



A Holocene Record of Endogenic Iron and Manganese Precipitation, Isotopic Composition of Endogenic Carbonate, and Vegetation History in a Lake-Fen Complex in Northwestern Minnesota

By Walter E. Dean and Lisa A. Doner



Open-File Report 2011–1106

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

For product and ordering information:
World Wide Web: <http://www.usgs.gov/pubprod>
Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth,
its natural and living resources, natural hazards, and the environment:
World Wide Web: <http://www.usgs.gov>
Telephone: 1-888-ASK-USGS

Suggested citation:

Dean, W.E., and Doner, L.A., 2011, A Holocene record of endogenic iron and manganese precipitation, isotopic composition of endogenic carbonate, and vegetation history in a lake-fen complex in northwestern Minnesota: U.S. Geological Survey Open-File Report 2011–1106, 41 p.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted material contained within this report.

Contents

Abstract	1
Introduction	2
Methods	4
Results	7
Little Shingobee Lake	7
Chronology	7
Sediment Components	9
Stable Isotopes of Carbon and Oxygen	17
Pollen Zones	21
Sediment Components in Little Shingobee Fen	23
Discussion	28
Carbonate and Detrital Clastic Deposition	28
Endogenic Fe and Mn	29
Stable Isotopes	29
Pollen Zones	34
Conclusions	36
Acknowledgments	37
References Cited	37
Appendix 1. Concentrations of Major, Minor, and Trace Components in Core LSL–B	link
Appendix 2. X-Ray Diffraction Intensities and Percentages of Dominant Minerals in Core LSL–B	link
Appendix 3.1. Results of Carbon and Oxygen Isotope Analyses of Ostracodes	link
Appendix 3.2. Results of Carbon and Oxygen Isotope Analyses of <i>Pisidium</i>	link
Appendix 4. Results of Carbon Analyses of Organic Carbon in Core LSL–B	link
Appendix 5. Percentages of Major Pollen Types in Core LSL–B	link
Appendix 6. Concentrations of Major, Minor, and Trace Components in Core LSF–10	link

Figures

1. A, Modern lakes of the Shingobee River Headwaters Area. B, Inferred extent of glacial Lake Willobee formed when a debris flow dammed the Shingobee River	3
2. Little Shingobee Lake and Little Shingobee Fen. Transects of cores of Carter and others (1997), and locations of cores LSL–B and LSF–10 also are shown	5
3. Age-depth model for Little Shingobee Lake core LSL–B from Little Shingobee Lake based on AMS radiocarbon dates	9
4. Sediment components in Little Shingobee Lake and Little Shingobee Fen	11
5. Major and minor components in sediments in core LSL–B from Little Shingobee Lake relative to depth in core	12
6. Percentages of allogenic (detrital) and endogenic components in sediments in core LSL–B from Little Shingobee Lake relative to depth in core. Ages of sediments from the age model in figure 3 are shown at the right of the diagram. Pollen zones are for cores from Little Shingobee Lake (Doner, this report), Shingobee Lake (Locke, 1995), and Elk Lake (Whitlock and others, 1993)	14
7. Percentages of total, detrital, and endogenic iron (Fe) and manganese (Mn) in sediments in core LSL–B from Little Shingobee Lake relative to depth in core. See text and figure 4 for methods of calculation of detrital and endogenic Fe and Mn. Ages of sediments from the age model in figure 3 are shown at the right of the Mn diagram	16

8. Stable isotope ratios of carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in the carbonate shells of the fingernail clam, <i>Pisidium</i> , and ostracodes picked from sediments in core LSL-B from Little Shingobee Lake relative to depth in core	18
9. Stable isotope ratios of carbon ($\delta^{13}\text{C}$) in organic carbon and percent organic carbon in sediments in core LSL-B from Little Shingobee Lake relative to depth in core	20
10. Pollen diagram for major pollen types in core LSL-B from Little Shingobee Lake relative to depth in core	22
11. Major and minor components in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core	24
12. Percentages of allogenic (detrital) and endogenic components in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core	25
13. Percentages of total, detrital, and endogenic iron (Fe) and manganese (Mn) in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core. See text and figure 4 for methods of calculation of detrital and endogenic Fe and Mn	27
14. Cross plots of values of $\delta^{18}\text{O}$ compared with $\delta^{13}\text{C}$ in endogenic carbonate (marl) from Elk, Williams, and Shingobee Lakes, and in ostracodes from Little Shingobee Lake for three time slices: 10 cal ka, 4 cal ka, and 2 cal ka. A fourth time slice (7 cal. ka) is added for Elk and Little Shingobee Lakes for which there is better time control.....	31

Table

1. Radiocarbon dates from Little Shingobee Lake core LSL-B.....	8
---	---

Abbreviations Used in This Report

cal. ka	thousand calendar years old
cal. yr	calendar year
cm	centimeter
cmblf	centimeters below lake floor
g	gram
ka	thousands of years old
ky	thousands of years
mm	millimeter
mm yr ⁻¹	millimeters per year
AMS	accelerator mass spectrometer
BP	before present
DIC	dissolved inorganic carbon
GMWL	global meteoric water line
IC	inorganic carbon
LMWL	local meteoric water line
OC	organic carbon
SHAEP	Shingobee Headwaters Aquatic Ecosystem Project
TC	total carbon
USGS	U.S. Geological Survey
VPDB	Vienna Pee Dee belemnite
XRD	X-ray diffraction

A Holocene Record of Endogenic Iron and Manganese Precipitation, Isotopic Composition of Endogenic Carbonate, and Vegetation History in a Lake-Fen Complex in Northwestern Minnesota

By Walter E. Dean¹ and Lisa A. Doner²

¹U.S. Geological Survey, MS 980 Federal Center, Denver, Colorado 80225

²Center for the Environment, MSC6317, Plymouth State University, Plymouth, New Hampshire 03264

Abstract

Little Shingobee Lake and Fen are part of an extensive network of lakes and wetlands in the Shingobee River headwaters area of northwestern Minnesota. Prior to about 9800 radiocarbon years, most of the lakes in the Shingobee watershed area were interconnected to form glacial Lake Willabee. From 9800 to 7700 radiocarbon years, the level of Lake Willabee fell as a result of breaching of a dam, leaving small separated basins containing the existing lakes and wetlands.

The dominant components in the sediments in a 9-meter core from Little Shingobee Lake (LSL-B), and lacustrine sediments under 3.3 meters of peat in a 17-meter core from Little Shingobee Fen (LSF-10) are detrital clastic material, endogenic CaCO₃, and organic matter. The detrital fraction in the Holocene section in core LSL-B varies considerably from 7 weight percent to 82 weight percent and closely parallels the concentration of detrital quartz measured by X-ray diffraction. The CaCO₃ concentration, which also varies considerably from 10 weight percent to 70 weight percent, is generally antithetic to the detrital concentration owing to the dilution of detrital material by CaCO₃, particularly during the early to middle Holocene (about 9000–6500 calendar years). The organic-matter content varies from 5 weight percent to 25 weight percent and, together with CaCO₃, serves to dilute the allogenic detrital fraction.

In both cores almost all of the iron (Fe) and manganese (Mn) is in endogenic minerals, presumed to be oxyhydroxide minerals, that are important components throughout the core; little Fe and Mn are contributed by detrital aluminosilicate minerals. The endogenic Fe mineral, calculated as Fe(OH)₃, forms a larger percentage of the sediment than endogenic organic material throughout most of the Holocene section in the LSL-B core and in the lacustrine sediments below the peat in the LSF-10 core. Biogenic silica as opal (biopal; diatom debris) was not measured, but the average calculated biopal is 5 percent in the LSL-B core and 15.5 percent in the LSF-10 core.

Values of $\delta^{18}\text{O}$ in mollusk (*Pisidium*) and ostracode shells increase by only about 20 per mil from the bottom to the top of the LSL-B core (about 12600–2200 calendar years). The remarkably constant oxygen-isotope composition throughout the Holocene suggests that environmental conditions affecting values of $\delta^{18}\text{O}$ (temperature, salinity, composition of the water, composition of precipitation) did not change greatly. Values of $\delta^{13}\text{C}$ in carbonate shells generally decreased by about 2 per mil from 9000 calendar years to 6000 calendar years, but they did not increase in organic carbon. This

mid-Holocene increase in $\delta^{13}\text{C}$ in shells but not in organic carbon is likely due to an increase in residence time.

A late Pleistocene forest dominated by spruce was replaced in the early Holocene by a pine forest. The pine forest migrated east during the middle Holocene and was replaced by an open sagebrush–oak savanna. The western migration of forests into northwestern Minnesota is marked first by a hardwood forest and finally a pine forest.

Introduction

The lakes and wetlands of the Shingobee River headwaters area in northwestern Minnesota (fig. 1A) have been intensively studied by the U. S. Geological Survey (USGS) and several universities for more than 20 years (Winter, 1997). The first initiative, the Interdisciplinary Research Initiative (IRI), focused mainly on Williams and Shingobee Lakes. Preliminary results of numerous IRI studies have been published in Winter (1997). Most of the studies concentrated on the waters of the lakes and watershed; less work has been done on the sediments. However, some results from analyses of surface sediments and longer sediment cores have been presented elsewhere (Schwalb and others, 1995; Dean and Bradbury, 1997; Locke and Schwalb, 1997; Dean and Schwalb, 2002; Schwalb and Dean, 2002). In recent years research expanded to include the entire Shingobee headwaters under the Shingobee Headwaters Aquatic Ecosystem Project (SHAEP). Research continued to be focused on waters and the watershed, but in addition long cores that collected the entire Holocene sediment sections were taken from Little Shingobee Lake, Little Shingobee Fen, and Steel Lake (Carter and others, 1997; Wright and others, 2004; Tian and others, 2005). Prior to about 9.8 thousand radiocarbon years ago (radiocarbon ka), most of the lakes in the Williams and Shingobee watershed area were interconnected to form glacial Lake Willobee (fig. 1B; Schwalb and Dean, 2002), which apparently formed when a debris flow dammed the Shingobee River (R.C. Melchior, 2010, unpub. data). From 9.8 to 7.7 radiocarbon ka, the level of glacial Lake Willobee fell, as a result of breaching of the dam, and left small separated basins containing the existing lakes and wetlands. At that time, Williams Lake became hydrologically isolated (it had no surface-water connection). The other lakes have surface inlets and outlets but also store a large component of groundwater from both shallow and deep sources (Rosenberry and others, 1997; Dean and others, 2003).

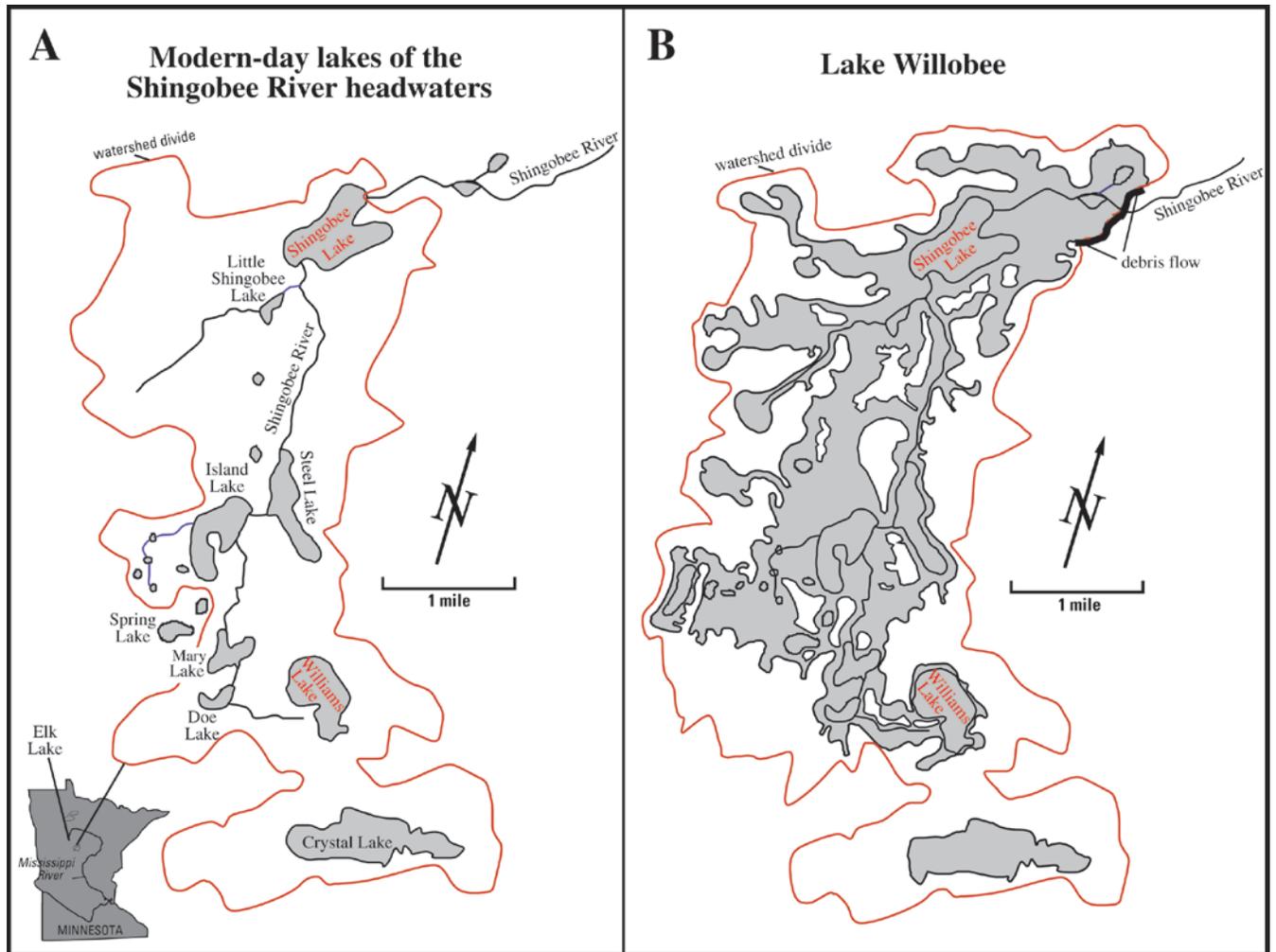


Figure 1. A, Modern lakes of the Shingobee River Headwaters Area. B, Inferred extent of glacial Lake Willobee formed when a debris flow dammed the Shingobee River.

Williams, Shingobee, and Steel Lakes are three of the lakes occupying basins on the floor of glacial Lake Willobee. The Holocene sediments in these lakes contain abundant endogenic carbonate (marl) (Dean and Schwalb, 2002; Schwalb and Dean, 2002; Tian and others, 2005; Dean, 2010, unpub. data). For sediment description, magnetic susceptibility, loss-on-ignition, pollen stratigraphy, and ostracode assemblages in cores from Williams and Shingobee Lakes, see Schwalb and others (1995) and Locke and Schwalb (1997). The SHAEP area has numerous seeps that precipitate an orange ferric hydroxide floc, and the groundwaters, especially in a deep aquifer (several tens of meters to more than 130 meters (m) below the surface), contain high concentrations of iron (Fe) and manganese (Mn) (Dean and others, 2003). The sediments of Shingobee Lake are unusual for a lake in a glaciated north-temperate region in that precipitation of Fe and Mn minerals, presumed to be X-ray amorphous oxyhydroxides, occurs at spring and fall overturn (Dean and others, 2003). As a result, the surface sediments of Shingobee Lake contain concentrations of Fe and Mn that are 7 and 27 times higher than can be explained by contributions of Fe and Mn from detrital aluminosilicates, and even higher

concentrations occur at depth in cores (Dean and Schwalb, 2002). Concentrations of dissolved Fe and Mn in the hypolimnion of Shingobee Lake at the end of summer stratification are several hundred times higher than after spring and fall overturn, and they are much higher than in shallow groundwaters. However, groundwater from deep wells (as deep as 130 m) contains high concentrations of Fe and Mn (as much as 14 parts per million (ppm) Fe and 0.5 ppm Mn; that is, they are major ions), and this deep groundwater is the most likely source of high concentrations of Fe and Mn that accumulate in the hypolimnion of Shingobee Lake at the end of summer stratification (Dean and others, 2003).

The Holocene dominant sediment components in Shingobee Lake are allogenic detrital material and endogenic CaCO₃, organic matter, Fe and Mn oxyhydroxides, and an unknown amount of biogenic silica (diatom debris). Because Little Shingobee Lake is in the same groundwater regime as Shingobee Lake, we assumed that the same would be true of the Holocene sediments in Little Shingobee Lake and the lake sediments that underlie 3.3 m of peat in Little Shingobee Fen. The purposes of this report are (1) to document the composition of sediment components in Little Shingobee Lake and Fen, and particularly whether excess (endogenic) Fe and Mn occur in the sediments; (2) to document the vegetation and climatic history of the region on the basis of pollen; and (3) to determine the sources of organic matter and how these sources may have changed with changes in productivity, vegetation, and hydrology. The dominance of endogenic Fe and Mn as compared with detrital Fe and Mn in the sediments of Shingobee Lake is highly unusual, and we wanted to see if chemical conditions in Little Shingobee Lake would duplicate endogenic formation of Fe and Mn. The vegetation history of the Shingobee River headwaters area is based on studies of Shingobee and Williams Lakes, but the age model for these lakes is questionable. Isotopic composition of organic matter in Williams and Shingobee Lakes shows distinct changes with time. In order to document the timing of events and changes recorded in the sediments, a good age model was needed, and we attempted to provide it.

Methods

Core LSL-B from Little Shingobee Lake was cored from the ice in 1998 with a modified square-rod Livingstone piston corer as an extension of a transect of cores across Little Shingobee Fen (Carter and others, 1997; transect B-B' and D-D' in fig. 2). The top meter of the core was too soupy to be recovered by the Livingstone corer, but the rest of the core was recovered; it consists of marl and gyttja. Core LSF-10 was cored from the surface of the fen along transect D-D' of Carter and others (1997). The top 3.3 m of the core consists of peat, but the rest of the core consists of marl, bottoming in sand. The cores are stored at the Limnological Research Center, University of Minnesota.

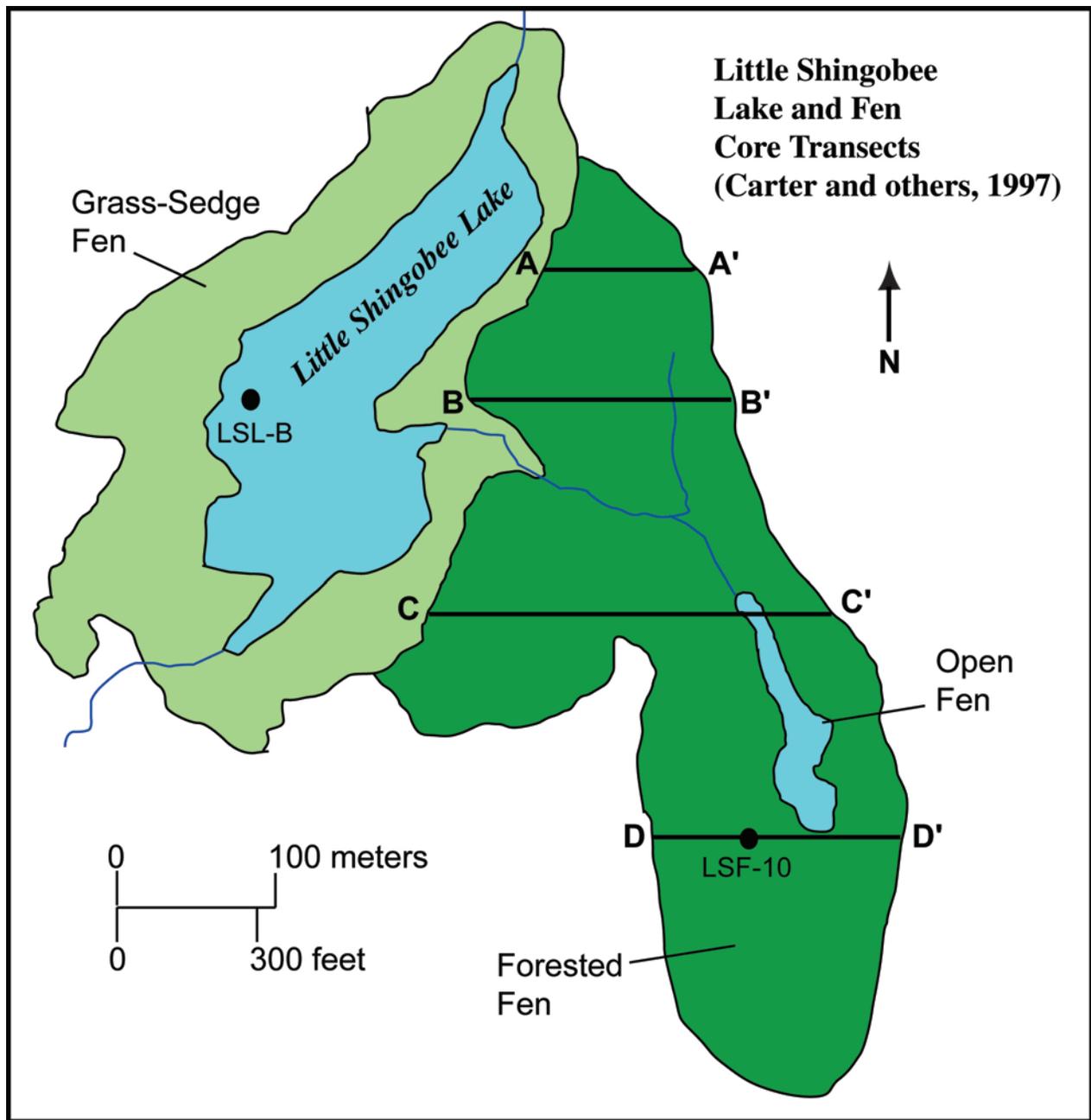


Figure 2. Little Shingobee Lake and Little Shingobee Fen. Transects of cores of Carter and others (1997), and locations of cores LSL-B and LSF-10 also are shown.

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 and others, 1985). Weight percent IC was converted to weight percent CaCO_3 by dividing by 0.12, the fraction of carbon in CaCO_3 . Organic carbon (OC) was determined as the

difference between TC and IC. The accuracy and precision of both TC and IC, determined from hundreds of replicate standards, usually are better than 0.10 wt percent.

Semiquantitative estimates of mineral contents in aliquots of carbon samples from core LSL-B were determined by standard X-ray diffraction (XRD) techniques (Moore and Reynolds, 1989). Each sample was packed into an aluminum holder and scanned from 15° to 50° 2 θ at 2° 2 θ /minute (min) by using Ni-filtered, Cu-K α radiation at 45 kilovolts and 30 milliamps. For each sample, raw XRD peak intensities, in counts per second, of the main peaks of minerals detected in each sample were converted to semiquantitative percentages by dividing the main peak intensity of a mineral by the sum of the main peak intensities of all minerals. These percentage calculations should be used with caution because they do not reflect the different X-ray mass absorption characteristics of different minerals.

Samples were analyzed for 40 major, minor, and trace elements in a multiacid digest of sediment samples by inductively coupled argon-plasma, atomic emission spectrometry (ICP-AES) by SGS Minerals Services, Toronto, Canada. Rock standards (USGS) were included with the sediment samples, and 5 percent of the samples were analyzed in duplicate. The precision, determined by analyzing rock standards and duplicate sediment samples, was better than 10 percent, and usually better than 5 percent at a concentration of 10 times the limit of detection. Only the results of analyses of aluminum (Al), titanium (Ti), iron (Fe), and manganese (Mn) will be discussed in this report.

The bulk-sediment samples remaining after XRD and ICP analyses were decalcified with hydrochloric acid for measurement of carbon isotopes in organic carbon. Therefore, measurements of ratios of stable isotopes of carbon and oxygen were made only on picked mollusk (the fingernail clam *Pisidium*) and ostracode shells. No attempt was made to pick only one species of ostracode or to separate juveniles from adults. Consequently, the isotope analyses on ostracode valves are on mixed adults and juveniles and mixed species, most likely *Candona acuta* and *Candona ohioensis*, which are the most common ostracodes in Shingobee Lake sediments (Schwalb and Dean, 2002). Powdered samples were reacted with dehydrated phosphoric acid under vacuum at 70°C. The resulting CO₂ was then dehydrated and purified in a high-vacuum gas-transfer system, and the isotope ratios determined with an isotope-ratio mass spectrometer.

Stable carbon-isotope ratios of bulk organic matter were determined by standard techniques on decalcified samples (Dean and others, 1986). A powdered sample was reacted with buffered acetic acid for 24 hours to dissolve carbonate minerals. The residue was then centrifuged, decanted, washed three times, and dried. The residue was then combusted at 1,000°C with copper oxide in a sealed quartz tube. The resulting CO₂ was then dehydrated and purified in a high-vacuum gas-transfer system, and the isotope ratios were determined with an isotope-ratio mass spectrometer. Duplicate analyses were made on all samples.

Results of carbon and oxygen analyses are reported in the usual per mil (‰) δ -notation relative to the Vienna Pee Dee Belemnite (VPDB) marine-carbonate standard for carbon and oxygen:

$$\delta\text{‰} = [(R_{\text{sample}}/R_{\text{VPDB}}) - 1] \times 10^3,$$

where R is the ratio (¹³C: ¹²C) or (¹⁸O: ¹⁶O). Precision is ± 0.1 per mil for oxygen and ± 0.06 per mil for carbon in carbonate and on the basis of duplicate analyses, it is usually better than 0.2 per mil for organic carbon.

Seventeen samples were analyzed for their contained pollen. Samples for pollen analysis were prepared by using standard procedures (Faegri and others, 1989). Spores of *Lycopodium clavatum* from Lund, Sweden, were added to each 0.5 gram (g) sample to provide a control basis for concentration estimates. Prepared pollen samples are stored with glycerin in capped glass vials. About 40–100

terrestrial pollen grains were counted for each of the 17 levels, and pollen percentages were based on the sum of terrestrial pollen.

Pollen identifications and counts were completed by using an Olympus BH2 microscope with a combined ocular and dry-lens magnification factor of 500. To avoid problems of differential sorting, pollen grains were identified along a minimum of five evenly spaced transects, covering either half the slide from midline to outer edge, or the full slide, until a minimum of 300 grains were identified, excluding spores, aquatic types, and pre-Quaternary types. The pollen types are grouped as trees, shrubs, herbs, aquatic, spores, pre-Quaternary, and indeterminate. Pollen percentages for each group were calculated relative to a total sum of trees, shrubs, herbs, and indeterminate types. Total pollen concentrations are derived from grains per gram of dry sediment and include all vascular pollen and spore types. Cyperaceae (sedges) in the temperate regions occur commonly as aquatic species and so are grouped as aquatic pollen. The multivariate analysis program CONISS (Grimm, 1987) generated Euclidean-distance dissimilarity values of terrestrial pollen and spores with more than 1 percent maximum occurrence (Overpeck and others, 1985). These values are displayed as hierarchical, polythetic agglomerative dendrograms with minimum-variance clustering so that samples that are most alike (least dissimilar) form tight clusters close to the axis (Gaugh, 1982). The dendrogram defines the pollen zones.

The pollen zonations defined for Little Shingobee Lake resemble those of Whitlock and others (1993) for Elk Lake just north of the SHAEP area in the headwaters of the Mississippi River (fig. 1A, inset), and Williams and Shingobee Lakes (Locke, 1995; Locke and Schwalb, 1997), but the chronologies of these zones are slightly different (discussed below).

Results

Little Shingobee Lake

Chronology

A total of 31 accelerator mass spectrometer (AMS) radiocarbon dates were obtained from samples of wood, mollusks, and bulk sediment from Little Shingobee Lake (table 1). Targets for AMS analyses were prepared in the USGS Radiocarbon Laboratory, Reston, Va., (WW numbers in table 1) and analyzed at the Lawrence Livermore Center for Accelerator Mass Spectrometry (CAMS). Ages were calibrated by using both the University of Washington's radiocarbon calibration program CALIB 4.3 (Stuiver and others, 1998) and the University of Cologne's online radiocarbon calibration program CalPal (<http://www.calpal.de>) (table 1). A depth-age diagram (fig. 3) shows that dates from mollusks are generally older than those from wood or bulk sediment, particularly at the base of the core, owing to the hard-water carbonate reservoir effect. For five horizons where there are dates from both mollusks and wood or sediment, the maximum difference is 1,130 years and the average difference is 338 years. To determine depth-age relations, we used the regression shown in figure 3 for wood and sediment only. All ages are expressed in thousands of calendar years before present (cal. ka BP), where "present" is AD 1950 and ranges of ages are expressed in thousands of years (k.y.).

Table 1. Radiocarbon dates from Little Shingobee Lake core LSL-B.

[AMS, accelerator mass spectrometer; cmblf, centimeters below lake floor; cal. ka BP, thousands of calendar years before present; sed., sediment WW#, U.S. Geological Survey Radiocarbon Laboratory number; yr BP, years before present]

Depth (cmblf)	Material	Dated on	USGS Radiocarbon Lab Numbers (WW#)	Age AMS ¹⁴ C (yr BP)	Error (years)	CALIB Age (cal. ka BP)	CalPal Age (cal. ka BP)
419.5	wood	10/4/1998	1916	4655	60	5.42	5.40
658-661.5	wood	10/4/1998	1917	10810	95	12.89	12.91
810-812	cone	10/4/1998	1918	10175	80	11.82	11.83
840-842	wood	10/4/1998	1919	10300	140	12.25	12.11
845.5-846	wood	10/4/1998	1920	10305	70	12.24	12.17
871-872	wood	10/4/1998	1921	10510	120	12.47	12.40
915-917	wood	10/4/1998	1922	10820	100	12.90	12.81
420-422	bulk sed.	12/29/1998	2104	5400	50	6.25	6.20
659-661	bulk sed.	12/29/1998	2103	10710	50	12.85	12.90
915-917	bulk sed.	12/29/1998	2101	12840	50	15.48	15.37
810-812	bulk sed.	12/29/1998	2102	16180	100	19.30	19.30
840-842	bulk sed.	12/29/1998	2109	13000	40	15.63	15.85
120-122	bulk sed.	6/19/1999	2359	2915	55	3.08	3.07
170-172	bulk sed.	6/19/1999	2360	3170	55	3.38	3.40
230-232	bulk sed.	6/19/1999	2361	3395	55	3.64	3.65
380-382	bulk sed.	6/19/1999	2362	5605	85	6.37	6.41
430-432	bulk sed.	6/19/1999	2363	5505	95	6.29	6.30
542-544	bulk sed.	6/19/1999	2364	6555	70	7.43	7.47
602-604	bulk sed.	6/19/1999	2365	8125	70	9.03	9.10
619-621	bulk sed.	6/19/1999	2366	8440	70	9.47	9.44
770-772	bulk sed.	6/19/1999	2367	16230	110	19.36	19.40
409-411	mollusks	2/16/1999	2150	4970	40	5.68	5.70
840-842	mollusks	2/16/1999	2151	11350	50	13.25	13.24
870-872	mollusks	2/16/1999	2152	12250	40	14.21	14.32
120-122	mollusks	7/13/1999	2374	2410	50	2.36	2.37
173	mollusks	7/13/1999	2375	3270	50	3.47	3.51
380-382	mollusks	7/13/1999	2376	4940	40	5.66	5.67
427.5	mollusks	7/13/1999	2377	5660	50	6.42	6.45
542-544	mollusks	7/13/1999	2378	7000	50	7.81	7.84
602-604	mollusks	7/13/1999	2379	8930	50	10.15	10.06
619-621	mollusks	7/13/1999	2380	8730	50	9.70	9.72

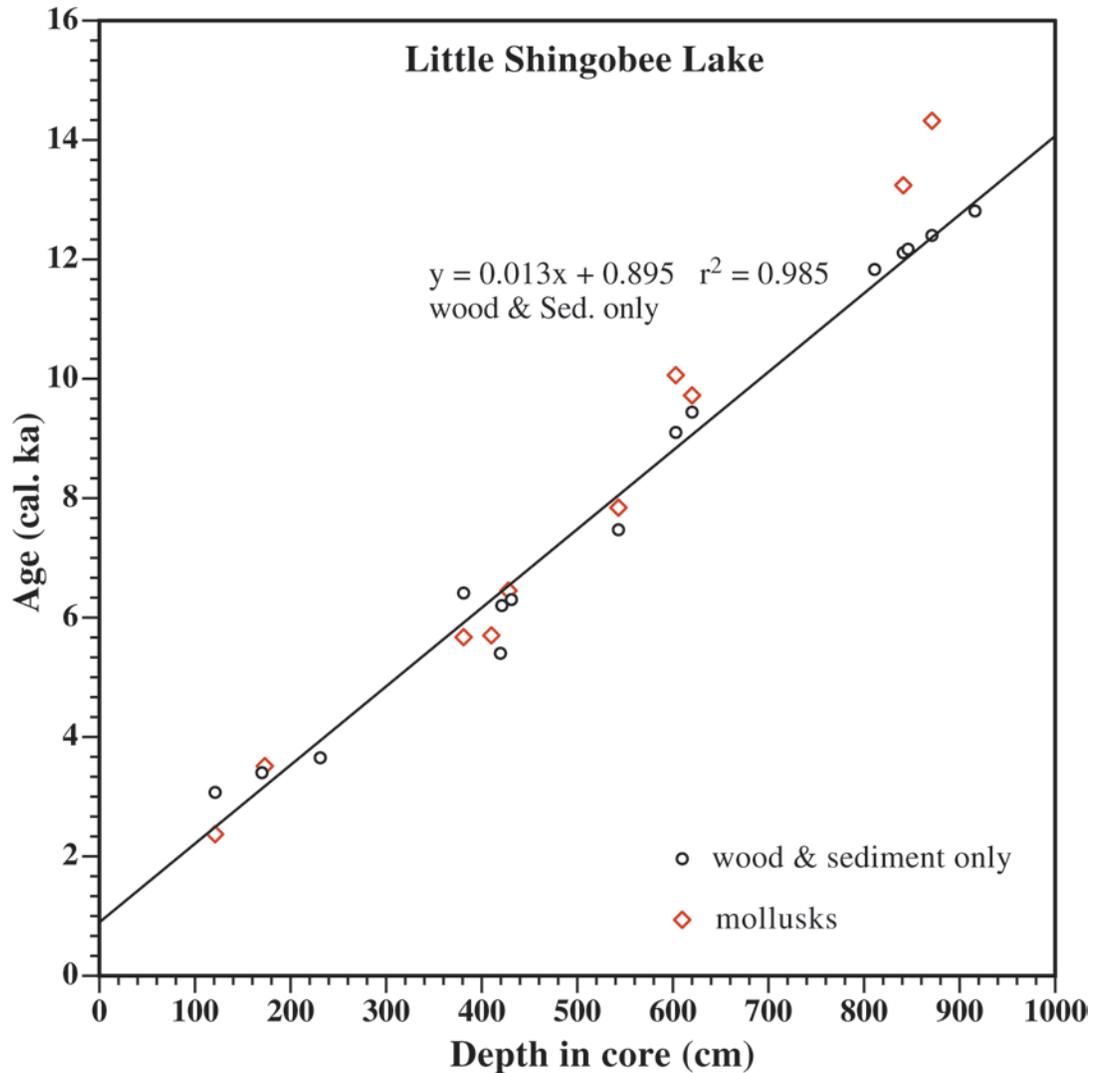


Figure 3. Age-depth model for Little Shingobee Lake core LSL-B from Little Shingobee Lake based on AMS radiocarbon dates.

Sediment Components

The dominant components in the sediments of Little Shingobee Lake are detrital clastic material (aluminosilicates), endogenic CaCO_3 , biogenic silica (biopal), and organic matter (fig. 4; appendix 1). A record of clastic influx into the lake was provided by measured concentrations of aluminum (Al) and titanium (Ti) (fig. 5) because their concentrations are largely unaffected by weathering and postdepositional alteration. The quartz content, determined by X-ray diffraction, provides another, independent measure of the detrital fraction (fig. 5). X-ray diffraction analyses of the high-detrital sections of the core show that they consist predominantly of quartz with minor dolomite, feldspar, and calcite, in that order of abundance (appendix 2). The percentage of dolomite in the high-detrital sections

is always higher than the percentages of feldspar and calcite, suggesting that the dolomite is detrital, derived from Paleozoic carbonate rocks in the drainage basin. Some of the calcite in these sections also may be detrital, but most is probably endogenic as in the low-detrital sections. A record of endogenic CaCO_3 is calculated from measured concentrations of IC and XRD calcite. A record of endogenic organic matter (OM) is provided by measured concentrations of OC. Biogenic silica calculated as opal (biopal) was calculated as the residual from the sum of all other components (fig. 4; appendix 1; discussed below).

Sediment Components in Little Shingobee Lake

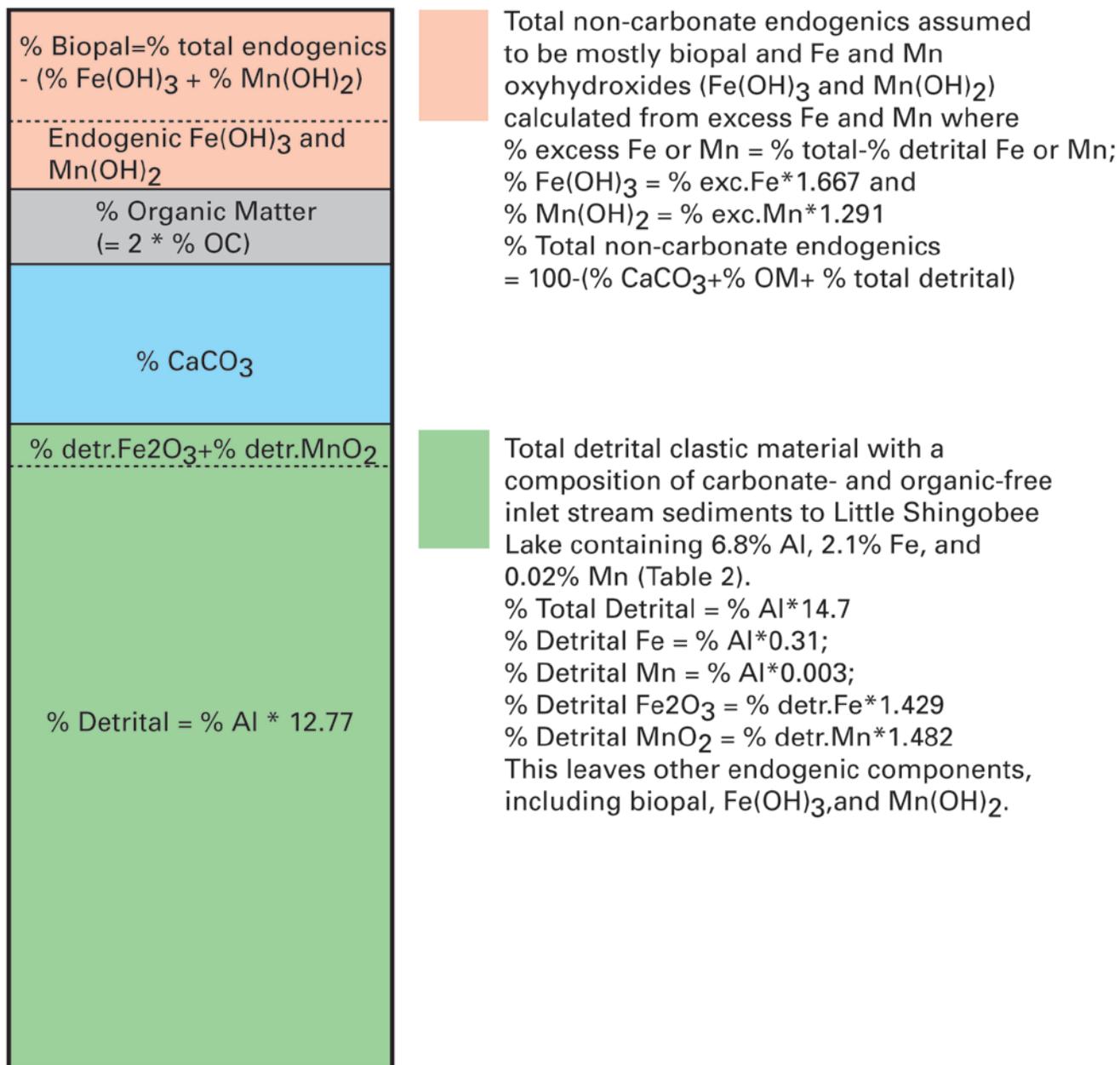


Figure 4. Sediment components in Little Shingobee Lake and Little Shingobee Fen.

Little Shingobee Lake

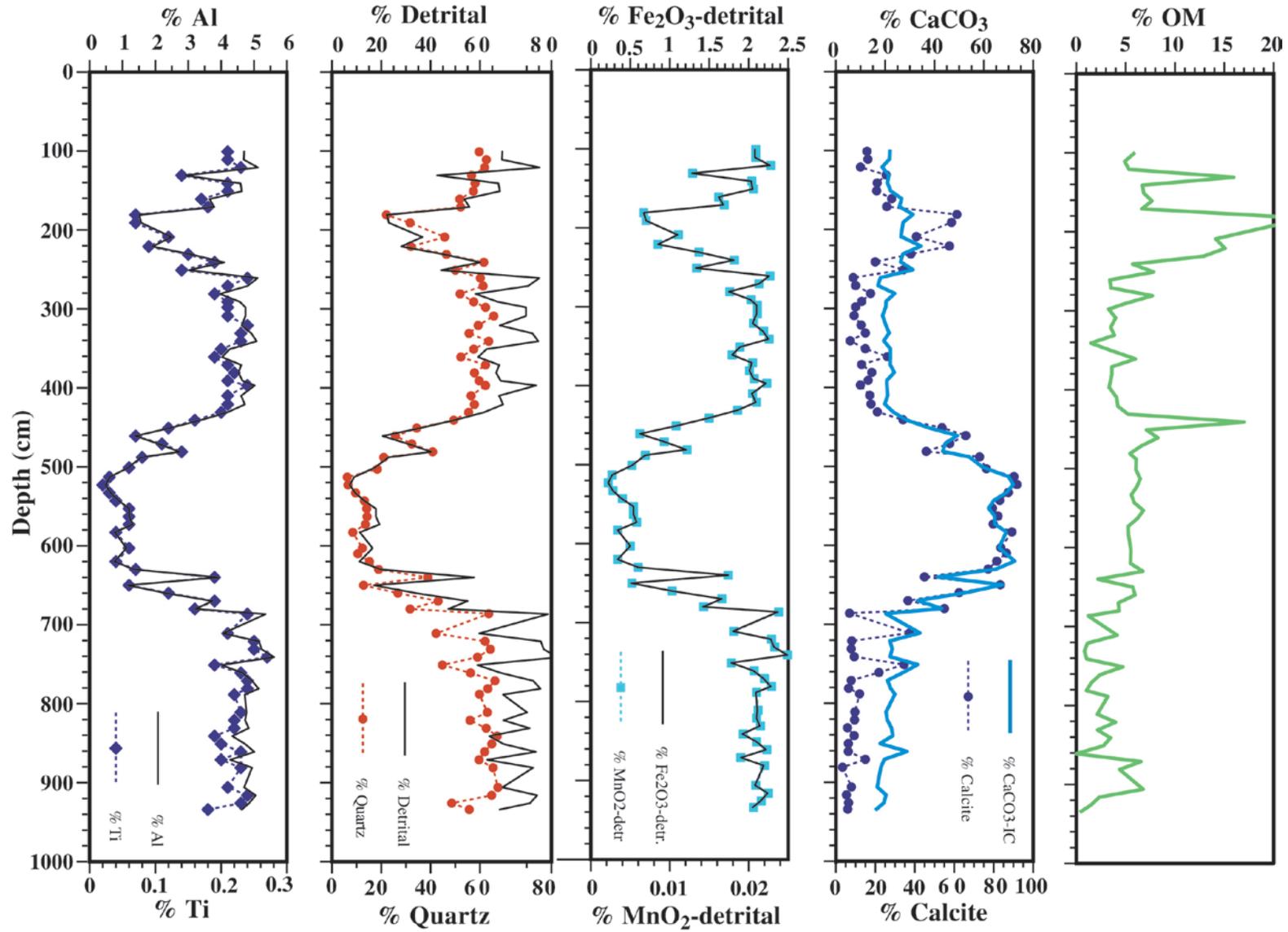


Figure 5. Major and minor components in sediments in core LSL-B from Little Shingobee Lake relative to depth in core.

The total detrital clastic fraction was calculated by assuming that the detrital rock debris in Little Shingobee Lake sediments has the same Al concentration as the carbonate- and organic-free sediment entering Little Shingobee Lake from the inlet at the south end of the lake (fig. 2) (6.8 percent Al). The calculated detrital fraction in core LSL-B varies considerably from 7 percent to 82 percent and closely parallels the concentration of detrital quartz measured by XRD (fig. 5). The CaCO₃ concentration, calculated from the measured IC concentration, also varies considerably from 10 percent to 70 percent and is generally antithetic to the detrital concentration (fig. 5). The CaCO₃ maxima between 660 and 420 centimeters (cm) depth (about 9–6.5 cal. ka) and 250 to 180 cm (about 4–3 cal. ka) are most likely due to dilution of clastic material with CaCO₃ rather than a decrease in the influx of detrital material. The OM content, equivalent to loss on ignition at 550°C, is twice the OC content, a relation that has been demonstrated for many Minnesota lakes (Dean, 1974) and, in particular, in cores from Shingobee and Williams Lakes (Dean and Schwab, 2002). The OM content in the core LSL-B varies from 5 percent to 25 percent (average, 6.6 percent) and, together with CaCO₃, serves to dilute the allogenic detrital fraction (fig. 5). The detrital Fe and Mn concentrations, expressed as weight percent Fe₂O₃ and MnO₂ (fig. 5), were calculated by assuming that the detrital fraction in Little Shingobee sediments has the same Fe/Al and Mn/Al ratios as carbonate- and organic-free inlet stream inlet sediments (0.31 and 0.003, respectively; fig. 4).

In the top 50 cm of the core LSL-B (100–150 cm) the sum of the major components of allogenic detrital clastic material, endogenic CaCO₃, and OM totals about 94 percent, leaving about 6 percent of other endogenic material (fig. 6). Detrital clastic material and CaCO₃ clearly dominate the sediments in Little Shingobee Lake. In most of the core, detrital material dominated (60–70 percent) but percent CaCO₃ had two distinct pulses, one during the early Holocene (700–450 cm; about 10–7 cal ka; fig. 6), and a second during the late Holocene (250–150 cm; about 4–3 cal. ka). The percentage of OM is relatively minor throughout most of the section except for a pulse of up to 10 percent coincident with the late Holocene pulse in CaCO₃ (fig. 6).

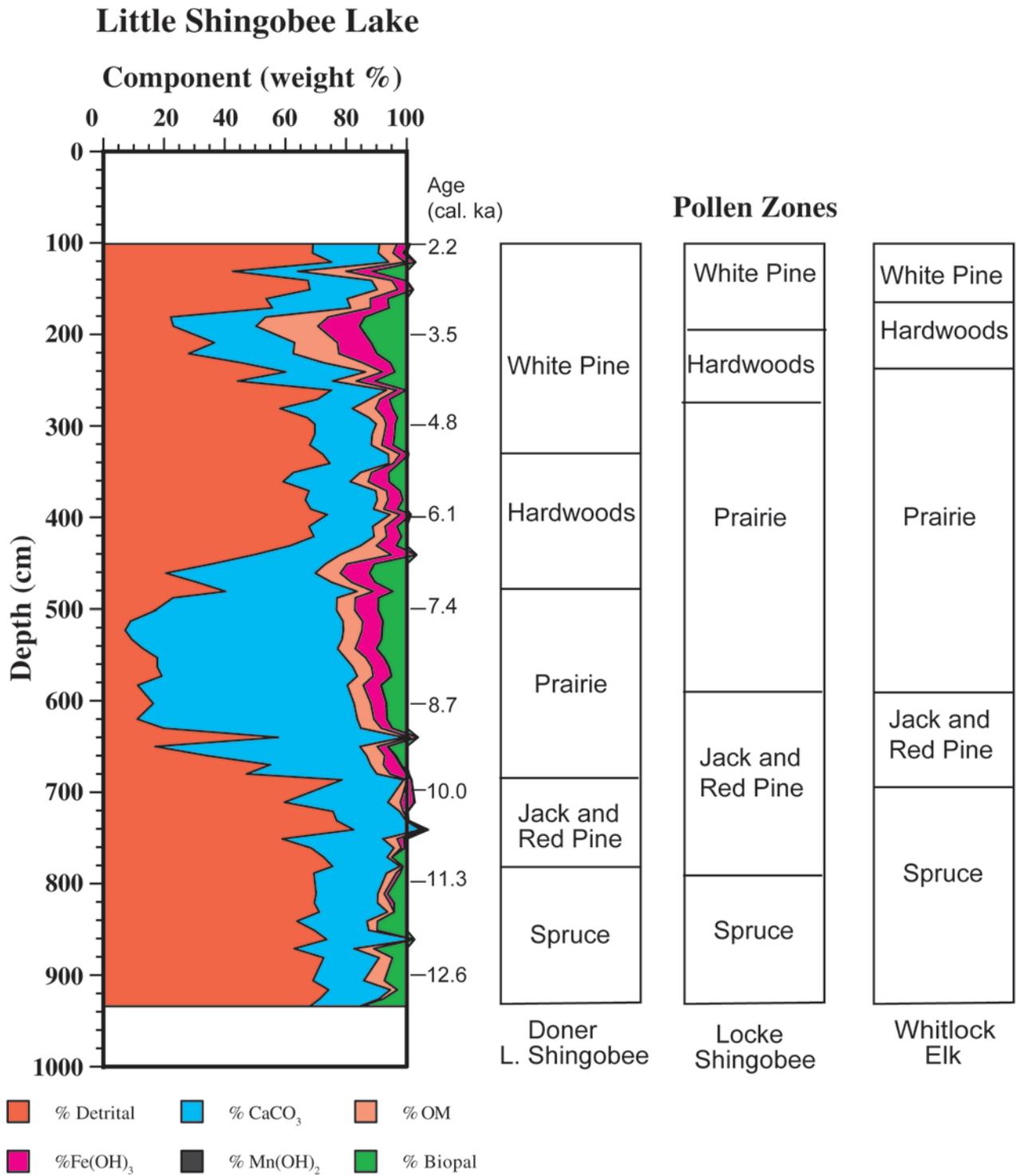


Figure 6. Percentages of allogenic (detrital) and endogenic components in sediments in core LSL-B from Little Shingobee Lake relative to depth in core. Ages of sediments from the age model in figure 3 are shown at the right of the diagram. Pollen zones are for cores from Little Shingobee Lake (Doner, this report), Shingobee Lake (Locke, 1995), and Elk Lake (Whitlock and others, 1993).

Because unusually high concentrations of endogenic Fe and Mn oxyhydroxides occur in the sediments of Shingobee Lake (Dean and Schwalb, 2002; Dean and others, 2003), they likely form a substantial part of the 6 percent of other endogenic components in Little Shingobee Lake. We define “excess” concentrations of Fe and Mn as the difference between the measured total Fe and Mn concentrations and the calculated detrital Fe and Mn concentrations (fig. 4). We then assume that the excess Fe and Mn are present as endogenic minerals, most likely as oxyhydroxides. The most oxidized species of Fe and Mn in natural waters are $\text{Fe}(\text{OH})_3$ and $\text{Mn}(\text{OH})_2$ (Wetzel, 2001), and we calculated excess Fe and Mn as these species for mass balance purposes. On the basis of these calculations, the average concentrations of excess Fe and Mn are as much as 2.6 and 10 times higher than can be explained by average contributions of Fe and Mn from detrital aluminosilicates and can be much higher (fig. 7). In fact, almost all of the Mn is endogenic (fig. 7). Endogenic $\text{Fe}(\text{OH})_3$ forms a larger percentage of the sediment than endogenic OM throughout most of the section (fig. 6). The section between 250 and 150 cm depth (about 4–3 cal. ka) is dominated by endogenic components CaCO_3 , $\text{Fe}(\text{OH})_3$, OM, and biopal (discussed below) (fig. 6).

Little Shingobee Lake

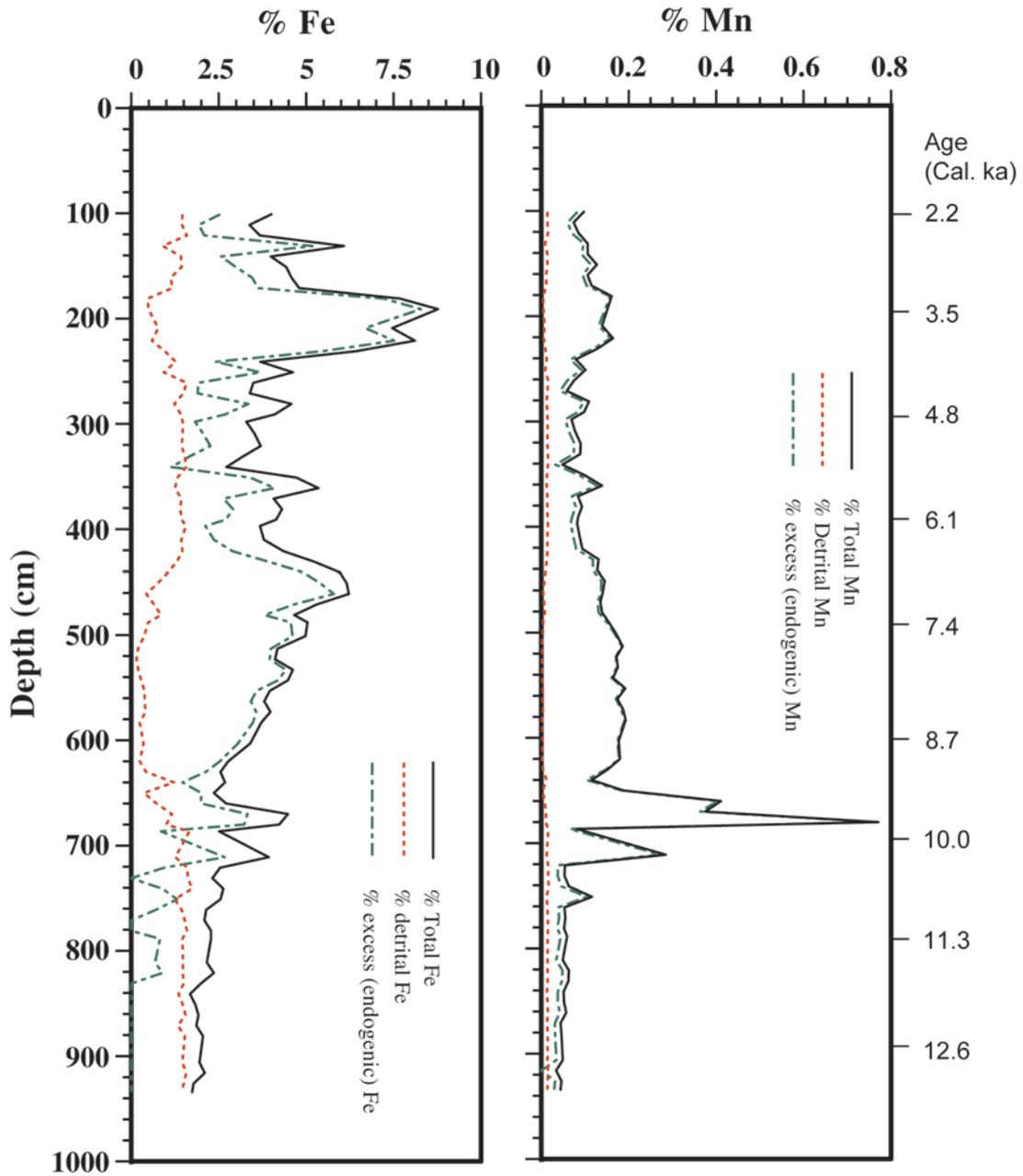


Figure 7. Percentages of total, detrital, and endogenic iron (Fe) and manganese (Mn) in sediments in core LSL-B from Little Shingobee Lake relative to depth in core. See text and figure 4 for methods of calculation of detrital and endogenic Fe and Mn. Ages of sediments from the age model in figure 3 are shown at the right of the Mn diagram.

Diatoms are a major component of the phytoplankton in both Williams and Shingobee Lakes (LaBaugh, 1997) and probably also in Little Shingobee Lake. Therefore, biogenic silica as opal (biopal) is likely a major part of the other endogenic material, but we do not have direct measurements of biopal. We calculated weight percent biopal as the difference between 100 percent and the sum of percentage detrital + percentage CaCO_3 + percentage OM + percentage $\text{Fe}(\text{OH})_3$ + percentage $\text{Mn}(\text{OH})_2$ (fig. 4). The average percentage of biopal is 5.1 percent but the total percentage is as high as 15.5 percent (fig. 6).

Stable Isotopes of Carbon and Oxygen

Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in *Pisidium* and ostracodes in Little Shingobee Lake show parallel trends but with considerable variation (fig. 8; appendix 3). Some of the variation in isotopic values in ostracodes is likely due to analysis of mixed adults and juveniles and mixed species. Values of $\delta^{18}\text{O}$ increase only slightly from -9 to -8 per mil between 900 and 800 cm depth (about 12–11 cal. ka) to around -7 per mil at 100 cm, but with a large negative excursion to less than -10 per mil in values in *Pisidium* between 100 and 150 cm. This negative excursion is defined by four data points and must be real, but because *Pisidium* and ostracodes are benthic, we see no reason for such a large excursion only in *Pisidium*. Values of $\delta^{13}\text{C}$ in ostracodes in pre-Holocene sediments (>700 cm) are -7 to -6 per mil before decreasing abruptly to -9.5 per mil at 650 cm. Values of $\delta^{13}\text{C}$ show a broad, well-defined, early Holocene peak in both ostracodes and *Pisidium*, increasing from around -9 per mil at 650 cm (about 9.5 cal. ka) to -8 between 600 and 400 cm (about 8.7 to 6.1 cal. ka). This ^{13}C peak is approximately coincident with that of percent CaCO_3 (fig. 5) but the ^{13}C peak begins and ends later, suggesting that carbonate saturation occurs before isotopic equilibrium of dissolved inorganic carbon (DIC) is achieved. Values of $\delta^{13}\text{C}$ in both ostracodes and *Pisidium* gradually decrease to about -9.5 per mil at 350 cm (about 5.5 cal. ka). The positive excursion in $\delta^{13}\text{C}$ in *Pisidium* is based on only one data point and may be analytical error.

Little Shingobee Lake

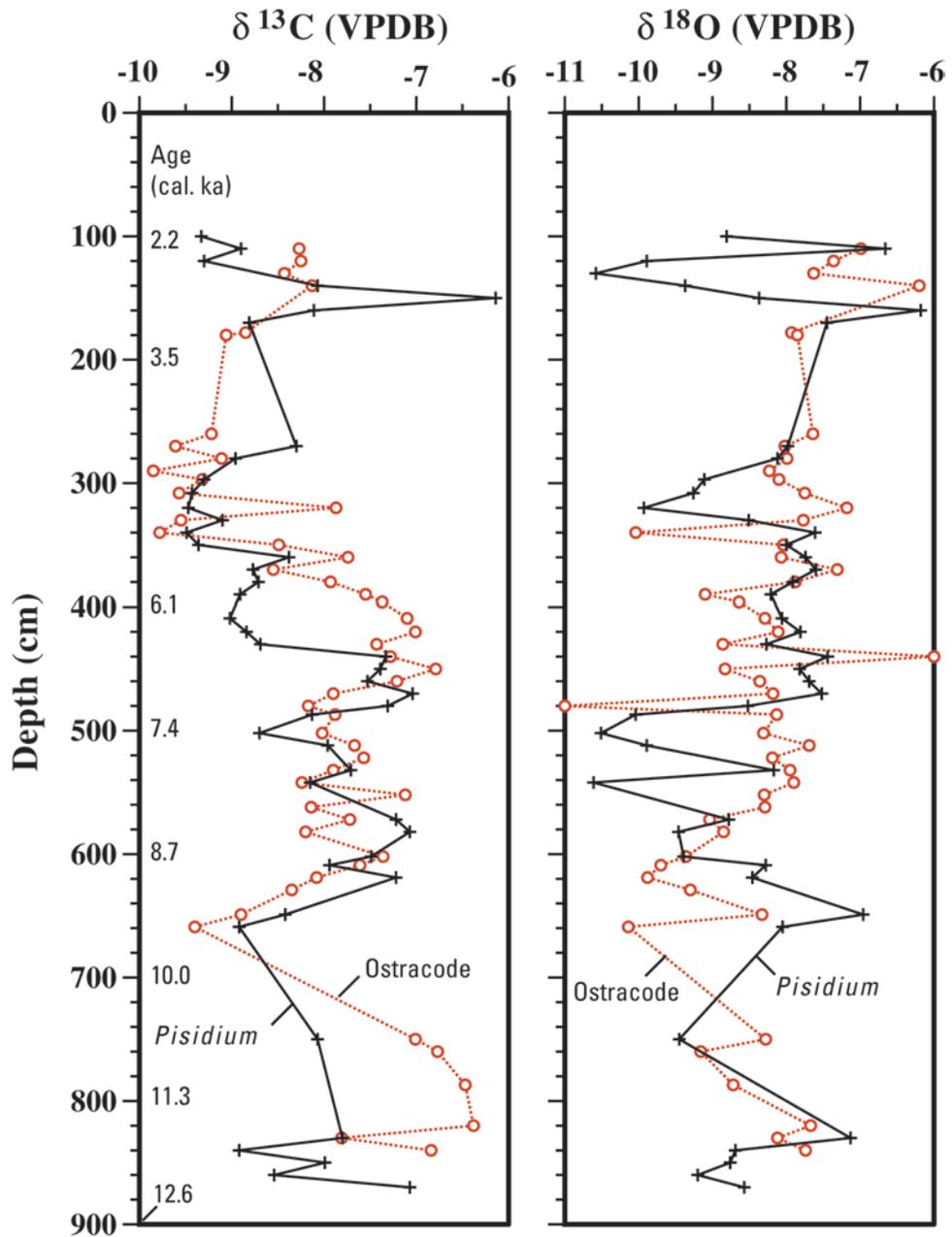


Figure 8. Stable isotope ratios of carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) in the carbonate shells of the fingernail clam, *Pisidium*, and ostracodes picked from sediments in core LSL-B from Little Shingobee Lake relative to depth in core.

Values of $\delta^{13}\text{C}$ in organic carbon in pre-Holocene sediments in Little Shingobee Lake (940–700 cm depth, about 13–10 cal. ka) vary considerably, ranging from –32 per mil to –25 per mil (fig. 9; appendix 4). However, in Holocene sediments (<700 cm) variations in values of $\delta^{13}\text{C}$ are much smaller (–30 per mil to –28 per mil), with a slight decrease of about 1.0 per mil upward in the section. The isotopic composition of OC does not correspond to any of the considerable variations in amount OC, especially in upper Holocene sediments (2 percent to >10 percent; fig. 9). In surface sediments in Minnesota lakes, those judged from plant pigments to be the most algal rich by Gorham and Sanger (1975) have values of $\delta^{13}\text{C}$ of –30 per mil to –31 per mil (Dean and Stuiver, 1993). Those judged by pigments to be most oxidized have values of $\delta^{13}\text{C}$ in the low –20s per mil. The most algal-rich surface sediments, and most ^{13}C depleted, are also the most hydrogen rich (lipid rich) as judged by Rock-Eval pyrolysis (Dean and Stuiver, 1993). On the basis of these criteria, the organic matter in Little Shingobee Holocene sediments with values of $\delta^{13}\text{C}$ of around –30 per mil should be algal. However, the increase in OC between 250 and 150 cm may be due to a greater influx of terrestrial organic matter, and the increase in $\delta^{13}\text{C}$ from –29 per mil to –27 per mil may reflect that origin.

Little Shingobee Lake

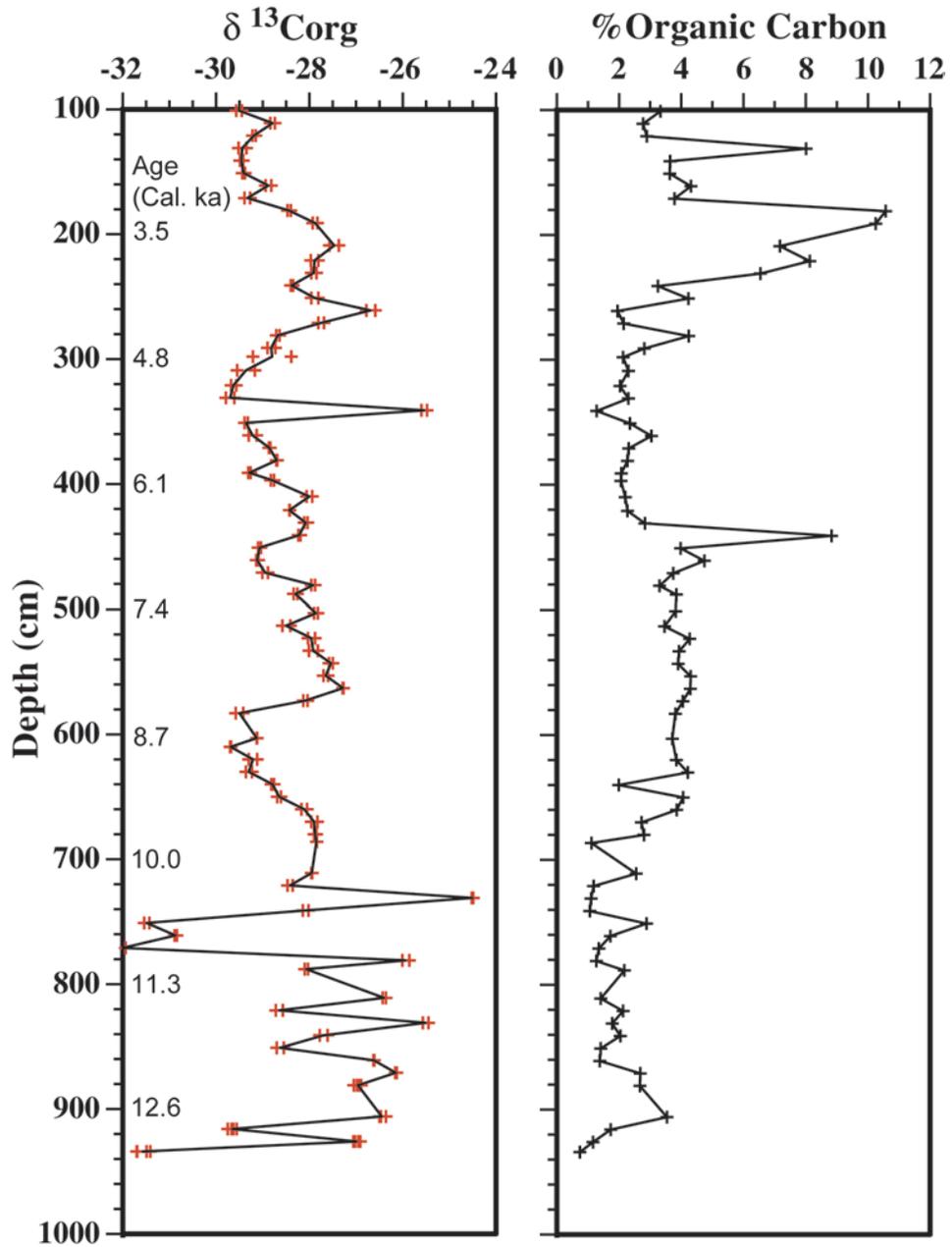


Figure 9. Stable isotope ratios of carbon ($\delta^{13}\text{C}$) in organic carbon and percent organic carbon in sediments in core LSL-B from Little Shingobee Lake relative to depth in core.

Pollen Zones

The basal sediments of late Pleistocene age (fig. 6; appendix 5) are dominated by spruce (*Picea*) and Cupressaceae (cypress). When the observed pollen types in core LSL-B are combined with those of Locke (1995) and Whitlock and others (1993), other abundant pollen types include *Larix* (larch), Gramineae (grass), Cyperaceae (sedge), and *Artemisia* (sagebrush).

The Jack/Red Pine zone of early Holocene age (fig. 6) is dominated by *Pinus banksiana* and *P. resinosa* (fig. 10). The boundary between the Pine and Prairie zones was dated at 7680 radiocarbon years (6560 calendar years (cal. yr)) in a piece of wood from the Williams Lake core. Dates on all other pollen-zone boundaries reported by Locke (1995) (fig. 6) for Williams and Shingobee Lakes are based on other pollen stratigraphies from northwestern Minnesota. Pollen zone boundaries for Elk Lake reported by Whitlock and others (1993) were dated by varve counts and radiocarbon dates.

Little Shingobee Lakes, core LSL-B, major pollen types.

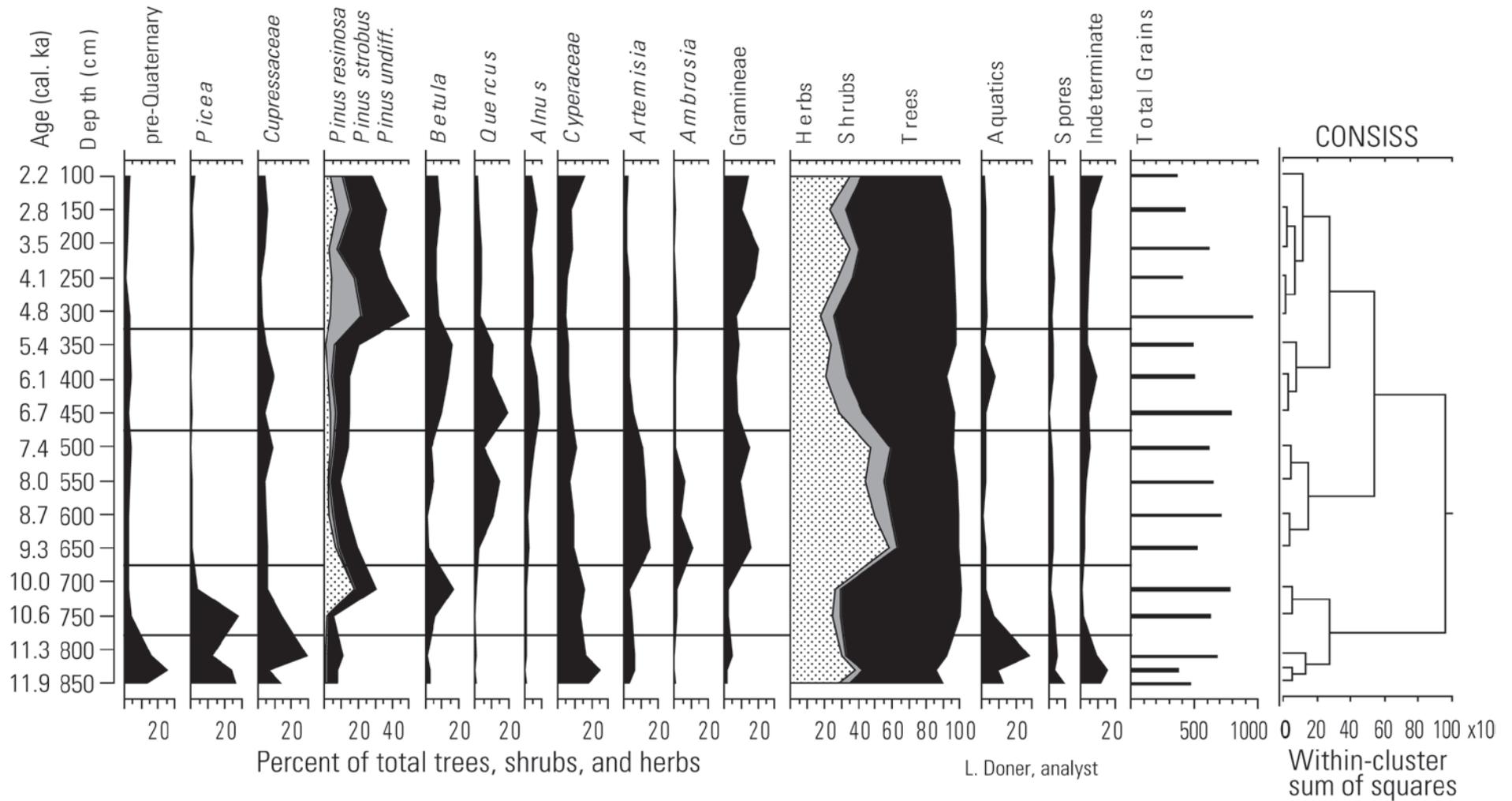


Figure 10. Pollen diagram for major pollen types in core LSL-B from Little Shingobee Lake relative to depth in core.

The Prairie zone pollen taxa are dominated by *Quercus* (oak), grass, and sagebrush (fig. 10). During this mid-Holocene period, the forest-prairie border in northwestern Minnesota migrated at least 100 km east of its present position, changing from pine forest to sagebrush-and-grass prairie and oak savanna (Whitlock and others, 1993). We use Wright's (1976) term "prairie period" for the mid-Holocene dry episode in northwestern Minnesota, marked simply by dry conditions with no necessary connotation of temperature (discussed later).

The return of the forest is marked by an increase in arboreal hardwood pollen taxa dominated by *Quercus* and *Betula* (birch) (fig. 10) but with important contributions from *Ostrya* (hornbeam) and pine. The hardwood forest was replaced by the return of a pine forest to northwestern Minnesota, this time dominated by white pine (*P. strobus*) but with substantial contributions from *P. banksiana* and *P. resinosa*.

Sediment Components in Little Shingobee Fen

The components in the sediments of Little Shingobee Fen (core LSF-10) can be calculated by using the same assumptions as for sediments in Little Shingobee Lake (fig. 4; appendix 6), again assuming that the detrital clastic fraction in the fen has the composition as the carbonate- and organic-free sediments entering the south end of the lake (fig. 2). The calculated total detrital fraction of sediments in core LSF-10 is considerably lower than in core LSL-B throughout most of the Holocene section of the core below the top 330 cm of peat and above 1,400 cm depth, averaging 4.4 percent (range, 1.3 percent to 31.0 percent) (fig. 11). CaCO₃ is by far the dominant component with an average of 61 percent. Between 1,400 and 330 cm, the next most abundant components are biopal (average, 16 percent) and OM (average, 13 percent) (fig. 12). Therefore, unlike the Holocene sediment section in core LSL-B with a dominant detrital component throughout most of its history, the sediment section in core LSF-10 was dominated by endogenic components (approximate ages to be determined below).

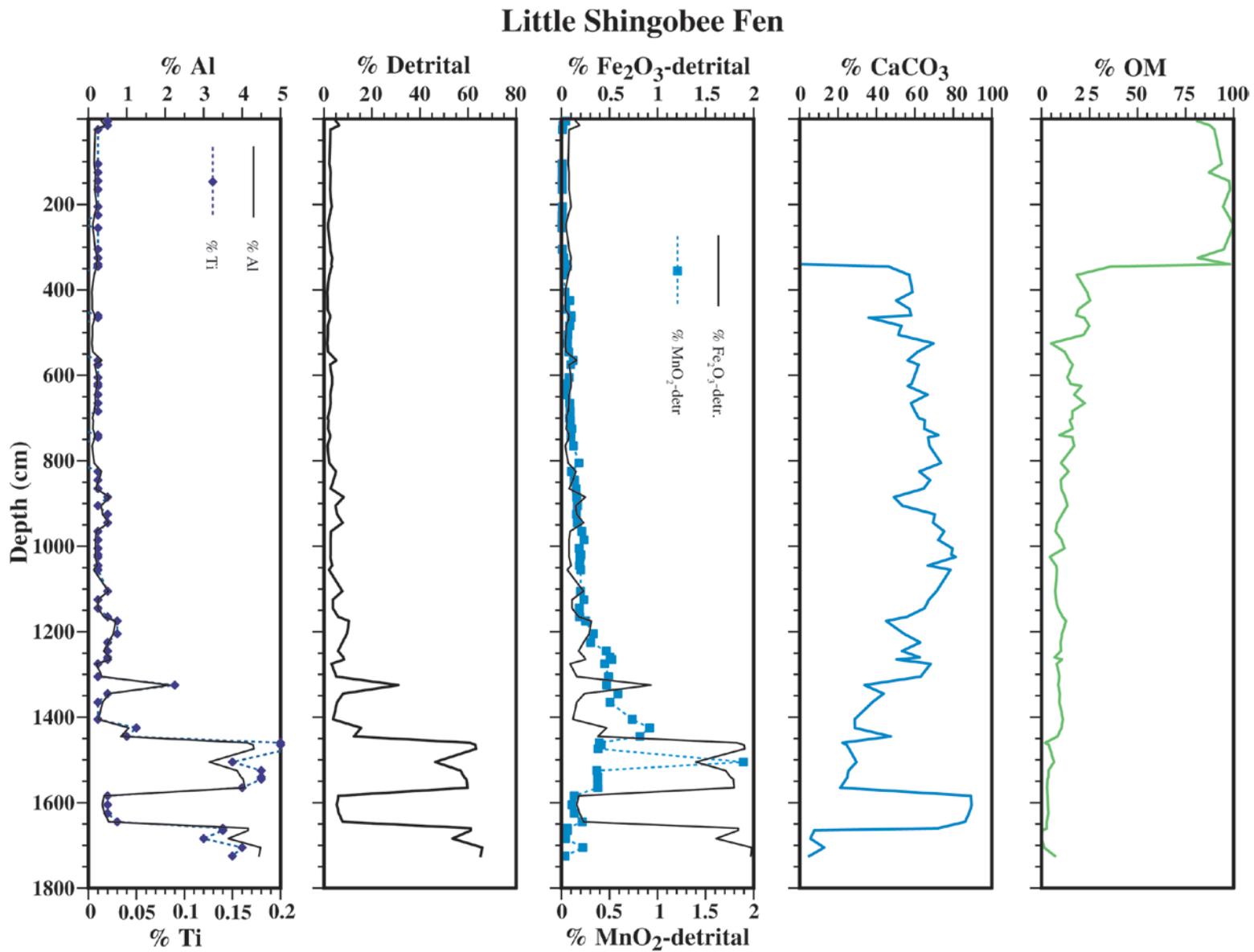


Figure 11. Major and minor components in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core.

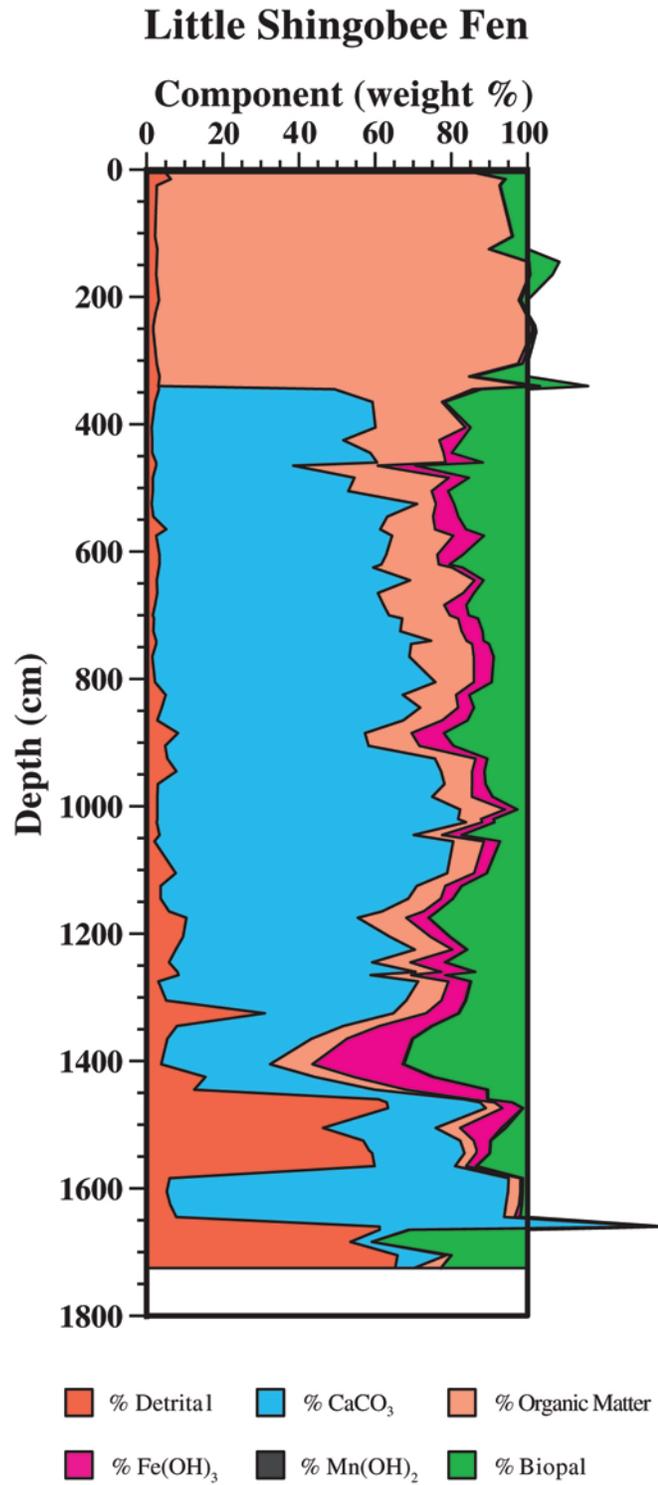


Figure 12. Percentages of allogenic (detrital) and endogenic components in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core.

Because the detrital fraction in core LSF-10 is so low, the contributions of detrital Fe and Mn are also low (expressed as Fe_2O_3 and MnO_2 ; fig. 11). However, as in core LSL-B, almost all of the Fe and Mn present in the sediments is endogenic (expressed as $\text{Fe}(\text{OH})_3$ and $\text{Mn}(\text{OH})_2$; fig. 13), even in the high-detrital clastic part of the section below 1,400 cm depth. On the basis of calculations of percentages of excess Fe and Mn (fig. 4), the average concentrations of excess Fe and Mn in core LSF-10 are 114 and 193 times higher than can be explained by contributions of Fe and Mn from average detrital aluminosilicates (fig. 13).

Little Shingobee Fen

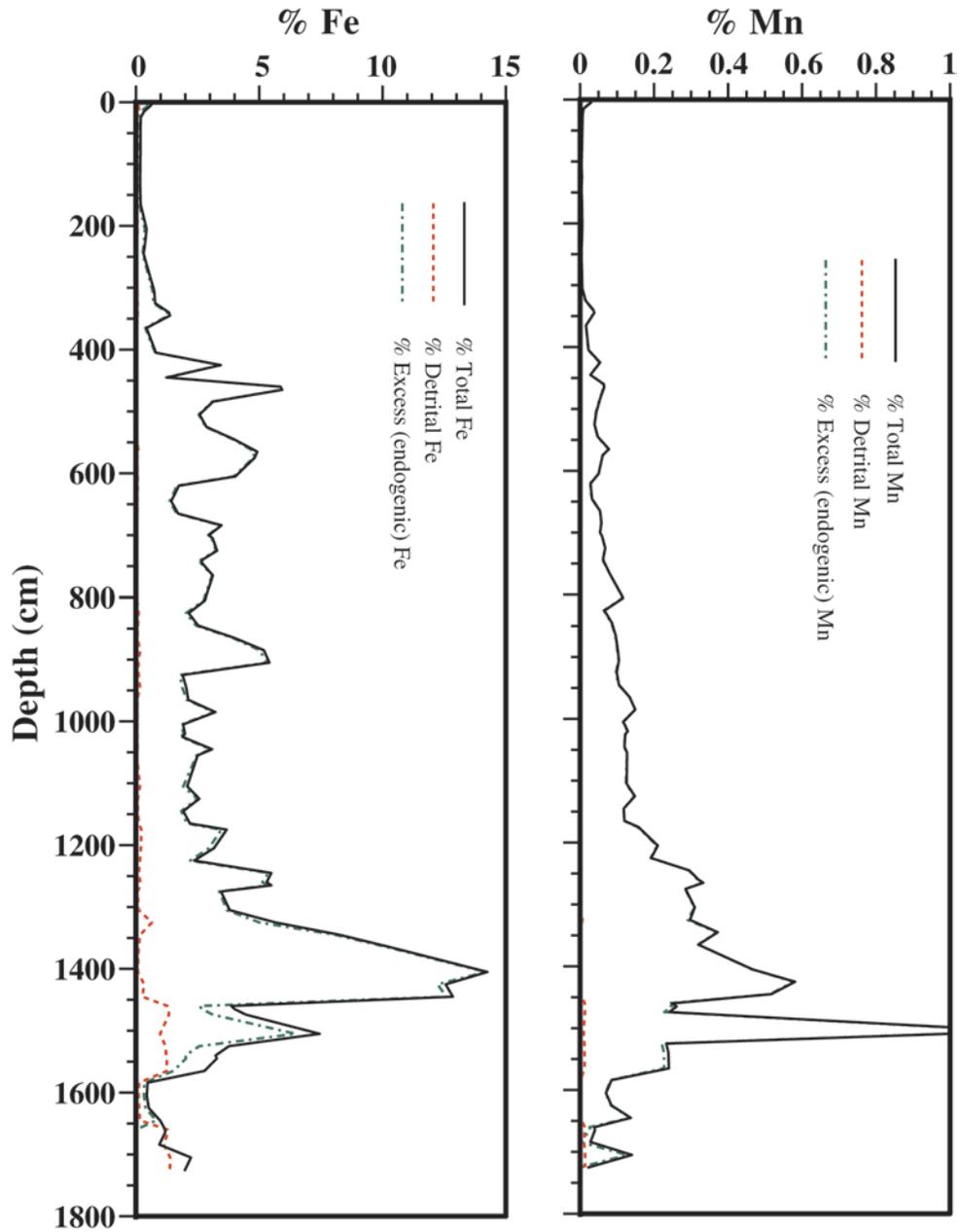


Figure 13. Percentages of total, detrital, and endogenic iron (Fe) and manganese (Mn) in sediments in core LSF-10 from Little Shingobee Fen relative to depth in core. See text and figure 4 for methods of calculation of detrital and endogenic Fe and Mn.

Discussion

Carbonate and Detrital Clastic Deposition

All present-day lakes and wetlands of the Shingobee River headwaters area were part of larger glacial Lake Willobee (fig. 1B). Once Lake Willobee drained, a sill separated Little Shingobee Lake and the lake that occupied the basin under the present-day fen. Little Shingobee Fen-lake filled with 11 m of mostly carbonate sediment (marl), culminating in 3.3 m of peat (fig. 12). The deepest part of the Little Shingobee Fen basin was 17 m, the thickness of the sediment in core LSF-10 (Carter and others, 1997). Wood from the sandy base of core LSF-9 (8 m) just east of LSF-10 was radiocarbon dated at 10345 years (about 12300 cal. yr; Carter and others, 1997), which may be the age of the base of LSF-9, or the wood could be old and redeposited. If the wood was not redeposited, and 12.3 cal. ka is a true date for the base of LSF-9, then that would also be the date of the sandy base of core LSF-10, which is in good agreement with our radiocarbon model for the base of core LSL-B (fig. 3). The bottom of the Little Shingobee Fen lake basin along transect C-C' (fig. 2) is mostly at about 6 m, and the bottom along transect B-B' is mostly at about 9 m (Carter and others, 1997).

Assuming that the base of core LSF-10 is indeed the same as the wood-dated base of core LSF-9 (12.3 cal. ka), and the top of the basal clastic layer in LSF-10 (about 1,450 cm depth, fig. 12) is the same age as the top of the basal clastic layer in LSL-B (about 10 cal. ka at 7 m, fig. 6), then the average Holocene sedimentation rate in LSF-10 is 1.5 mm yr^{-1} , which is considerably faster than in either LSL-B (0.7 mm yr^{-1}) or Shingobee Lake (0.9 mm yr^{-1} ; Schwalb and Dean, 2002). The basal detrital clastic layer in LSF-10 differs from that in LSL-B in that a 1-m-thick carbonate layer is sandwiched in the detrital layer in LSF-10 (fig. 12). That carbonate material (calcite and dolomite) may be detrital as is the minor CaCO_3 (~20 percent) in the basal detrital layer in LSL-B (fig. 5), derived from calcareous glacial drift in the drainage basin (Itasca Moraine; Moores and Norton, 1997). The basal detrital layer in LSL-B has a higher percentage of dolomite (average, 16 percent) than calcite (average, 10 percent), further evidence of Paleozoic carbonate-derived calcareous drift.

Once glacial Lake Willobee drained, the Holocene sediments in Little Shingobee Fen-lake and Shingobee Lake (Schwalb and Dean, 2002) remained at a similar composition, consisting mostly of 70–80 percent CaCO_3 , presumed to be mostly endogenic, with 330 cm of peat at the top of LSF-10 (fig. 12). The sediments in core LSL-B are different in that the Holocene marl is interrupted by a 2-m-thick detrital clastic layer (fig. 6), whereas detrital material in LSF-10 is very minor throughout the Holocene section (fig. 12). This difference may be because the sill between Little Shingobee Lake and Little Shingobee Fen-lake prevented detrital material from entering the fen-lake basin. Holocene sedimentation in Williams Lake was initially similar to that in the other three lakes, with 80 percent CaCO_3 in sediments above the detrital base (Dean and Schwalb, 2002). This early pulse of CaCO_3 deposition may have been the result of postglacial leaching of CaCO_3 from the calcareous Itasca moraine (Moores and Norton, 1993). Unlike the other three lakes, however, Williams Lake became progressively closed hydrologically. As productivity in Williams Lake increased, decomposition of produced organic matter caused the hypolimnion to become more acidic, dissolving CaCO_3 that was produced in the epilimnion (Dean and Schwalb, 2002). By about 5000 ^{14}C yr, the sedimentary organic carbon content in Williams Lake was greater than 10 percent (greater than 20 percent OM), and sedimentary CaCO_3 was completely dissolved in the water column and surface sediments, as it is today.

Endogenic Fe and Mn

As discussed above, the late Pleistocene influx of detrital material in Little Shingobee Lake (below 700 cm depth in core LSL-B; >10 cal. ka; figs. 5 and 6) is likely equivalent to the pulse of detrital material at the base of core LSF-10 (below 1,500 cm; figs. 11 and 12), with the difference that in LSF-10 there is a 1-m-thick CaCO₃ layer between 1,550 and 1,650 cm (fig. 11). Therefore, it is likely that the peak in endogenic Mn in core LSF-10 at 1,500 cm (fig. 13) is equivalent to the endogenic Mn in core LSL-B at 660 cm (about 9.5 cal. ka; fig. 7), with similar bulk-sediment Mn contents (about 0.8 percent). However, the endogenic Fe peak in core LSF-10 (up to 14 percent between 1,300 cm and 1,500 cm; fig. 12) is much higher than in LSL-B (about 5 percent; fig. 7) and occurs after the endogenic Mn peak. As discussed above, prior to 9.8 radiocarbon ka (9.3 cal. ka), all of the lakes in the Shingobee River headwaters were connected as part of a larger glacial Lake Willobee (fig. 1B; Schwab and Dean, 2002). At that time the sediments of Williams, Shingobee, and Little Shingobee Lakes, and what is now Little Shingobee Fen, all contained high concentrations of Fe and Mn (Dean and Schwab, 2002).

The base of the varved sediment section in Elk Lake (10–8 varve ka) (fig. 1A inset), also contained high concentrations of Fe (about 5 percent) and Mn (about 2 percent). Dean (1993) suggested that the high concentrations of Fe and Mn in lower Holocene sediments in Elk Lake were caused by leaching of Fe and Mn from glacial till in the drainage basin early in the lake's history. The most likely source of high concentrations of Fe and Mn that accumulate in the hypolimnion of Shingobee Lake today is not shallow groundwater but rather a deep till aquifer that overlies Cretaceous bedrock (Dean and others, 2003). Therefore, it seems likely that the source of Fe and Mn that precipitated as endogenic oxyhydroxide minerals that accumulated in the pre-Holocene sediments of Lake Willobee, represented by the sediments in Williams, Shingobee, and Little Shingobee Lakes and Little Shingobee Fen, was postglacial activation of that deep till aquifer.

In observations of individual annual laminations (varves) from Elk Lake, an orange ferric hydroxide (?) gel usually forms distinct seasonal (summer) laminations (Anderson, 1993). The orange ferric hydroxide laminae are usually underlain by thinner, black laminae, probably composed of manganese oxyhydroxide. The common appearance of a fairly thick seasonal lamina of ferric hydroxide gel in Elk Lake varves indicates that much of the precipitated endogenic iron hydroxide is incorporated into the reduced sediments and not remineralized; the same is true of manganese oxyhydroxides. Ferric hydroxide colloids tend to be fairly stable (Tipping and others, 1981; Davison and Seed, 1983; Stauffer and Armstrong, 1986) which may explain why they survive in reducing hypolimnion and sediment pore waters. As in Elk Lake, the high concentrations of endogenic Fe and Mn in the sediments of the SHAEP lakes probably form at fall overturn when high concentrations of dissolved Fe and Mn that accumulate in the anoxic hypolimnion during summer stratification mix with oxygenated epilimnetic waters (Megard and others, 1993; Dean and others, 2003).

Stable Isotopes

Once glacial Lake Willobee drained, the carbon and oxygen isotope composition of endogenic and ostracode-shell carbonate should be similar in lower Holocene sediments in all of the residual lakes on the floor of glacial Lake Willobee, at least initially. Apparently they were not (fig. 14). These differences are due mainly to vital and environmental effects. Benthic ostracodes reflect the isotopic composition of bottom waters. During summer stratification, hypolimnion $\delta^{18}\text{O}$ in Shingobee Lake is about 1.5 per mil lower than the epilimnion $\delta^{18}\text{O}$ (Kendall and others 1997), and the hypolimnion $\delta^{13}\text{C}$ is about 3 per mil lower than the epilimnion DIC (R.G. Striegl, USGS, written commun., 2008). Culture experiments and studies of living ostracodes and modern lake waters have shown that some ostracode

species calcify out of isotopic equilibrium with the water (Xia and others, 1997a; von Grafenstein and others, 1999). Also, if ostracodes molt throughout a wide range of temperatures (in different seasons), the isotopic signature reflects an integrated seasonal signal (Xia and others, 1997b). Oxygen-isotope values may display positive offsets from equilibrium of about 2 per mil.

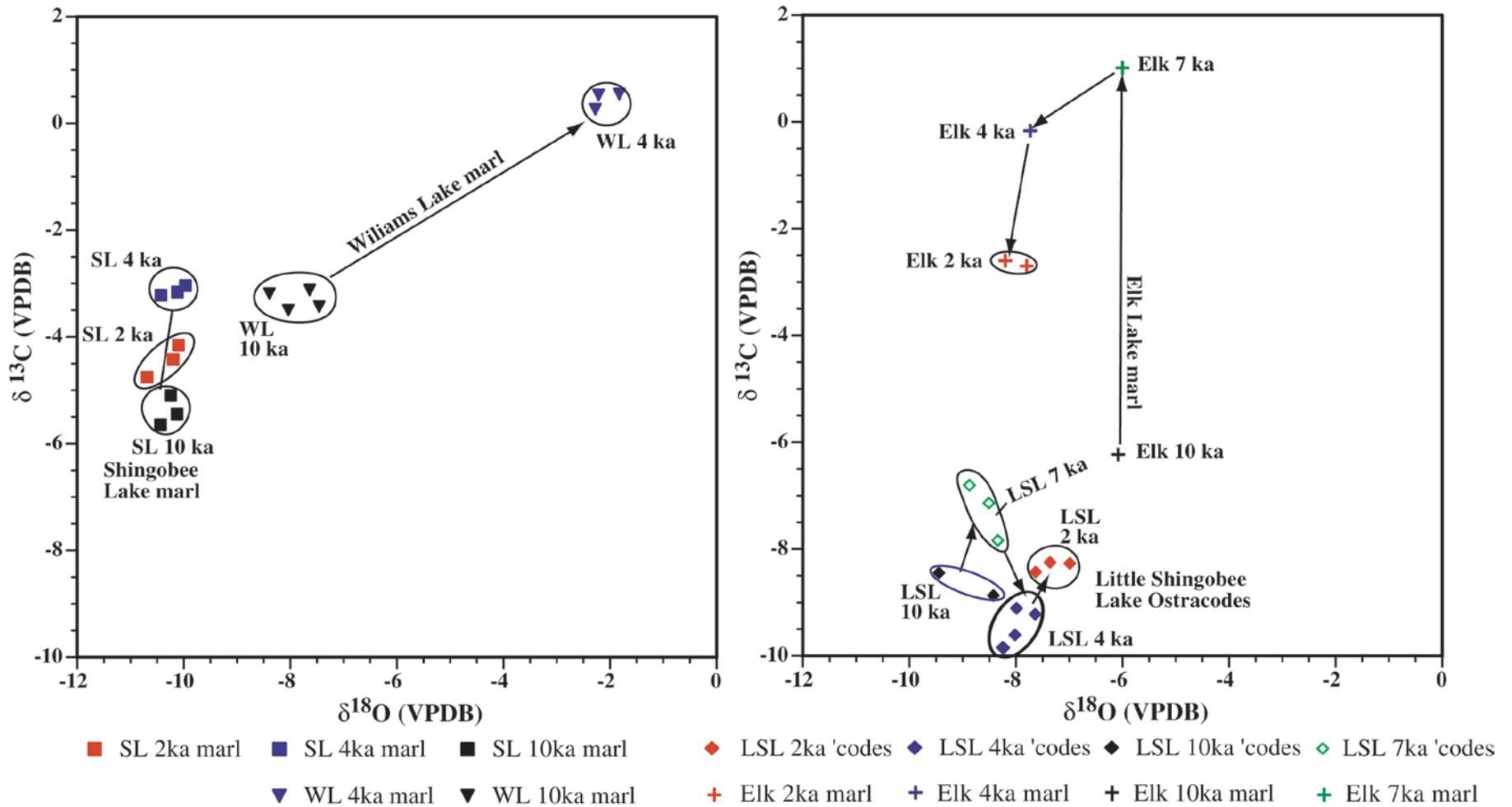


Figure 14. Cross plots of values of $\delta^{18}\text{O}$ compared with $\delta^{13}\text{C}$ in endogenic carbonate (marl) from Elk, Williams, and Shingobee Lakes, and in ostracodes from Little Shingobee Lake for three time slices: 10 cal ka, 4 cal ka, and 2 cal ka. A fourth time slice (7 cal. ka) is added for Elk and Little Shingobee Lakes for which there is better time control.

Ostracodes that grew in both Shingobee and Williams Lakes at the beginning of the Holocene have lower values of $\delta^{13}\text{C}$ and higher values of $\delta^{18}\text{O}$ than the marl (carbonate in bulk sediment) in which they occur (Schwalb and Dean, 2002), reflecting that positive equilibrium. Schwalb and Dean (2002) also found that all Holocene sediments in Shingobee Lake had values of $\delta^{18}\text{O}$ in marl that were between 3 per mil and 6 per mil lower than values in ostracodes, and in Williams Lake, marl values were 4 per mil to 9 per mil lower than in ostracodes. In fact, values of $\delta^{18}\text{O}$ in Shingobee Lake marl changed very little throughout the Holocene section (about -10 per mil; fig. 14). Values of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in ostracodes in Williams and Shingobee Lakes are much more variable than the marl values because several ostracodes species had to be used, and juvenile ostracodes were analyzed at levels where adults were not present (Schwalb and Dean, 2002). Also, if ostracodes molt throughout a wide range of temperatures (in different seasons), the isotopic signature reflects an integrated seasonal signal (Xia and others, 1997b). Ostracodes are present throughout the entire section in Shingobee Lake, but in Williams Lake ostracodes are present only in lower Holocene sediments, whereas bulk-sediment CaCO_3 persisted until about 4 radiocarbon ka (4.5 cal. ka). For this study, only picked ostracodes and *Pisidium* were analyzed, and no attempt was made to separate ostracode species for analysis. On the basis of all of these considerations, the isotopic values for Little Shingobee marl deposited at 10 cal. ka (not measured) should have lower values of $\delta^{18}\text{O}$ and higher values of $\delta^{13}\text{C}$ than the ostracodes.

The most obvious changes in postglacial Lake Willobee isotopic compositions are the marked increases in values of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in Williams Lake marl between 10 cal. ka and 4 cal. ka (fig. 14). This increase reflects the evolution of Williams Lake to a closed-basin lake. Today, a diagram of $\delta^{18}\text{O}$ and δD of rain water in the Shingobee River headwaters area defines a local meteoric water line (LMWL) that is almost identical to the global meteoric water line (GMWL) (Kendall and others, 1997). Most river, lake, and groundwater samples, on the other hand, have values of $\delta^{18}\text{O}$ that are higher than the LMWL; those higher values indicate a strong evaporation signal with Williams Lake, which has the highest values of $\delta^{18}\text{O}$. Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measured in samples collected during late summer on a transect along the Shingobee River and through Little Shingobee and Shingobee Lakes increase downstream along the Shingobee River transect from -11 per mil to -7 per mil for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, indicating an evaporation trend and longer residence time downstream (Kendall and others, 1997). Williams Lake, on the other hand, had values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ that are enriched in ^{13}C and ^{18}O by about 5 per mil and 6 per mil, respectively, relative to the most ^{13}C - and ^{18}O -enriched samples from Little Shingobee and Shingobee Lakes.

The remarkably constant oxygen-isotope composition throughout the Holocene in Shingobee Lake marl (Dean and Schwalb, 2002; Schwalb and Dean, 2002; fig. 14) and Little Shingobee Lake ostracodes (figs. 8 and 14) suggests that environmental conditions affecting values of $\delta^{18}\text{O}$ (temperature, salinity, composition of the water) did not change greatly. The oxygen-isotope composition of Williams Lake marl did change markedly as the lake evolved from an open to a closed basin (fig. 14).

In Shingobee Lake marl, there is a considerable increase in values of $\delta^{13}\text{C}$ during the prairie period between 10 cal. ka and 4 cal. ka (about 4 per mil), then about a 2 per mil decrease between 4 cal. ka and 2 cal. ka (fig. 14). The mid-Holocene increase in values of $\delta^{13}\text{C}$ (about 3 per mil) in Shingobee Lake is fairly broad and extends from about 7 radiocarbon ka (about 7.8 cal. ka) to 3.5 radiocarbon ka (about 3.8 cal ka) (Schwalb and Dean, 2002). The mid-Holocene increase in values of $\delta^{13}\text{C}$ (about 2 per mil) in ostracodes in Little Shingobee Lake is also broad, increasing from about -9 per mil to -7 per mil, extending from about 9.5 cal. ka to about 5 cal. ka with a maximum of -7 per mil at about 7 cal. ka (figs. 8 and 14). By 4 cal. ka values of $\delta^{13}\text{C}$ are back down to where they were at 9.5 ka (about -9 to -10 per mil; figs. 8 and 14). The marl in the varved sediments of Elk Lake also has a mid-Holocene

maximum in values of $\delta^{13}\text{C}$ that is even pronounced, going from -6 per mil at 10 cal. ka to $+1$ per mil at 7 cal. ka (fig. 14). Values of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are generally higher in marl from Elk Lake than in marl from Shingobee Lake due to the longer residence time of this 30-m-deep lake.

The most commonly cited model for enrichment of surface waters by ^{13}C is increased productivity with removal of ^{13}C -depleted OC leaving reservoirs of ^{13}C -enriched surface-water DIC and CO_2 (Hollander and McKenzie, 1991; McKenzie and Hollander, 1993; Bernasconi and others, 1997; Hollander and Smith, 2001; Meyers and Teranes, 2001; Myrbo and Shapley, 2006). Today values of $\delta^{13}\text{C}$ in surface waters of Shingobee and Little Shingobee Lakes are -11 to -12 per mil (R.G. Striegl, USGS, written commun., 2008). Values for waters in Williams Lake are much higher, about -4 per mil for $\delta^{13}\text{C}$ (R.G. Striegl, USGS, written commun., 2008). During the spring and summer (April to September), values of $\delta^{13}\text{C}$ in DIC in the epilimnion increase by 1.40 per mil in Williams Lake and 1.24 per mil in Shingobee Lake because of photosynthetic uptake of lake CO_2 that is enriched in ^{12}C (Striegl and Michmerhuizen, 1998; Striegl and others, 2001). By late August of 1997, values of $\delta^{13}\text{C}$ in CO_2 in the epilimnion of Williams Lake were -10 per mil and those in the hypolimnion were -12 per mil; epilimnion values in the more productive Shingobee Lake were -15 per mil and hypolimnion values were -19 per mil; epilimnion values in Little Shingobee Lake were -17 per mil and hypolimnion values were -20 per mil (R.G. Striegl, USGS, written commun., 2008). Resulting values of $\delta^{13}\text{C}$ in DIC in the epilimnion and hypolimnion of these three lakes were -3 per mil and -5 per mil for Williams, -8 per mil and -12 per mil for Shingobee, and -10 and -13 for Little Shingobee. Clearly the productivity model was working in these three lakes, resulting in the transfer of ^{13}C -depleted organic (CO_2) and inorganic (DIC) carbon from the epilimnion to the hypolimnion, leaving ^{13}C -enriched carbon in the organic and inorganic reservoirs in the epilimnion. The increase in values of $\delta^{13}\text{C}$ in marl in both Williams and Shingobee Lakes in mid-Holocene sediments (fig. 14; Schwalb and Dean, 2002) suggests that at least some of this increase in values of $\delta^{13}\text{C}$ in the DIC reservoirs is due to the productivity model. Dean and Stuiver (1993) attributed the sharp increase in values of $\delta^{13}\text{C}$ in OC in the varved sediments of Elk Lake during the prairie period to an increase in production of more hydrogen-rich, algal organic matter.

Dean and Schwalb (2002) suggested that some of the mid-Holocene $\delta^{13}\text{C}$ -enrichment in marl and OC in sediments of Williams and Shingobee might be due to the change in the drainage basin from the C_3 -plant-dominated pine forest to C_4 -plant-dominated prairie grasses having values of $\delta^{13}\text{C}$ that average about -27 and -12 per mil, respectively, a result of their different photosynthetic pathways (O'Leary, 1988; Cerling and Quade, 1993; Meyers and Teranes, 2001). The mid-Holocene increase in $\delta^{13}\text{C}$ of OC in Shingobee Lake marl is about 4 per mil, but in Williams Lake marl the increase is about 10 per mil. Dean and Schwalb (2002) thought that the difference (6 per mil) was due to hydrology; the other 4 per mil may represent vegetation change in the drainage basin during the early Holocene. The fact that values of $\delta^{13}\text{C}$ in OC in Shingobee Lake decreased to early Holocene levels following reforestation during the late Holocene suggests that vegetation change in the drainage basin and not productivity was the main cause of the increase in $\delta^{13}\text{C}$ in OC in Shingobee Lake in the mid-Holocene, and probably some of the increase of 10 per mil in Williams Lake.

Values of $\delta^{13}\text{C}$ in marl also increased in mid-Holocene sediments in Williams and Shingobee Lakes indicating that the entire surface-water carbon reservoir was enriched in ^{13}C . Values of $\delta^{13}\text{C}$ in the shells of *Pisidium* and ostracodes in Little Shingobee Lake increase in the mid-Holocene section from about -9 per mil at 660 cm depth to -7 per mil at 600 cm (about 9 cal ka) and remain high at -7 per mil to -8 per mil until 440 cm (about 6.5 cal ka) (fig. 8). However, unlike in the sediments of Williams, Shingobee, and Elk Lakes, values of $\delta^{13}\text{C}$ in OC in Little Shingobee sediments did not

increase in the mid-Holocene (fig. 9). Values remain between -28 per mil and -30 per mil throughout the entire Holocene section. Values of percent OC in Little Shingobee Lake sediments increased from about 1 percent to 4 percent during the mid-Holocene, suggesting that productivity had increased, but a lack of an increase in $\delta^{13}\text{C}$ in OC suggests that productivity did not increase.

The sharp increases in $\delta^{13}\text{C}$ of marl (fig. 14) and OC (Dean and Schwab, 2002) in mid-Holocene sediments in Williams Lake, relative to the more modest increases in marl and OC in Shingobee Lake sediments, indicate that the hydrologic closing of Williams Lake had a major role in the carbon-isotope signatures in the sediments. As mentioned earlier, values of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the Shingobee River transect of Kendall and others (1997) in the dry late summer increased from -11 per mil to -7 per mil, indicating an evaporation trend. Kendall and others concluded that the increase in $\delta^{13}\text{C}$ along the transect reflects hydrologic processes (residence time) and not biological recycling (productivity). Therefore, the mid-Holocene increase in $\delta^{13}\text{C}$ in carbonate shells but not in OC in Little Shingobee Lake sediments is likely due to longer residence time during the dry prairie period and not due to productivity. Some of the larger mid-Holocene increases in values of $\delta^{13}\text{C}$ in sediments of Shingobee and Elk Lakes are probably also due to hydrology although some of the increases are due to productivity, as suggested by the mid-Holocene increase in $\delta^{13}\text{C}$ in OC in both lakes. Some of the mid-Holocene increases in values of $\delta^{13}\text{C}$ are undoubtedly due to changes from forest to prairie. At this time we do not have the data to measure the influence of these three factors (productivity, vegetation change, and hydrology) on the isotopic composition of DIC and OC in these lakes, although hydrology was obviously a dominant factor in Williams Lake. All three could explain the mid-Holocene increases in $\delta^{13}\text{C}$ in Williams and Shingobee Lakes.

Pollen Zones

We compare the timing of pollen zones in Little Shingobee Lake with those in Shingobee Lake (Locke, 1995), and Elk Lake (Whitlock and others, 1993) in figure 6. The main tie point in the chronology of Shingobee Lake is a radiocarbon date of a piece of wood of about 7,700 years ago at the horizon of the forest/prairie border. The other pollen zones are extrapolated from dated zone boundaries in other lakes in northwestern Minnesota, including Elk Lake. We have calibrated those radiocarbon ages reported by Locke by using the online radiocarbon calibration program CalPal. The varve timescale in Elk Lake has been well correlated with the radiocarbon timescale (Anderson and others, 1993; Sprowl, 1993; review by Dean and others, 2002a). For the pollen-zone boundaries in Little Shingobee we tried to use the same criteria used by Whitlock and others (1993) for Elk Lake on our limited sampling. We would like to see a better correspondence for the prairie period but it is not evident in the pollen diagram (fig. 10). The beginning of the prairie period is defined by a decrease in *Pinus* and increases in *Quercus*, *Artemisia*, and Gramineae (fig. 10). The end of the prairie period is defined by a decrease in *Artemisia* and an increase in *Betula*. We are encouraged that the pollen zones in Little Shingobee Lake match changes in lithology. Most notable of these changes is the marked increase in CaCO_3 between 700 cm and 400 cm depth (10 cal. ka and 6 cal. ka (fig. 6). In the white pine zone there are marked increases in endogenic CaCO_3 , OM, $\text{Fe}(\text{OH})_3$, and biopal (fig. 6) that correspond with the warm Prairie Period as defined in core LSL-B. This increase is probably in response to a slight increase in temperature at the beginning of the white pine zone (see discussion below).

The reconstructed climate of northwestern Minnesota in the Spruce zone was cold and relatively dry (Whitlock and others, 1993). Numerical modeling of the Elk Lake pollen data by Bartlein and Whitlock (1993) suggests that the temperature in northwestern Minnesota was about 5°C lower in January than at present and 2.5° lower in July. Precipitation was about 200 mm less annually than today.

The Jack/Red Pine zone of early Holocene age was slightly drier and warmer than the Spruce zone, with closest modern analogs in northern Wisconsin (Whitlock and others, 1993). Reconstruction of annual precipitation by comparing the Elk Lake data with modern pollen data shows that the early-middle Holocene transition (8.5 to 7.8 cal. ka) is marked by an abrupt decrease in precipitation of about 200 millimeters per year (mm yr^{-1}) (Bartlein and Whitlock, 1993). *Artemisia* is the most distinctive vegetation of prairie environments west of the Shingobee River headwaters area. An expansion of sagebrush pollen in abundance at about 10 cal. ka in Little Shingobee Lake (about 8.7 varve years in Elk Lake) marks the initial expansion of the prairie eastward. Reviewing all of the evidence from Elk Lake, including pollen, diatoms, ostracodes, geochemistry, mineralogy, and varve thickness, Bradbury and others (1993) and Dean and others (2002a) concluded that between about 8.6 and 8.0 cal. ka (on the basis of varve counts), Elk Lake went from a well-stratified lake in a pine forest that protected the lake from wind mixing, to a well-mixed lake in dry, open prairie and oak savanna receiving wind-blown dust as the polar front moved north into northern Canada, and that the most abrupt change occurred at 8.2 cal. ka within about 100 years. The only other varve-calibrated lake record from Minnesota is from Lake of the Clouds in the Boundary Waters Canoe Area of northeastern Minnesota (Craig, 1972). In that record *Chenopod* pollen blown from western Minnesota became important at 8.2 cal. ka.

The Prairie zone pollen taxa also had abundant *Quercus* and *Gamineae*. During this mid-Holocene period, the forest-prairie border in northwestern Minnesota migrated at least 100 km east of its present position, changing from pine forest to sagebrush-and-grass prairie and oak savanna (Whitlock and others, 1993). The average annual precipitation during the prairie period was about 100 mm lower than at present, and July temperature continued an increasing trend begun in the pine zone to about 2°C warmer at the end of the prairie period (Bartlein and Whitlock, 1993). Modern pollen analogs for this period are located in the prairies along the North Dakota–Canadian border. Ostracode and diatom data from Elk Lake (Forester, 1987; Bradbury and Dieterich-Rurup, 1993) suggest that the early part of the mid-Holocene in northwestern Minnesota was cooler throughout the year than at present.

On the basis of the Elk Lake varve-calibrated record, after 8.2 cal. ka, westerly winds became increasingly dominant (Bradbury and others, 1993; Dean and others, 2002a). High concentrations of Al, quartz, and plagioclase feldspar indicate an increase in influx of relatively unweathered detrital clastic material moved by the wind and forming thicker varves (Dean, 1993). The effects of increased temperature and evaporation between 7.2 varve ka and 6.5 varve ka produced the highest salinity in the history of Elk Lake, as evidenced by ostracode assemblages (Forester and others, 1987) and presence of aragonite needles in the sediments (Dean, 1993). The increase in temperature and evaporation is manifested in Little Shingobee Lake sediments by the marked increase in endogenic CaCO_3 from about 20 percent in the pine zone (>700 cm) to 60 percent to 70 percent throughout the prairie period (fig. 5). This increase in CaCO_3 is the most distinctive feature of the prairie period in Little Shingobee Lake. Maxima of eolian indicators in Elk Lake were reached at about 5.8 varve ka. Evidence for increased aridity and eolian activity during the mid-Holocene in the Great Plains and Rocky Mountain region is abundant, with predominantly westerly or northwesterly winds (see review by Dean and others, 1996).

Increased productivity in Elk Lake during the prairie period is evidenced by high concentrations of algal pigments (Sanger and Hay, 1993), increases in $\delta^{13}\text{C}$ in both endogenic CaCO_3 and hydrogen-rich OM (discussed above). Increased productivity in Little Shingobee Lake during the prairie period is evidenced by increases in $\delta^{13}\text{C}$ in CaCO_3 of shells (fig. 8) and increases in OM and biopal (fig. 6).

The return of the forest is marked by an increase in arboreal hardwood pollen taxa dominated by *Quercus* and *Betula* but with significant contributions from *Ostrya* and *Pinus*. Precipitation and temperature reconstructions show that going into the hardwood zone annual precipitation increased to values greater than present, and July temperature remained slightly greater than at present (Bartlein and

Whitlock, 1993). This Hardwood zone has modern analogs in the hardwood-conifer forests of the southern Great Lakes region where the climate is wetter than that of the prairie period.

The White Pine zone marks the return of pine forest to northwestern Minnesota, this time dominated by white pine (*P. strobus*) but with important contributions from *P. banksiana* and *P. resinosa*. White pine reached northeastern Minnesota from the Great Lakes region by about 7.2 cal. ka but was unable to spread west during the prairie period (Whitlock and others, 1993). Its appearance marks a western retreat of the forest-prairie border characterized by warm, moist conditions in northwestern Minnesota. At the beginning of the white pine zone, July temperature was about 1.5°C higher than at present, January temperature was about 2°C higher, and precipitation was about 100 mm greater (Bartlein and Whitlock, 1993). All three climate variables decreased through the zone to modern values. The increase in temperature appears to have been enough to trigger increases in endogenic inorganic components in the middle of the White Pine zone in Little Shingobee Lake including CaCO₃ and Fe(OH)₃ and an increase in productivity as evidenced by increases in endogenic OM and biopal (fig. 6). This increase in productivity may also be manifested by an increase in values of δ¹³C in *Pisidium* (fig. 8), although there are few values.

Most paleolimnologic parameters in the Elk Lake record remain relatively constant during the last 4 ky, which includes the Hardwood and White Pine zones. Bradbury and others (1993) concluded that overall the last 4 ky of the Elk Lake record represents the establishment of modern climatic and environmental regimes. However, there are fluctuations of some paleolimnologic parameters that may be associated with decadal to centennial variability in modern climates, such as the Little Ice Age (Anderson, 1993; Dean, 2002). Fluctuations in many paleolimnologic parameters in the last 1,500 years of Elk Lake history are documented by Bradbury and others (2002), Dean (2002), and Dean and others, (2002b).

Conclusions

1. The major components in the Holocene sediments in both Little Shingobee Lake and Little Shingobee Fen are allogenic detrital clastic material (aluminosilicates), endogenic CaCO₃, and organic matter. The main difference is that in Little Shingobee Fen CaCO₃ is by far the dominant component with little change through the Holocene section with an average of 61 percent CaCO₃. Shingobee Lake sediments are dominated by detrital material (7 percent to 82 percent) interrupted by several major pulses of CaCO₃ that diluted the detrital material. The lack of detrital material in Little Shingobee Fen (average of 4.4 percent) may have been because the sill that separated Little Shingobee Lake and the lake that occupied the basin under the present-day fen restricted inflow of detrital material. The organic matter content in Holocene sediments of Little Shingobee Fen (average 13 percent) is about twice that of Little Shingobee Lake sediments (6 percent).
2. An early Holocene carbonate pulse resulted in the accumulation of about 80 percent CaCO₃ in the sediments of both Little Shingobee Lake and Fen and also in the sediments of nearby Williams and Shingobee Lakes. This pulse of CaCO₃ deposition was likely the result of postglacial leaching of CaCO₃ from the calcareous glacial drift in the drainage basin into the lakes that triggered endogenic calcite precipitation.
3. Almost all of the Fe and Mn in the sediments in both Little Shingobee Lake and Fen is endogenic, even in the late glacial detrital sediments, and is assumed to reside in oxyhydroxide minerals. The source of high concentrations of Fe and Mn that accumulate in the hypolimnion of Shingobee Lake today is not shallow groundwater but rather is a deep aquifer that overlies

Cretaceous bedrock. Therefore, it seems likely that the source of Fe and Mn that precipitated as endogenic minerals that accumulated in the sediments of Little Shingobee Lake and Little Shingobee Fen, as well as those in Williams and Shingobee Lakes, was postglacial activation of that deep aquifer.

4. Values of $\delta^{18}\text{O}$ in carbonate shells in Little Shingobee Lake sediments are remarkably constant throughout the Holocene, indicating that environmental conditions affecting oxygen-isotope composition were fairly constant. However, there is an increase in $\delta^{13}\text{C}$ in mid-Holocene in carbonate shells but not in organic carbon, and this increase is likely due to longer residence time during the dry prairie period.
5. The most striking change in the vegetation of Shingobee River headwater area, and northwestern Minnesota in general, is the transition from late Pleistocene and early Holocene forests of spruce and then pine to a mid-Holocene open sagebrush-oak savanna. Forests returned to northern Minnesota during the late Holocene, first as a hardwood forest followed by a return to a pine forest.

Acknowledgments

This work was funded by the U.S. Geological Survey Global Change and Climate History and Earth Surface Dynamics Programs. We thank Lesleigh Anderson, Don Rosenberry, and Tom Winter for helpful comments on an earlier version of this paper. Cores are archived at LacCore (National Lacustrine Core Repository), Department of Geology and Geophysics, University of Minnesota—Twin Cities.

References Cited

- Anderson, R.Y., 1993, The varve chronometer in Elk Lake—Record of climatic variability and evidence for solar/geomagnetic- ^{14}C -climate connection, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 46–68.
- Anderson, R.Y., Bradbury, J.P., Dean, W.E., and Stuiver, Minze, 1993, The varve chronology of Elk Lake sediments—Coring, sampling, and time-series construction, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 37–44.
- Bartlein, P.J., and Whitlock, Cathy, 1993, Paleoclimatic interpretation of the Elk Lake pollen record, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 275–294.
- Bernasconi, S.M., Barbieri, Alberto, and Simona, Marco, 1997, Carbon and oxygen isotope variations in sedimenting organic matter in Lake Lugano: *Limnology and Oceanography*, v. 42, p. 1755–1765.
- Bradbury, J.P., Cumming, B.E., and Laird, K.A., 2002, A 1,500-year record of climatic and environmental change in Elk Lake, Minnesota—III. Measures of past primary productivity: *Journal of Paleolimnology*, v. 27, p. 320–331.
- Bradbury, J.P., Dean, W.E., and Anderson, R.Y., 1993, Holocene climatic and limnologic history of the north-central United States as recorded in the varve sediments of Elk Lake, Minnesota—A synthesis, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 309–328.

- Bradbury, J.P., and Dieterich-Rurup, Katherine, 1993, Holocene diatom paleolimnology of Elk Lake, Minnesota, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 215–238.
- Carter, Virginia, Gammon, P.T., and Rybicki, N.B., 1997, Vegetation of Little Shingobee Fen, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River headwaters area, north-central Minnesota: U. S. Geological Survey Water Resources Investigations Research 96–4215, p. 161–166.
- Cerling, T.E., and Quade, Jay, 1993, Stable carbon and oxygen isotopes in soil carbonates, *in* Swart, P.K., Lohmann, K.C., McKenzie, Judith, and Savin, Samuel, eds., Climate change in continental isotopic records: American Geophysical Union Geophysical Monograph 78, p. 217–231.
- Craig, A.J., 1972, Pollen influx to laminated sediments—A pollen diagram from northeastern Minnesota: *Ecology*, v. 53, p. 46–57.
- Davison, W., and Seed, G., 1983, The kinetics of oxidation of ferrous iron in synthetic and natural waters: *Geochimica et Cosmochimica Acta*, v. 47, p. 67–79.
- Dean, W.E., Jr., 1974, Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition—Comparison with other methods: *Journal of Sedimentary Petrology*, v. 44, p. 242–248.
- Dean, W.E., 1993, Physical properties, mineralogy, and geochemistry of Holocene varved sediments from Elk Lake, Minnesota, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 135–158.
- Dean, W.E., 2002, A 1,500-year record of climatic and environmental change in Elk Lake, Minnesota—II. Geochemistry, mineralogy, and stable isotopes: *Journal of Paleolimnology*, v. 27, p. 301–319.
- Dean, W.E., Ahlbrandt, T.S., Anderson, R.Y., and Bradbury, J.P., 1996, Regional aridity in North America during the middle Holocene: *The Holocene*, v. 6, p. 145–155.
- Dean, W.E., Anderson, R.Y., Bradbury, J.P., and Anderson, D., 2002b, A 1,500-year record of climatic and environmental change in Elk Lake, Minnesota I—Varve thickness and gray-scale density: *Journal of Paleolimnology*, v. 27, p. 287–299.
- Dean, W.E., Arthur, M.A., and Claypool, G.E., 1986, Depletion of ^{13}C in Cretaceous marine organic matter—Source, diagenetic, or environmental signal?: *Marine Geology*, v. 70, p. 119–158.
- Dean, W.E., and Bradbury, J.P., 1997, Transects of organic carbon, calcium carbonate, and diatoms in surface sediments of Williams and Shingobee Lake, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River headwaters area, north-central Minnesota: U.S. Geological Survey Water Resources Investigations Research 96–4215, p. 117–130.
- Dean, W.E., Forester, R.M., and Bradbury, J.P., 2002a, Early Holocene change in atmospheric circulation in the Northern Great Plains—An upstream view of the 8.2 ka cold event: *Quaternary Science Reviews*, v. 21, p. 1763–1775.
- Dean, W.E., Neff, B., Rosenberry, D., Winter, T.C., and Parkhurst, R., 2003, The significance of ground water to the accumulation of iron and manganese in the sediments of two hydrologically distinct lakes in north-central Minnesota—A geological perspective: *Ground Water*, v. 41, p. 951–963.
- Dean, W.E., and Schwalb, Antje, 2002, The lacustrine carbon cycle as illuminated by the waters and sediments of two hydrologically distinct hardwater lakes in northwestern Minnesota: *Journal of Sedimentary Research*, v. 72, p. 416–431.

- Dean, W.E., and Stuiver, Minze, 1993, Stable carbon and oxygen isotope studies of the sediments of Elk Lake, Minnesota, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 163–180.
- Engleman, E.E., Jackson, L.L., Norton, D.R., and Fischer, A.G., 1985, Determination of carbonate carbon in geological materials by coulometric titration: *Chemical Geology*, v. 53, p. 125–128.
- Faegri, Knut, Kaland, P.E., Krzywinski, Knut, 1989, Textbook of pollen analysis, 4th ed.: New York, Blackwell, 328 p.
- Forester, R.M., 1987, Late Quaternary paleoclimate records from lacustrine ostracodes, *in* Ruddiman, W.F., and Wright, H.E., Jr., eds., The geology of North America, v. K-3, chapter 12, North America and adjacent oceans during the last deglaciation: Geological Society of America, p. 261–276.
- Gaugh, H.G., Jr., 1982, Multivariate analysis in community ecology: New York, Cambridge University Press, 298 p.
- Gorham, Eville, and Sanger, J.E., 1975, Fossil pigments in Minnesota lake sediments and their bearing upon the balance between terrestrial and inputs to sedimentary organic matter: *Verhandlungen International Vereinigung für Limnologie*, v. 19, p. 267–273.
- Grimm, Eric, 1987, CONISS—A Fortran 77 program for stratigraphically constrained cluster analysis by the method of incremental sum of squares: *Computers and Geosciences*, v. 13, p. 13–35.
- Hollander, D.J., and McKenzie, J.A., 1991, CO₂ control on carbon-isotope fractionation during aqueous photosynthesis—A paleo-pCO₂ barometer: *Geology*, v. 19, p. 929–932.
- Hollander, D.J., and Smith, M.A., 2001, Microbially mediated carbon cycling as a control on the $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA)—New models for interpreting isotopic excursions in the sedimentary record: *Geochimica et Cosmochimica Acta*, v. 65, p. 4321–4337.
- Kendall, Carol, Evans, W.C., Reddy, M.M., and Schuster, P.F., 1997, Application of stable isotopes in the Shingobee River headwaters area, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River Headwaters Area, north-central Minnesota: U.S. Geological Survey Water Resources Investigations Research 96–4215, p. 63–70.
- LaBaugh, J.W., 1997, The plankton communities of Shingobee and Williams Lakes, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River Headwaters Area, north-central Minnesota: U.S. Geological Survey Water Resources Investigations Research 96–4215, p. 97–104.
- Locke, S.M., 1995, A paleohydrologic model applied to the Holocene sediment stratigraphy of two lakes in north-central Minnesota: Minneapolis, University of Minnesota, Ph.D. dissertation, 258 p.
- Locke, S.M., and Schwalb, Antje, 1997, Sediment stratigraphy and paleolimnological characteristics of Williams and Shingobee Lakes, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River Headwaters Area, north-central Minnesota: U.S. Geological Survey Water Resources Investigations Research 96–4215, p. 187–192.
- McKenzie, J.A., and Hollander, D.J., 1993, Oxygen-isotope record in recent carbonate sediments from Lake Greifen, Switzerland (1750–1986)—Application of continental isotopic indicator for evaluation of changes in climate and atmospheric circulations patterns, *in* Swart, P.K., Lohman, K.C., McKenzie, J.A., and Savin, Samuel, eds., Climate change in continental isotope records: American Geophysical Union Monograph 78, p. 101–111.
- Megard, R.O., Bradbury, J.P., and Dean, W.E., 1993, Climatic and limnologic setting of Elk Lake, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 19–36.

- Meyers, P.A., and Teranes, J.L., 2001, Sediment organic matter, *in* Last, W.M., and Smol, J.P., eds., Tracking environmental change using lake sediments, v. 2: Dordrecht, The Netherlands, Kluwer Academic Publishers, p. 239–269.
- Moore, D.M., and Reynolds, R.C., Jr., 1989, X-ray diffraction and identification and analysis of clay minerals: Oxford, U.K., Oxford University Press, 332 p.
- Moores, H.D., and Norton, A.R., 1997, Glacial landscape evolution of the Itasca/St. Croix moraine interlobate area including the Shingobee River Headwaters Area, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River Headwaters Area, north-central Minnesota: U.S. Geological Survey Water Resources Investigations Research 96–4215, p. 11–18.
- Myrbo, Amy, and Shapley, M.D., 2006, Seasonal water-column dynamics of dissolved inorganic carbon stable isotope compositions ($\delta^{13}\text{C}_{\text{DIC}}$) in small hardwater lakes in Minnesota and Montana: *Geochimica et Cosmochimica Acta*, v. 70, p. 2699–2714.
- O’Leary, M.H., 1988, Carbon isotopes in photosynthesis: *BioScience*, v. 38, p. 328–336.
- Overpeck, J.T., Webb, Thompson, III, and Prentice, I.C., 1985, Quantitative interpretation of fossil pollen spectra—Dissimilarity coefficients and the method of modern analogs: *Quaternary Research*, v. 23, p. 87–108.
- Rosenberry, D.O., Winter, T.C., Merk, D.A., Leavesley, G.H., and Beaver, L.D., 1997, Hydrology of the Shingobee River Headwaters Area, *in* Winter, T.C., ed., Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River headwaters area, north-central Minnesota: U. S. Geological Survey Water Resources Investigations Research 96–4215, p. 19–24.
- Sanger, J.E., and Hay, R.J., 1993, Fossil pigments in Holocene varved sediments, Elk Lake, Minnesota, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 181–188.
- Schwalb, Antje, and Dean, W.E., 2002, Reconstruction of hydrological changes and effective moisture from north-central USA lake sediments: *Quaternary Science Reviews*, v. 21, p. 1541–1554.
- Schwalb, Antje, Locke, S.M., and Dean, W.E., 1995, Ostracode $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ evidence of Holocene environmental changes in the sediments of two Minnesota lakes: *Journal of Paleolimnology*, v. 14, p. 281–296.
- Stauffer, R.E., and Armstrong, D.E., 1986, Cycling of iron, manganese, silica, phosphorus, calcium and potassium in two stratified basins of Shagawa Lake, Minnesota: *Geochimica et Cosmochimica Acta*, v. 50, p. 215–229.
- Striegl, R.G., Kortelainen, Pirkko, Chanton, J.P., Wickland, K.P., Bugna, G.C., and Rantakari, Miitta, 2001, Carbon dioxide partial pressure and ^{13}C content of north temperate and boreal lakes at spring ice melt: *Limnology and Oceanography*, v. 46, p. 941–945.
- Striegl, R.G., and Michmerhuizen, C.M., 1998, Hydrologic influence on methane and carbon dioxide dynamics in two north-central Minnesota lakes: *Limnology and Oceanography*, v. 43, p. 1519–1529.
- Stuiver, Minze, Reimer, P.J., Bard, Edouard, Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, Bernd, McCormac, Gerry, Van der Plicht, Johannes, and Spurk, Marco, 1998, INTCAL98 radiocarbon age calibration, 24,000–0 cal BP: *Radiocarbon*, v. 40, p. 1041–1083.
- Sprowl, D.R., 1993, On the precision of the Elk Lake varve chronology, *in* Bradbury, J.P., and Dean, W.E., eds., Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276, p. 69–74.
- Tian, Jian, Brown, T.A., and Hu, F.S., 2005, Comparison of varve and ^{14}C chronologies from Steel Lake, Minnesota, USA: *The Holocene*, v. 15, p. 510–517.

- Tipping, E., Woof, C., and Cooke, D., 1981, Iron oxide from a seasonally anoxic lake: *Geochimica et Cosmochimica Acta*, v. 45, p. 1441–1419.
- Von Grafenstein, Ulrich, Erlenkeuser, Helmut, and Trimborn, Peter, 1999, Oxygen and carbon isotopes in modern fresh-water ostracod valves—Assessing vital offsets and autoecological effects of interest for palaeoclimate studies: *Palaeogeography, Palaeoclimatology, and Palaeoecology*, v. 148, p. 133–152.
- Wetzel, R.G., 2001, *Limnology—Lake and river ecosystems* (3d ed): San Diego, Calif., Academic Press, 1006 p.
- Whitlock, Cathy, Bartlein, P.J., and Watts, W.A., 1993, Vegetation history of Elk Lake, in Bradbury, J.P., and Dean, W.E., eds., *Elk Lake, Minnesota—Evidence for rapid climate change in the north-central United States: Geological Society of America Special Paper 276*, p. 251–274.
- Winter, T.C., ed., 1997, *Interdisciplinary Research Initiative—Hydrological and biogeochemical research in the Shingobee River Headwaters Area, north-central Minnesota: U. S. Geological Survey Water Resources Investigations Research 96–4215*, 210 p.
- Wright, H.E., Jr., 1976, The dynamic nature of Holocene vegetation: *Quaternary Research*, v. 24, p. 115–120.
- Wright, H.E., Jr., Stefanova, Ivana, Tian, Jian, Brown, T.A., and Hu, F.S., 2004, A chronological framework for the Holocene vegetational history of central Minnesota—The Steel Lake pollen record: *Quaternary Science Reviews*, v. 23, p. 611–626.
- Xia, J., Ito, Emi, and Engstrom, D.R., 1997a, Geochemistry of ostracode calcite—An experimental determination of oxygen isotope fractionation: *Geochimica et Cosmochimica Acta*, v. 61, p. 377–382.
- Xia, J., Ito, Emi, and Engstrom, D.R., 1997b, Variation of stable-isotope and trace-element composition of lacustrine ostracodes from the northern Great Plains, part 2—The effects of lake water chemistry and seasonal temperature variation on *Candona rawsoni*: *Geochimica et Cosmochimica Acta*, v. 61, p. 383–391.