hypolimnion of Shingobee Lake during summer stratification, reaching concentrations that are hundreds of times higher than at spring overturn, much like the situation in Elk Lake. (Note that Fe and Mn concentrations in Williams Lake in Figure 10 are in μg L^{-1} whereas those in Shingobee Lake are in mg L^{-1}.) However, unlike Elk Lake, which accumulates Fe and Mn in the hypolimnion only during the summer, the concentration of Mn begins to build up in the hypolimnion of Shingobee Lake soon after fall overturn and, in some years, remains high throughout the year (Fig. 10D). The concentration of Fe does not build up after fall overturn (Fig. 10C), further evidence that Mn is more easily reduced.

Surface Sediments.—The effect of the carbon pump on the carbon cycle in Williams and Shingobee can be seen in the amounts of OC and CaCO$_3$ that have accumulated in surface sediments (Figs. 2, 3). The lack of CaCO$_3$ in the sediments of Williams Lake and the distinct inverse relation between percent OC and percent CaCO$_3$ in Shingobee Lake (Fig. 3) illustrate how high production of OC in the epilimnion can increase dissolution of CaCO$_3$ in the hypolimnion. That this inverse relation between OC and CaCO$_3$ cannot be due to simple dilution will be demonstrated below using mass accumulation rates.
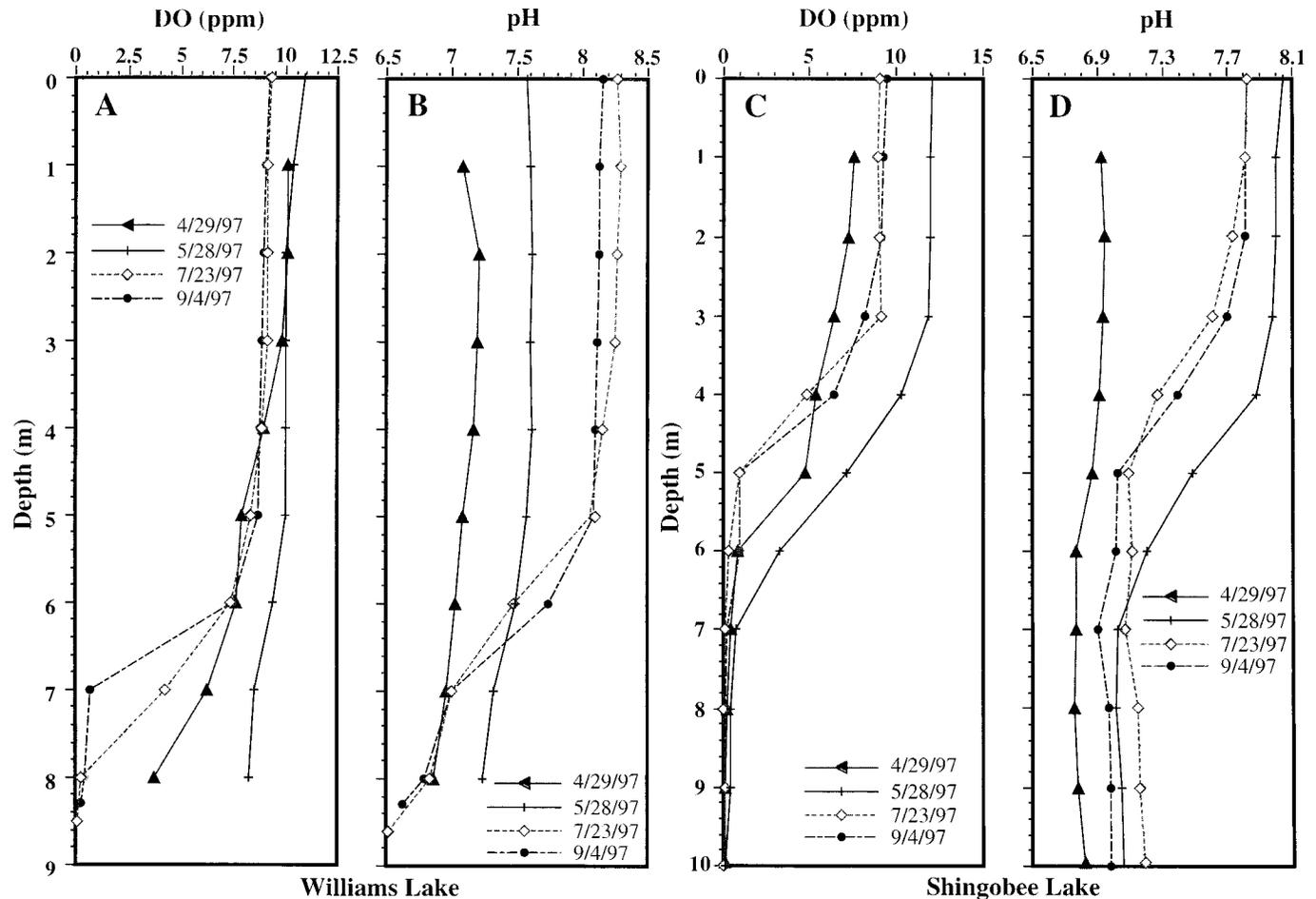
FIG. 9.—Profiles of dissolved oxygen (DO) and pH in Williams Lake (A and B, respectively) and in Shingobee Lake (C and D, respectively) for four dates in 1997.

Sample SL-4, from the deepest part of the lake (Fig. 1), clearly stands out as anomalous (Fig. 3). Intuitively, we would expect such high-carbonate, low-OC characteristics to be more typical of sediments from a marl bench in the littoral zone, where most of the carbonate is skeletal debris (molluscs and ostracodes) and carbonate precipitated on leaves and stems of aquatic macrophytes (e.g., McConnaughey et al. 1994; McConnaughey et al. 1997). Conversely, we would expect sediments from the deepest part of the lake, with a thicker and more acidic hypolimnion, to have lower carbonate and higher OC content. The abundance of $CaCO_3$ in sample SL-4 remains unexplained. One possibility is that this part of the lake is recharged by one or more springs with carbonate-rich ground waters with a relatively high CO_2 concentration (Dean and Bradbury 1997). Loss of CO_2 when the ground water enters the lake may increase the pH locally and trigger the precipitation of $CaCO_3$. Monthly profiles of several parameters, including pH, have been made in Shingobee Lake since 1989 (unpublished data, IRI database). The pH of the hypolimnion usually is < 8 (e.g., Fig. 9D), but values > 9 are common with a maximum of 9.9. Values could be even higher at the mouth of a spring.

Sample SL-4 also has an anomalously low diatom concentration, dominated by planktonic species, which are badly corroded and broken (Dean and Bradbury 1997). A sublacustrine spring with alkaline, carbonate-rich waters at the location of sample SL-4 may also explain the poor diatom preservation. This spring apparently is also enriched in Fe and Mn (Fig. 3) (see discussion below). The existence of this spring was confirmed in March 2000 by Dallas Hudson of Walker, Minnesota, the resident manager at the IRI site. There was very little snowfall in northwestern Minnesota

during the winter of 1999–2000, and by the end of March there was about one meter of clear ice on Shingobee Lake. The ice over the location of sample SL-4 was clouded with bubbles throughout its entire thickness. Bubbles in the water column were later confirmed with an acoustic fish finder (D. Hudson personal communication).

Little $CaCO_3$ is produced in the epilimnion of Williams Lake. Most is produced in the littoral zone on the leaves of aquatic macrophytes and as the calcareous alga *Chara* (McConnaughey et al. 1994), and none accumulates in the profundal zone (Fig. 2). The hypolimnion of Shingobee Lake is just as undersaturated with respect to calcite as that of Williams Lake and is thicker (Fig. 9). However, so much $CaCO_3$ is produced in the epilimnion that much escapes dissolution in the hypolimnion and sediments. Therefore, the differences in OC and $CaCO_3$ concentrations in the sediments of Williams and Shingobee Lakes simply may be due to differences in mass accumulation rates (MARs). In Shingobee Lake, OM has a higher benthic accumulation rate than in Williams Lake, as indicated by the higher OC MAR (Table 3). In the surface sediments of Shingobee Lake, the IC MAR is about 60% of the OC MAR (Table 3). In Williams Lake, on the other hand, the concentration of OC, in the absence of dilution by $CaCO_3$, is about three times higher than in Shingobee Lake, even though the OC MAR is lower than in Shingobee Lake (less than half; Table 3).

We have seen that as a consequence of the carbon pump, high concentrations of dissolved Fe and Mn accumulate in the hypolimnion of Shingobee Lake, but the question remains whether Fe and (or) Mn minerals precipitate in Shingobee Lake during overturn and accumulate in the sediments as they do in Elk Lake. The concentrations and accumulation rates
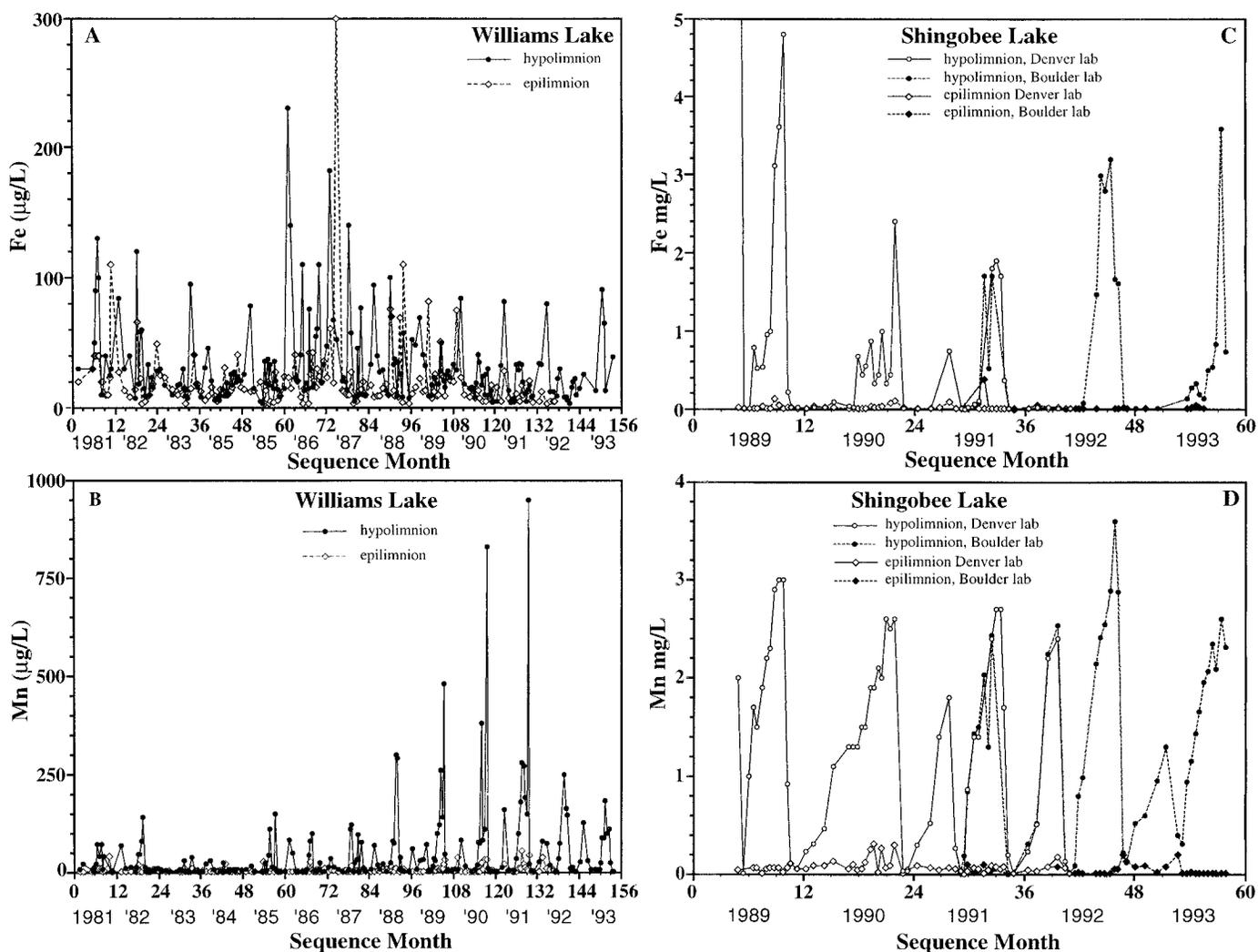
FIG. 10.—Concentrations of **A)** Fe, and **B)** Mn in the epilimnion and hypolimnion of Williams Lake for the period 1981 to 1993, and **C)** Fe and **D)** Mn in the epilimnion and hypolimnion of Shingobee Lake for the period 1989 to 1993.

(Table 3) of Fe and, especially, Mn in surface sediments of Shingobee Lake are much higher than in those of Williams Lake (compare Figs. 2 and 3). Although no Fe- and Mn-bearing minerals were detected by X-ray diffraction, we suspect that, as in Elk Lake, most of the Fe is precipitated as X-ray amorphous ferric hydroxide, and most of the manganese is precipitated as X-ray amorphous manganese oxyhydroxides.

There are several ways by which we can obtain an estimate of the amounts of Fe, Mn, and P present in amorphous oxyhydroxides in the surface sediments of Williams and Shingobee Lakes. The first estimate is from the cof concentrations of Fe and Mn in surface sediments (Table 3). These concentrations should represent the amounts of Fe and Mn contributed from detrital clastic material and any authigenic Fe and Mn minerals present (such as oxyhydroxides). If we assume that the sediments of Williams Lake contain no authigenic Fe or Mn oxyhydroxides, then the cof concentrations of Fe, Mn, and P in Williams Lake sediments should be similar to concentrations in some average source material such as average continental crust or average shale. The Fe, Mn, and P concentrations in average upper continental crust (UCC) are 3.1 wt. %, 0.05 wt. %, and 0.067 wt. %, respectively (Wedepohl 1995). Comparison of these values to average cof concentrations in Williams Lake sediments (Table 3) suggests that these sediments do not contain excess Fe or Mn (i.e., the Fe and Mn are from detrital clastic material) but do contain excess P, most likely as

organic P and (or) authigenic phosphate. The sediments of Shingobee Lake, on the other hand, contain 4.5 times more Fe and 15 times more Mn (Table 3) than can be explained by detrital clastic material (UCC), presumably as Fe and Mn oxyhydroxides. Excess P is most likely present as both organic P and P adsorbed on Fe and Mn oxyhydroxides.

Because the carbonate- and organic-free material contains other components in addition to detrital clastic material and authigenic Fe and Mn oxyhydroxides, particularly biogenic silica from diatom debris, a second but similar method of estimating the amount of authigenic Fe and Mn present is to use the inorganic geochemistry to calculate excess Fe and Mn. To do this, we assume that all of the aluminum (Al) is present in detrital clastic (aluminosilicate) minerals and that the Fe/Al and Mn/Al ratios of those aluminosilicate minerals are the same as in some standard reference material such as UCC. On the basis of this assumption, the detrital concentration of any metal (M) in a sample of lake sediment is calculated as

$$[M]_{detrital} = [Al]_{sample} * [M/Al]_{UCC.}$$

The excess amount is calculated as

$$[M]_{excess} = [M]_{total} - [M]_{detrital}.$$

Results of calculations for excess Fe, Mn, and P are given in Table 3. These result show that the surface sediments of Williams Lake contain little

excess Fe, no excess Mn, and a considerable amount of excess P (five times the detrital contribution), presumably as organic and (or) authigenic P. The sediments of Shingobee Lake, on the other hand, contain 7 times more Fe, 27 times more Mn, and 18 times more P than can be explained by detrital contributions.

The ultimate source of Fe and Mn in the lakes is from inflowing waters. LaBaugh (1997a) concluded from major-ion concentrations in groundwater, the Shingobee River, and Shingobee Lake that the ground water must have a considerable influence on the chemical characteristics of Shingobee River and Shingobee Lake. Ground-water seepage is the dominant influx of water into Williams Lake (58–76%; LaBaugh et al. 1995), but the Fe and Mn contents of that ground water are much lower than those of the Shingobee River (Table 1). The source of the high Fe and Mn concentrations in the Shingobee River and Shingobee Lake (Table 1) is unknown. However, because Shingobee Lake is at the end of the regional hydrologic flow system (Rosenberry et al. 1997), it might be that Shingobee Lake is receiving ground water from a deeper aquifer, perhaps reflecting discharge from underlying Cretaceous shales (T.C. Winter personal communication). This possibility is presently being tested by analyses of waters from deep piezometers, and preliminary analyses indicate that these deeper sources are higher in total Fe and Mn (i.e., unfiltered samples; Renee Parkhurst personal communication).

The concentrations of Fe and Mn in surface sediments in Shingobee Lake are highest in sample SL-4 (Fig. 4). As we discussed earlier, a sublacustrine spring at the location of sediment sample SL-4 probably is responsible for the high $CaCO_3$ content in that sample. It appears that the spring is also bringing in substantial amounts of Fe and Mn from the deeper, regional ground-water flow system. Therefore, from all of the above considerations, we conclude that the carbon pump has a considerable effect on the redox cycles of Fe and Mn in Shingobee Lake.

Long Cores.—Sediments in the spruce zone in both Williams and Shingobee Lakes contain about 80 wt. % $CaCO_3$ (Figs. 5, 6). We have suggested that during the early Holocene the two lakes were part of a larger lake, ''Lake Willobee,'' formed by a debris flow across the Shingobee River and with a shoreline that was about 7 m above the present level of Williams Lake, the highest of the two lakes, on the basis of lacustrine marl deposits at that elevation (Schwalb and Dean 2002). Once the debris flow was breached, the remaining depressions were filled to form the existing lakes and wetlands. The most convincing evidence for the existence of Lake Willobee comes from the carbon- and oxygen-isotope composition of ostracode shells and bulk carbonate (marl; Schwalb et al. 1995; Schwalb and Dean 2002). These data show that the waters of both lakes had identical values of $\delta^{13}C$ (Fig. 7) and $\delta^{18}O$ during the spruce period, but the waters of Williams Lake ''evolved'' during the early Holocene, increasing by about 10‰ in both $\delta^{13}C$ (Fig. 7) and $\delta^{18}O$. Values of $\delta^{18}O$ in Shingobee Lake remained unchanged throughout the Holocene, although values of $\delta^{13}C$ increased about 3‰ during the mid-Holocene, probably in response to vegetation change as discussed above.

The $CaCO_3$ contents of lower Holocene sediments provide additional evidence for the existence of Lake Willobee. Shingobee Lake continued accumulating $CaCO_3$ in sediments at the same high rate, but the $CaCO_3$ content of sediments in Williams Lake began to decline as the lake evolved from a hydrologically open lake to a hydrologically closed lake (Schwalb et al. 1995; Schwalb and Dean 2002). The decline in $CaCO_3$ in the sediments of Williams Lake from 80% at the bottom of the core to its disappearance at 320 cmblf (ca. 5000 yr B.P.) is mirrored by an increase in OC content from 2 to > 30 wt. % (Fig. 5). Dean (1999) suggested that a decrease, and eventual elimination, of $CaCO_3$ in profundal sediments with increasing OC-burial may be due to greater dissolution of $CaCO_3$ in an anoxic hypolimnion and corrosive pore waters (i.e., due to an increasingly active carbon pump through the early Holocene).

Today, the carbon pump has a large effect on the Fe and Mn biogeochemical cycles in Shingobee Lake, but the effects in the past on either Shingobee or Williams are less known. The concentrations of Fe, Mn, and total sulfur (S) are all high in the lower Holocene sediments of both lakes (Figs. 11, 12). This may be further evidence for the existence of Lake Willobee. The cof concentration of Al is shown here as a measure of changes in the detrital fraction. The mineral residences of Fe, Mn, and S in sediments from the cores, like those in surface sediments, are not known because concentrations are too small to be detected by X-ray diffraction and (or) the minerals are X-ray amorphous. Because the concentrations of both Fe and S are high, these two elements probably exist as pyrite (FeS_2). The concentrations of sulfate in both lakes today are low (Table 1), but the region is underlain by Cretaceous rocks known to contain gypsum (T.C. Winter personal communication). Therefore, gypsum may have been a source of sulfate for sulfate reduction early in the histories of both lakes. Unlike Fe, minerals that contain reduced Mn (Mn-II) are less common. One mineral that does contain Mn-II is rhodochrosite ($MnCO_3$); this mineral is rare in lacustrine sediments but has been detected by X-ray diffraction in the sediments of Elk Lake (Dean, 1993, 1999; Nuhfer et al. 1993). Another rare mineral that contains Mn-II is kutnahorite [(Ca, Mn)CO_3], which has been detected by X-ray diffraction in the varved sediments of Mina Lake in west-central Minnesota (Stevens 1997). Because of the high carbonate content of the lower Holocene sediments of both Williams and Shingobee Lakes, it is entirely possible that the Mn resides in rhodochrosite and (or) kutnahorite in concentrations below detection by X-ray diffraction, or it may simply be substituting for Ca in calcite.

In the sediments of Elk Lake, some Fe and Mn are present as an Fe–Mn–P mineral (rockbridgeite; Nuhfer et al. 1993), as corroborated by concentrations of P that covary with those of Fe and Mn (Dean 1999, 2002). The concentrations of P in lower Holocene sediments in Williams Lake, like those of Fe and Mn, are elevated relative to middle and upper Holocene sediments (Fig. 11). The P may reside in an Fe–Mn–P mineral such as rockbridgeite that is not detectable by X-ray diffraction, or it may be adsorbed onto ferric hydroxide, which is an efficient scavenger of P (Stauffer and Armstrong 1986). In the sediments of Shingobee Lake, however, P is not high in lower Holocene sediments (Fig. 12) but increases upward, suggesting that it is not coprecipitated with Fe and Mn. The presence of these geochemical indicators of reducing conditions in the bottom waters of both lakes during the early Holocene suggests that perhaps the bottom waters of these two lakes were connected as a larger lake (Lake Willobee) with an oxygen-deficient hypolimnion. The presence of high concentrations of Fe, Mn, and S in lower Holocene sediments in Shingobee Lake coincides stratigraphically with the presence of laminated sediments (Fig. 6), indicating that the bottom of Lake Willobee at the locality of present Shingobee Lake was anoxic, at least seasonally. At that locality, it is estimated that the water depth was 44 m (Schwalb and Dean 2002). In contrast, we estimate that Lake Willobee would have been 17 m shallower at the locality of present Williams Lake and perhaps oxic enough to permit the existence of a bioturbating benthic fauna that destroyed laminations. We conclude that the carbon pump is operating today to a high degree on the redox cycles of Fe and Mn in Shingobee Lake, but the pump may have been less efficient until several thousand years ago.

CONCLUSIONS

Extensive data on the sediments, limnology, biogeochemistry, and hydrology of hydrologically closed Williams Lake and hydrologically open Shingobee Lake and their watersheds provide a unique opportunity to investigate biogeochemical cycling that should have wide applicability to other hardwater lakes of the world. Some of the major conclusions are listed below.

1. Phytoplankton productivity in the epilimnions of Williams and Shingobee Lakes removes CO_2 and raises the pH of the water. Respiration of that fixed carbon in the hypolimnion produces CO_2 and lowers the pH. This simple ''carbon pump'' has a profound effect on $CaCO_3$ production

Williams Lake

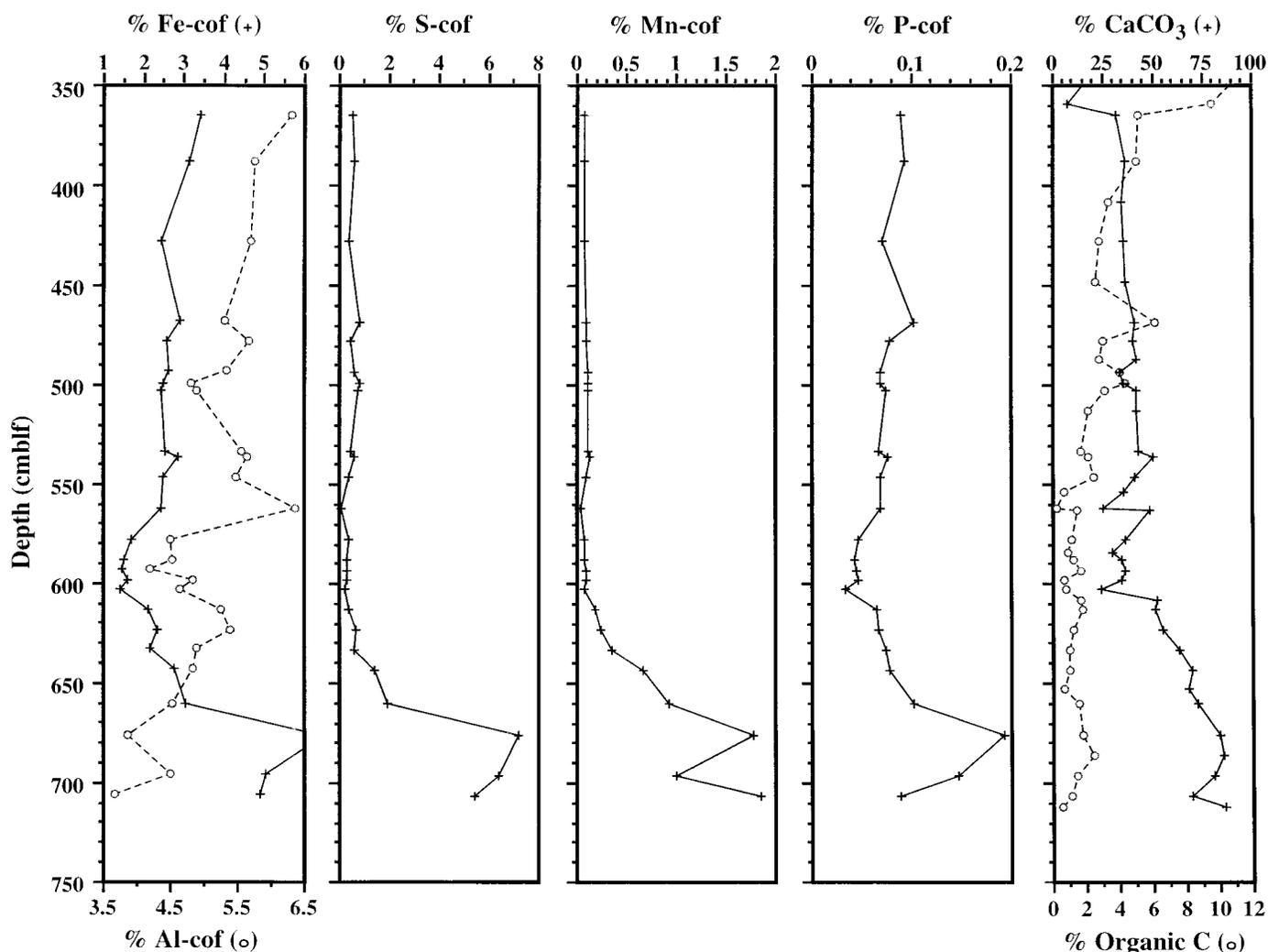FIG. 11.—Profiles of percentages of Fe, Al, S, Mn, P, CaCO₃ and Organic carbon in samples from the bottom 4 m of the Williams Lake J core. Percentages of Fe, S, Mn, and P are calculated on a carbonate- and organic-free basis (cof; see text for method of calculation).

and preservation. Any CaCO₃ that forms in the epilimnion of Williams Lake does not survive in the undersaturated hypolimnion. In response to higher rate of phytoplankton productivity in the epilimnion of Shingobee Lake, and a higher rate of decomposition in the hypolimnion, the hypolimnion in that lake is oxygen deficient and undersaturated with respect to calcite most of the year. In spite of an unfavorable environment for preservation of CaCO₃ in the hypolimnion of Shingobee Lake, such a large amount is produced each summer in the epilimnion that the surface sediments contain an average of 46 wt. % CaCO₃.

2. Because of the oxygen-deficient hypolimnion of Shingobee Lake, high concentrations of redox-sensitive ions like Fe^{2+} and Mn^{2+} build up there during summer stratification. Williams Lake is well oxygenated for at least six months each year, and high concentrations Fe^{2+} and Mn^{2+} do not build up seasonally in the hypolimnion.

3. As a consequence of the high concentrations of Fe^{2+} and Mn^{2+} in the hypolimnion of Shingobee Lake during periods of stratification, Fe and Mn minerals precipitate when oxygen-deficient hypolimnetic waters mix with well-oxygenated epilimnetic waters. Surface sediments of Shingobee Lake contain up to 20 wt. % Fe and 1 wt. % Mn on a carbonate- and organic-free basis. Although no Fe or Mn minerals have been identified by

X-ray diffraction in the surface sediments, the mineral residences are most likely amorphous oxyhydroxides. Because ferric hydroxide is an efficient adsorber of phosphate, the surface sediments of Shingobee Lake also contain elevated levels of P.

4. The lower Holocene sediments in both lakes contain about 80% CaCO₃, and that level was maintained in the sediments of Shingobee Lake throughout most of the Holocene. In Williams Lake, however, dissolution of CaCO₃ began about 9000 years ago. Accumulation of CaCO₃ ended about 5000 yr B.P. as the lake became hydrologically closed. The high concentrations of CaCO₃ in lower Holocene sediments of both lakes is but one line of evidence that the two lakes were initially part of a larger lake, Lake Willobee.

5. Lower Holocene sediments of Williams and Shingobee Lakes contain high concentrations of Fe, S, and Mn. The presence of these geochemical indicators of reducing conditions in the bottom waters of both lakes during the early Holocene is further evidence that they were connected as a larger lake. The high concentrations of Fe, Mn, and S in lower Holocene sediments in Shingobee Lake coincides stratigraphically with the presence of laminated sediments, indicating that the deepest waters of the larger Lake Willobee was anoxic, at least seasonally.
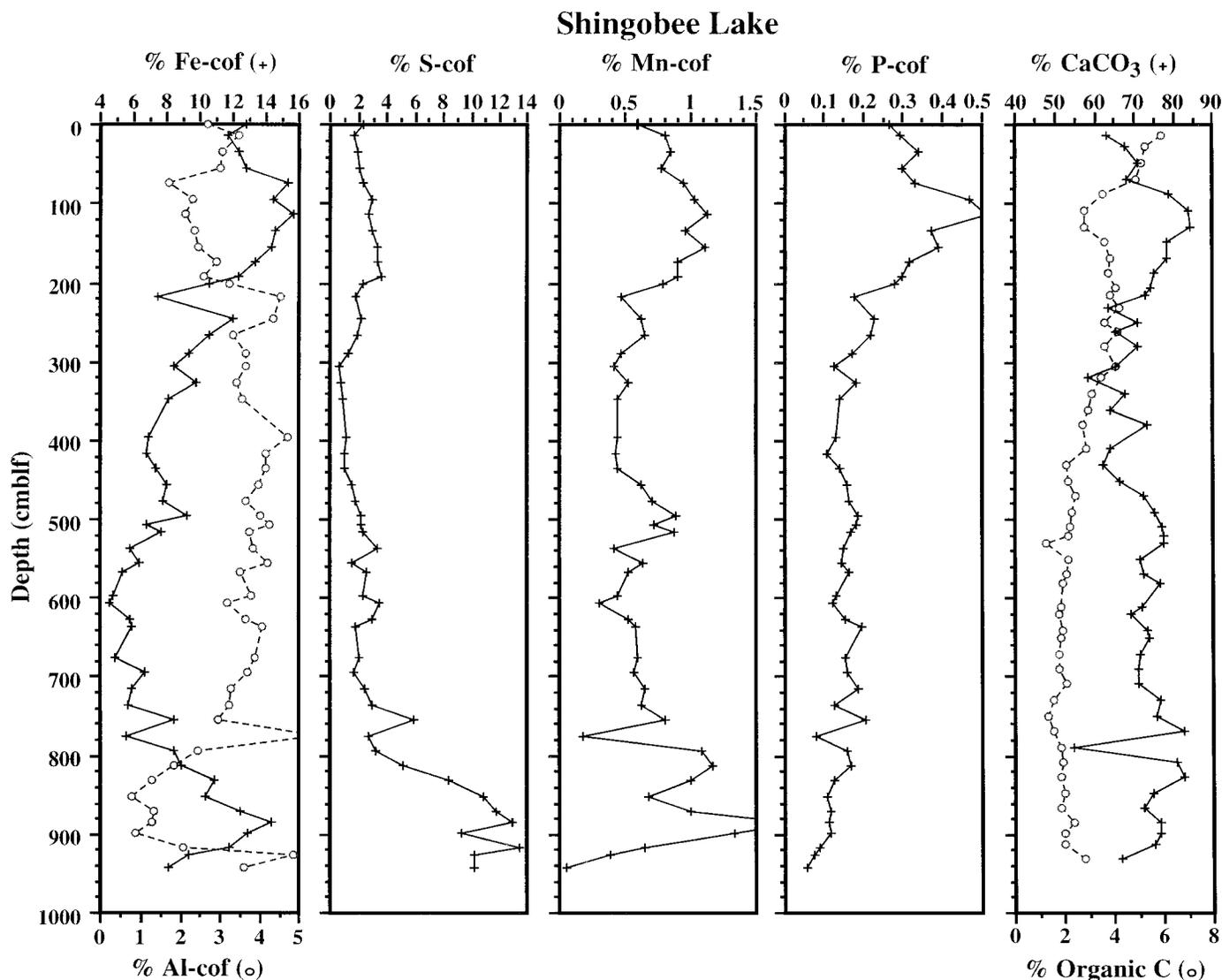
Shingobee Lake

F<small>IG</small>. 12.—Profiles of percentages of Fe, Al, S, Mn, P, CaCO$_3$ and Organic carbon in samples from the Shingobee Lake H core. Percentages of Fe, Al, S, Mn, and P are calculated on a carbonate- and organic-free basis (cof; see text for method of calculation).

6. Values of δ^{13}C in both bulk carbonate and organic matter increase by about 10‰ in lower to mid-Holocene sediments in Williams Lake and by about 4‰ in sediments deposited in Shingobee Lake over the same time interval. We estimate that about 7‰ of the 10‰ increase in Williams Lake sediments is due to hydrologic closure of the lake, and the rest is due to change in dominant flora of the drainage basin from C$_3$ forest to C$_4$ prairie vegetation.

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