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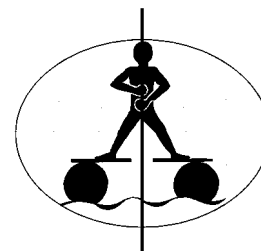
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Dean, Walter E., "The Carbon Cycle and Biogeochemical Dynamics in Lake Sediments" (1999). *USGS Staff -- Published Research*. 312.

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## The carbon cycle and biogeochemical dynamics in lake sediments\*



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Received 9 December 1997; accepted 4 May 1998

*Key words:* CaCO<sub>3</sub>, organic carbon, iron, manganese, eutrophication

### Abstract

The concentrations of organic carbon (OC) and CaCO<sub>3</sub> in lake sediments are often inversely related. This relation occurs in surface sediments from different locations in the same lake, surface sediments from different lakes, and with depth in Holocene sediments. Where data on accumulation rates are available, the relation holds for organic carbon and CaCO<sub>3</sub> accumulation rates as well. An increase of several percent OC is accompanied by a decrease of several tens of percent CaCO<sub>3</sub> indicating that the inverse relation is not due to simple dilution of one component by another. It appears from core data that once the OC concentration in the sediments becomes greater than about 12%, the CO<sub>2</sub> produced by decomposition of that OC and production of organic acids lowers the pH of anoxic pore waters enough to dissolve any CaCO<sub>3</sub> that reaches the sediment-water interface. In a lake with a seasonally anoxic hypolimnion, processes in the water column also can produce an inverse relation between OC and CaCO<sub>3</sub> over time. If productivity of the lake increases, the rain rate of OC from the epilimnion increases. Biogenic removal of CO<sub>2</sub> and accompanying increase in pH also may increase the production of CaCO<sub>3</sub>. However, the decomposition of organic matter in the hypolimnion will decrease the pH of the hypolimnion causing greater dissolution of CaCO<sub>3</sub> and therefore a decrease in the rain rate of CaCO<sub>3</sub> to the sediment-water interface.

### Introduction

The sediments of moderately to highly productive (mesotrophic to eutrophic) temperate lakes typically contain olive-green sediments rich in organic matter (> 20% organic matter by loss on ignition at 550 °C, > 10% organic carbon) called gyttja (Hansen, 1959; Wetzel, 1975). Because many of these lakes are in basins underlain by calcareous glacial drift, they contain calcium-magnesium-bicarbonate-rich ('hard') waters and precipitate calcium carbonate (CaCO<sub>3</sub>), mostly as low-magnesium calcite, during summer. This CaCO<sub>3</sub> may dilute the concentration of organic matter somewhat and produce a calcareous sediment called marl (Dean, 1981). The largest reservoir of organic

carbon (OC) in a lake is dissolved OC, which is usually greater than particulate OC. It is this particulate OC, however, that is the dominant source of organic matter in the sediments; some dissolved OC may be incorporated in the sediments by adsorption on clays and carbonate.

Plant pigment studies of Minnesota lake sediments (Sanger & Gorham, 1970; Gorham & Sanger, 1975) showed that most of the organic matter in an average Minnesota lake is autochthonous, and that only in the least productive of the lakes in northeastern Minnesota does allochthonous terrestrial organic matter make significant contributions to sedimentary organic matter. Autochthonous organic matter is enriched in proteinaceous, low molecular weight, H- and N-rich compounds with low C/N ratios (typically < 10; Meyers & Ishiwatari, 1993). Allochthonous terrestrial organic matter is enriched in humic, high molecular weight, C-rich compounds, and C/N ratios tend to be

\*This paper was presented at the 7th International Symposium on Palaeolimnology (1997), held at Heiligkreuztal, Germany.

much higher, with values typically between 20 and 30 (Meyers & Ishiwatari, 1993).

The average OC and  $\text{CaCO}_3$  concentrations in profundal surface sediments of 46 representative lakes throughout Minnesota are 12% (range 3–29%) and 16% (range 3–46%), respectively (Dean et al., 1993). Sediments in the littoral and sublittoral areas of hard-water lakes usually contain less organic matter and such more  $\text{CaCO}_3$  than profundal sediments. The average OC/N ratio in the sediments of those 46 Minnesota lakes is 9.0 (range 7.6–14), and the only sediments with OC/N ratios > 11 were from 5 of 10 lakes in northeastern Minnesota (Dean et al., 1993). For comparison, the average OC concentration in profundal surface sediments in the English Lake District is 7.0% (range 4.0–13%) and the average OC/N ratio is 12.2 (range 9.4–14.1) (Gorham et al., 1974; Dean et al., 1988) with little variation with lake primary productivity. Plant pigment analyses of sediments from English lakes demonstrated that in those lakes, as in Minnesota lakes, much of the organic matter is autochthonous (Gorham et al., 1974).

In this paper, I will examine how the biogeochemical cycles of OC and  $\text{CaCO}_3$  interact to determine the ultimate burial of these two components in sediments. I will mainly use examples from Minnesota where I have the most information and experience, and which is also a region with a particularly dense concentration and variety of lakes. I will first look at the concentrations of OC and  $\text{CaCO}_3$  in surface sediments, and then examine variations in OC and  $\text{CaCO}_3$  in cores from several lakes to see how burial of these two forms of carbon have changed with time. Finally, I will give an example of how the carbon cycle in a lake can profoundly influence the biogeochemical cycles of some other elements.

## Methods

Estimates of percent total organic matter and percent  $\text{CaCO}_3$  in samples of surface sediments and in samples from several cores were determined by loss on ignition (LOI) at 550 and 1000 °C, respectively (Dean, 1974). Concentrations of OC, total nitrogen, and total hydrogen in samples of surface sediments were determined chromatographically as  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ , respectively, using a Hewlett-Packard CHN analyzer (Dean, 1974). Total carbon (TC) and inorganic (carbonate; CC) carbon were determined in samples from cores using a coulometer (Engleman et al., 1985). OC was calculated as the difference between TC and CC.

Percent  $\text{CaCO}_3$  was calculated by multiplying % CC by 8.33. In general, the amount of organic matter determined by loss on ignition at 550 °C (% LOI-550) is twice the organic carbon content. Therefore, percent organic matter can be estimated by multiplying % OC by two. There is excellent agreement between these two methods, and also between %  $\text{CaCO}_3$  determined by LOI and %  $\text{CaCO}_3$  calculated from % CC (Dean, 1974). These agreements will be illustrated for samples from several cores.

## $\text{CaCO}_3$ and organic carbon in surface sediments of Minnesota lakes

The water chemistry of Minnesota lakes is closely controlled by the steep climatic gradient from east to west across the state and continuing into the Dakotas, and, to a lesser degree, by differences in surficial and bedrock geology (Gorham et al., 1983). One manifestation of this climatic gradient is the rapid increase in salinity of lake waters from east to west from Wisconsin, across Minnesota, and into the Dakotas (Figure 1). The 0.7 log total dissolved cations contour in Figure 1 approximately corresponds to the zero precipitation minus evaporation contour, with net precipitation to the east of that line, and net evaporation to the West. Lakes of northeastern Minnesota and northwestern Wisconsin (groups 1 and 2 of Gorham et al., 1983; Figure 2) contain dilute bicarbonate waters with conductivities <141 microsiemens per centimeter ( $\mu\text{S}$ ) and log total cations <0.1 milliequivalent per liter (epm) and are located on Precambrian bedrock. This region is heavily forested and has a positive balance of precipitation minus evaporation. The most dilute of the group 1 lakes are close to rainwater in composition. Group 3 lakes in central Minnesota (Figure 2) contain calcium-magnesium bicarbonate waters of intermediate salinity (141–500  $\mu\text{S}$ ; log total cations 0.1–0.7 epm) and are in calcareous drift. The compositions of waters from group 3 lakes in Minnesota are given in Table 1 along with % OC and %  $\text{CaCO}_3$  in their sediments. Group 3 lakes occur in both forested and prairie regions with a slight positive or slight negative balance of precipitation minus evaporation. Group 4 lakes, in the prairie region of southwestern Minnesota (Figure 2) and the Dakotas, have a distinctly negative balance of precipitation minus evaporation, and have conductivities of 501–7078  $\mu\text{S}$  (log total cations 0.7–1.9 epm). The surficial deposits of this region contain gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) derived from

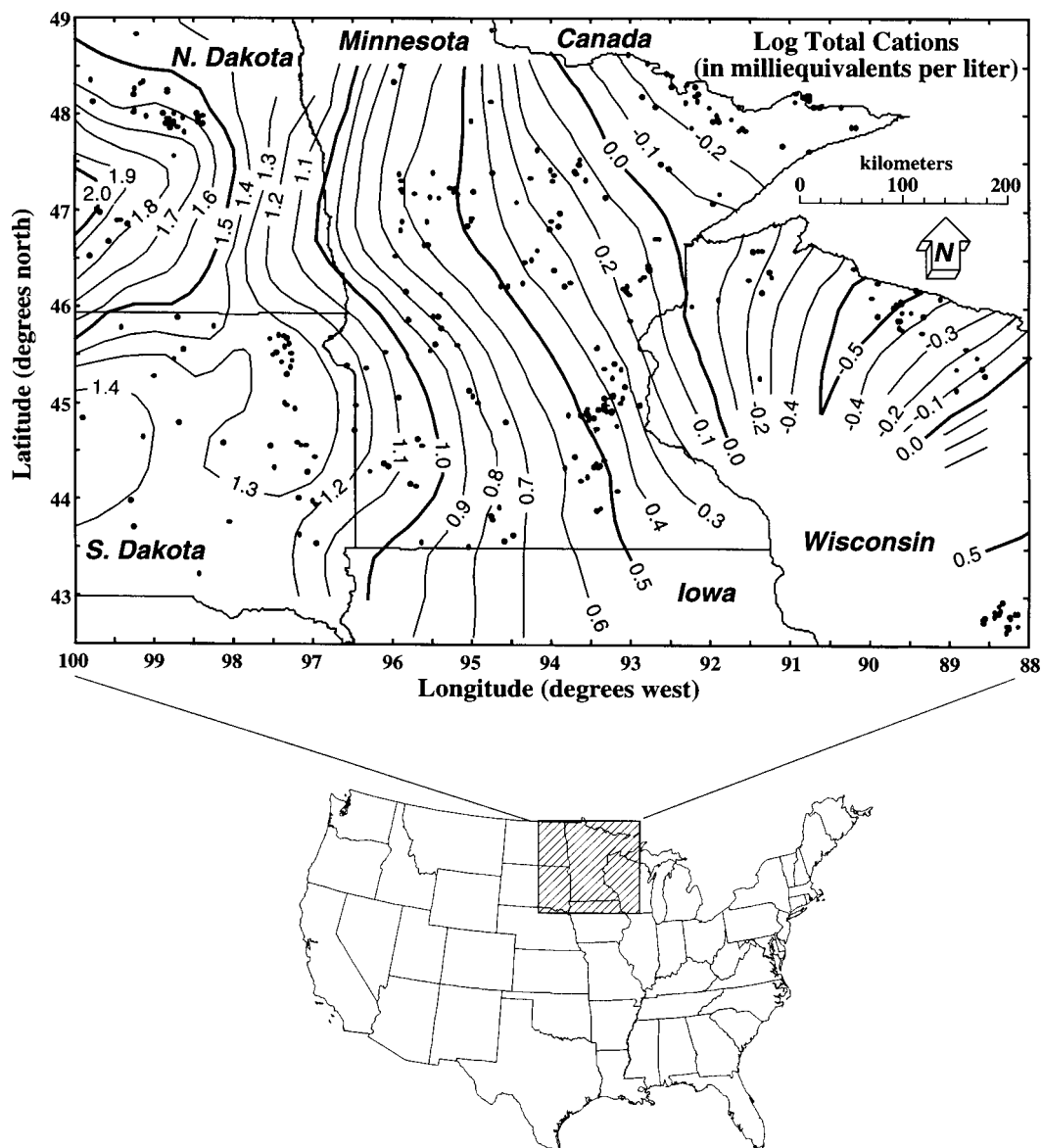


Figure 1. Contour map of log total cation concentration in milliequivalents per liter (epm) in lake waters in Wisconsin, Minnesota, North Dakota and South Dakota. Black dots represent locations of lakes sampled and reported in Gorham et al., 1982 and 1983). Raw data were gridded, smoothed, and contoured using 'Surface III' software developed by the Kansas Geological Survey. Major-ion data for these lakes are available in Gorham et al. (1982) or from the author.

Cretaceous shale. As a result, sulfate replaces bicarbonate as the dominant anion. Because of loss of calcium by  $\text{CaCO}_3$  precipitation, and gain of sodium and magnesium from Cretaceous shales, sodium and magnesium are the dominant cations in group 4 lakes. Group 5 lakes lack outlets and have very high salinities (conductivity  $> 7078 \mu\text{S}$ ; log total cations  $> 1.9$  epm); they occur mainly in western South and North Dakota.

All but the most dilute group 3 lakes precipitate  $\text{CaCO}_3$  as low-Mg calcite (Dean et al. 1993; Dean and Megard, 1993). Precipitation of  $\text{CaCO}_3$  begins when log total cations is greater than about 0.3 epm (Figure 3A). The basic concentration- $\text{CaCO}_3$  precipitation model can be envisioned as beginning with a beaker of group 2 water and transporting it across central Minnesota's steep climatic gradient, concentrating it by evaporation,

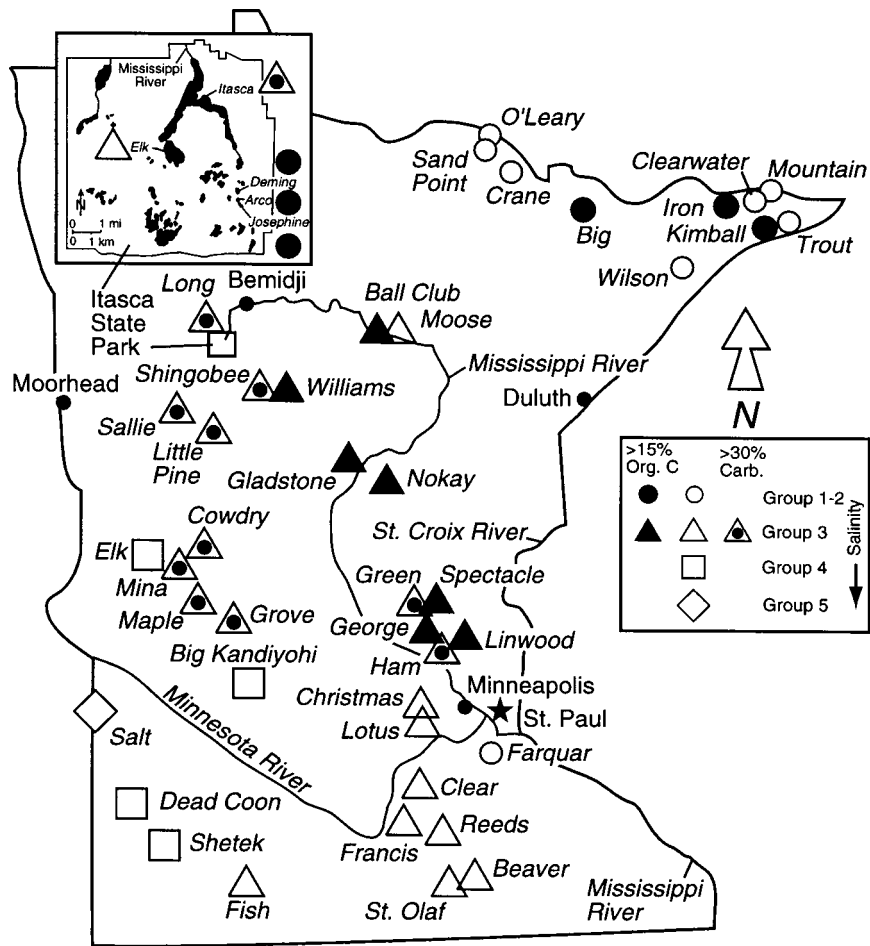


Figure 2. Map showing locations of 47 lakes for which there are data on water chemistry (Gorham et al., 1982 and 1983) and sediment chemistry (Dean & Gorham, 1976; Dean et al., 1993; Dean & Bradbury, 1997). Symbols reflect water-salinity groups (groups 1-2, 3, 4, and 5) of Gorham et al. (1983), modified to separate those lakes with profundal sediments rich in carbonate (> 30%  $\text{CaCO}_3$ ), those rich in organic matter (> 30% organic matter), and those with intermediate contents of both carbonate and organic matter (Dean & Gorham, 1976; Dean et al., 1993).

and then precipitating  $\text{CaCO}_3$  once the concentration reaches about 0.3 epm log total cations, at which time calcium constitutes about 60% of the cations and magnesium constitutes about 35% (Figure 3B). Once  $\text{CaCO}_3$  precipitation begins, the calcium content, as percent of total cations, decreases markedly and that of magnesium increases. In group 4 lakes of southwestern Minnesota, the simple evaporation-precipitation model breaks down as additional ions are added, mainly from Cretaceous shales. Carbonate precipitates in group 4 lakes but in lower amounts because of the lower calcium concentration, and often as a mixture of low-Mg calcite, high-Mg calcite, and dolomite because of the high Mg:Ca ratio in the waters (Dean & Gorham, 1976; Dean & Megard, 1993).

The organic content of surface sediments appears to be more of a function of preservation than of production. The lakes with high sedimentary organic contents in Itasca Park (Deming, Arco, and Josephine, inset, Figure 2) are meromictic and their sediments consist almost entirely of well-preserved algal remains. As mentioned earlier, the plant pigment studies of Gorham and Sanger (Sanger & Gorham, 1970; Gorham & Sanger, 1975) have shown that most of the sedimentary organic matter in Minnesota lakes is of algal origin. In most of the group 3 lakes with > 30% organic matter (> 15% OC; Figure 2), the higher organic content is due to lack of dilution by  $\text{CaCO}_3$ . Initially, I was perplexed as to why two lakes very close to each other, in the same glacial till, and with similar

Table 1. Chemical compositions of waters, and concentrations of organic carbon and calcium carbonate in surface sediments, of selected lakes in north-central Minnesota

Lake	Specific Conductance ( $\mu\text{S}$ )	Concentration in milliequivalents per liter							Percent	
		Ca	Mg	Na	K	Cl	SO <sub>4</sub>	Alkalinity	Organic Carbon	CaCO <sub>3</sub>
Ball Club <sup>2</sup>	249	1.720	0.944	0.131	0.035	0.017	0.138	2.630	17.1	5.6
Cowdry <sup>2</sup>	362	1.324	2.700	0.250	0.130	0.027	0.448	3.709	10.8	31.3
Elk <sup>2</sup>	266	1.646	1.378	0.313	0.045	0.019	0.068	3.250	9.5	19.0
George <sup>2</sup>	167	1.016	0.588	0.127	0.021	0.039	0.125	1.588	17.3	3.1
Gladstone <sup>2</sup>	162	1.204	0.534	0.161	0.026	0.010	0.060	1.816	20.9	3.8
Green <sup>2</sup>	206	1.084	0.984	0.134	0.029	0.028	0.141	2.069	10.6	30.9
Grove <sup>2</sup>	349	1.568	2.242	0.180	0.100	0.066	0.437	3.480	11.2	35.6
Ham <sup>2</sup>	188	1.048	0.916	0.156	0.039	0.048	0.163	1.924	12.7	37.4
Itasca <sup>2</sup>	284	1.388	1.820	0.278	0.044	0.030	0.055	3.454	10.8	35.0
Linwood <sup>2</sup>	171	1.032	0.652	0.115	0.019	0.034	0.122	1.658	15.9	10.5
Little Pine <sup>2</sup>	311	1.856	1.699	0.192	0.053	0.034	0.124	3.437	8.5	46.3
Long <sup>2</sup>	274	1.291	1.234	0.157	0.023	0.051	0.073	3.210	6.0	40.2
Maple <sup>2</sup>	390	1.182	2.534	0.280	0.140	0.077	0.387	4.162	9.6	42.6
Mina <sup>2</sup>	460	1.832	3.157	0.440	0.110	0.192	1.508	3.644	8.8	39.4
Moose <sup>2</sup>	254	1.730	0.880	0.164	0.052	0.023	0.109	2.700	8.4	28.4
Nokay <sup>2</sup>	238	1.828	0.613	0.120	0.030	0.021	0.093	2.464	19.5	15.8
Sallie <sup>2</sup>	361	1.368	2.377	0.516	0.123	0.167	0.492	3.606	9.5	46.3
Shingobee <sup>1</sup>	341	2.095	1.398	0.252	0.043	0.101	0.079	1.398	8.8	46.2
Spectacle <sup>2</sup>	181	0.956	0.760	0.143	0.039	0.042	0.096	1.747	21.1	3.5
Williams <sup>1</sup>	145	0.998	0.567	0.052	0.028	0.011	0.043	1.478	24.6	0.23

<sup>1</sup>Data on water chemistry are from LaBaugh (1997); OC and CaCO<sub>3</sub> values are averages from Dean and Bradbury (1997). <sup>2</sup>Data on water chemistry are from Gorham and others (1982); data on OC and CaCO<sub>3</sub> are from Dean and Gorham (1976).

water chemistries had such different sediment characteristics (e.g. compare, for example, Ball Club and Moose Lakes, and Linwood and Ham Lakes in Table 1). The sediment characteristics for most of the lakes shown in Figure 2 are based on one sample of surface sediment collected from the deepest part of the lake (Dean & Gorham, 1976). For Elk, Williams, and Shingobee Lakes, I have analyses of surface sediments collected along depth transects, and the ranges in contents of CaCO<sub>3</sub> are considerable (bars in Figure 3A). There is also an inverse relation between contents of OC and CaCO<sub>3</sub> in the surface sediments of a particular lake. In the surface sediments of Shingobee Lake, for example, the OC contents range from 4–14% and the CaCO<sub>3</sub> contents range from 24–73% (Dean & Bradbury, 1997). The difference in OC is 10% whereas the difference in CaCO<sub>3</sub> is 50%, so the inverse relation cannot be one of simple dilution of one component by the other. This inverse relation between OC for Shingobee Lake sediments, and for all of the group 3 lakes with characteristics tabulated in Table 1, is shown in Figure 4.

The greatest insight into the inverse relation between OC and CaCO<sub>3</sub> came from the study of surface sediments and cores from Williams and Shingobee Lakes

(Figure 2) against a background of more than 10 years of intense hydrological and limnological investigations of these two lakes (LaBaugh et al., 1995; Averett & Winter, 1997). Shingobee Lake is hydrologically open with the Shingobee River as both the inlet and outlet, and has a residence time of about seven months. Williams Lake is hydrologically closed with only ground water inflow and outflow, and a residence time of about four years. The OC and CaCO<sub>3</sub> characteristics of surface sediments in Shingobee Lake are shown in Figure 4. The surface sediments of Williams Lake, on the other hand, contain an average of 25% OC and essentially no CaCO<sub>3</sub> (Dean and Bradbury, 1997) even though CaCO<sub>3</sub> does precipitate in Williams Lake during the summer (McConnaughey, et al., 1995). The distinct inverse relation between OC and CaCO<sub>3</sub> in surface sediments in a transect across Shingobee Lake and in surface sediments from group 3 lakes of central Minnesota (Figure 4) illustrates how burial of a large amount of OC can increase dissolution of CaCO<sub>3</sub>. The total salinity (specific conductance) and calcium concentrations in Williams Lake are distinctly lower than those of Shingobee Lake (Table 1). Calcite saturation measurements in Williams Lake by McConnaughey, et al. (1995 and 1997) show that the lake is over-

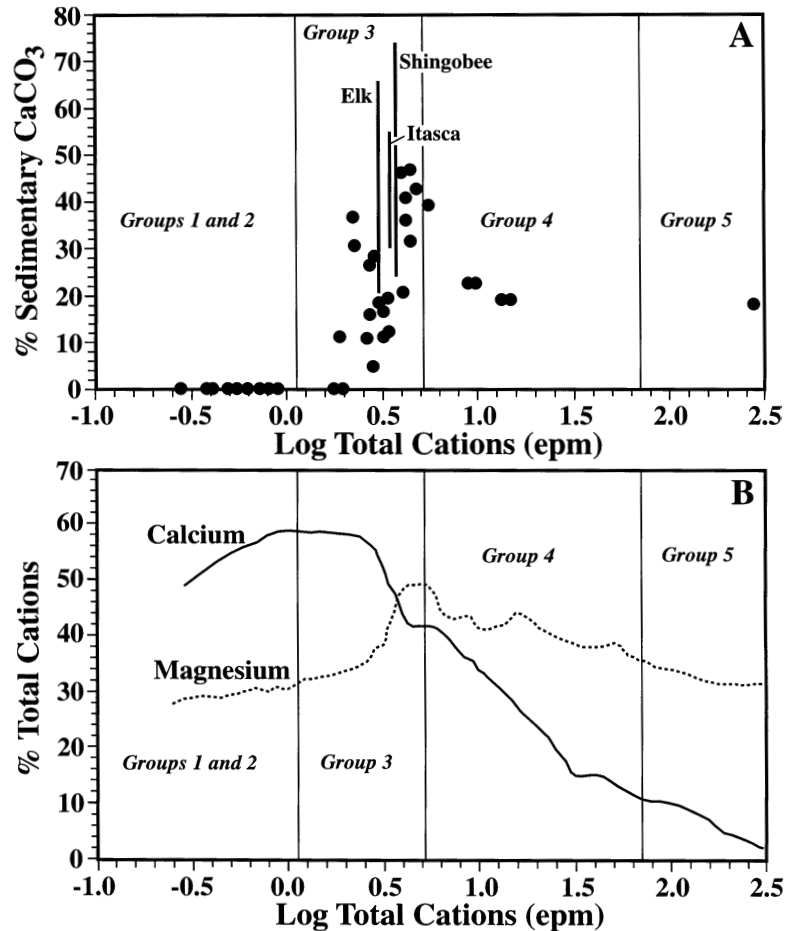


Figure 3. (A) Percent CaCO<sub>3</sub> in profundal sediments of 47 Minnesota lakes versus log total cation concentration (in milliequivalents per liter, epm) in surface waters from the same lakes. Ranges of % CaCO<sub>3</sub> in surface sediments from six localities in Elk Lake, six localities in Lake Itasca, and six localities in Shingobee Lake are also shown (vertical lines). (B) Smoothed curves, using a 21-point weighted moving average, showing relative proportions (as percent total cations) of dissolved calcium and magnesium versus log total cation concentration (in milliequivalents per liter, epm) in surface waters from 219 lakes in Wisconsin, Minnesota, North Dakota, and South Dakota (Figure 1; Data of Gorham et al., 1982). Groups 1-2, 3, 4, and 5, separated by vertical lines, refer to the water chemistry groups of Gorham et al. (1983).

saturated with calcite at a depth of 1 m during the summer, and is undersaturated at all times below 8 m. Therefore, the differences in OC and CaCO<sub>3</sub> concentrations in the sediments of Williams and Shingobee Lakes may simply be due to differences in accumulation rates. The salinities and calcium concentrations in low-CaCO<sub>3</sub> lakes Spectacle, Linwood, and George also are relatively low, but not that much lower than those of Ham and Green which are high-CaCO<sub>3</sub> lakes (Figure 2; Table 1). Also, Nokay and Ball Club, with CaCO<sub>3</sub>-poor sediments have salinities and calcium concentrations that are higher than those in high-CaCO<sub>3</sub> lakes. I conclude, therefore, that the inverse relation between

OC and CaCO<sub>3</sub> is not due to water chemistry alone, but must be due to greater dissolution of CaCO<sub>3</sub> in OC-rich sediments. A higher OC content of the sediments will result in a lower pH of interstitial waters due to decomposition of that organic matter and accumulation of organic acids, and, therefore, greater dissolution of CaCO<sub>3</sub>. In Elk Lake in Itasca State Park (Figure 2 inset) the range in % CaCO<sub>3</sub> in surface sediments is about as large as that in surface sediments from Shingobee Lake (Figure 3). The point plotted for surface sediment in Elk Lake in Figure 4 (Elk-surf; ca. 10% CaCO<sub>3</sub>, 11% OC) is the lowest CaCO<sub>3</sub> content and highest OC content measured for

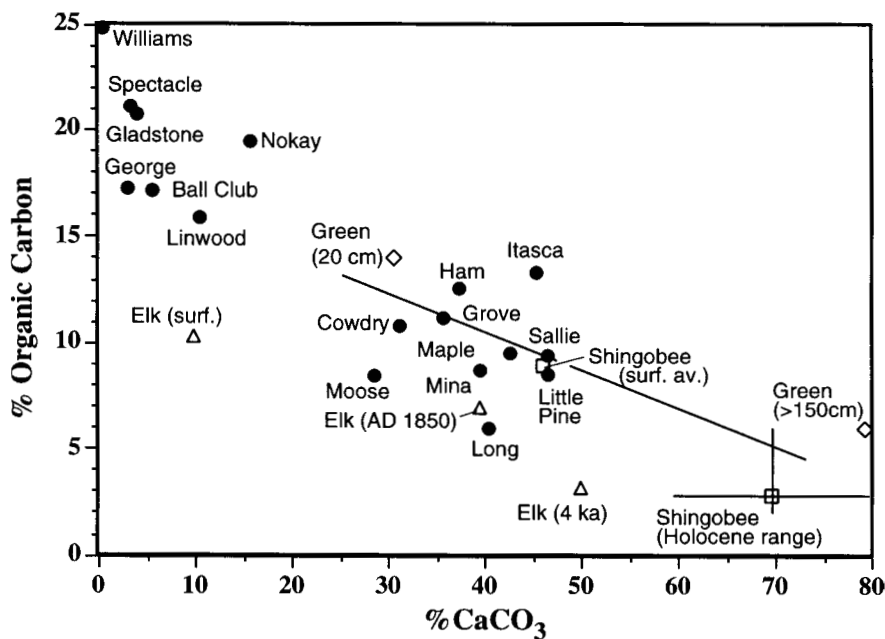


Figure 4. Cross plot of %  $\text{CaCO}_3$  vs. % organic carbon in surface sediments from central Minnesota lakes (group 3 lakes, Figure 2). Horizontal and vertical lines labeled 'Shingobee (Holocene range)' represents the ranges of concentrations of  $\text{CaCO}_3$  and organic carbon measured in Holocene sediments in Shingobee Lake (Figure 5). The square symbol at the intersection of the horizontal and vertical lines represents the average concentrations of  $\text{CaCO}_3$  and organic carbon in Holocene sediments in Shingobee Lake. The diagonal line is the best fit line ( $r = 0.92$ ;  $n = 6$ ) for the range of concentrations of  $\text{CaCO}_3$  and organic carbon measured in surface sediments in Shingobee Lake (Dean & Bradbury, 1997), and the square symbol labeled 'Shingobee (surf. av.)' is the average of the surface-sediment measurements. The symbol labeled 'Green (20 cm)' is the composition of Green Lake sediments at 20 cm depth, and the point labeled 'Green (> 150 cm)' is the average composition of Green Lake sediments below 150 cm (Figure 8A). The points labeled 'Elk (4 ka)', 'Elk (AD 1850)', and 'Elk (surf.)' are the compositions of sediments from the deepest part of Elk Lake deposited about 4,000 years ago, 150 years ago, and 20 years ago, respectively (Figure 7).

surface sediments in that lake. That point was plotted for Elk Lake because that sample came from the deepest part of the lake (30 m) which is where samples were collected from all of the other lakes plotted in Figure 4. The sediments in the marl bench in the littoral and sublittoral areas of Elk Lake contain up to 70%  $\text{CaCO}_3$ . In deep lakes like Elk Lake, much of the  $\text{CaCO}_3$  precipitated in the epilimnion is dissolved in the anoxic hypolimnion. More is dissolved at the sediment-water interface before it is buried, and even more is dissolved in corrosive pore waters. In shallow lakes like Shingobee (maximum depth of 10.6 m) and Williams (maximum depth 9.6 m), the amount of  $\text{CaCO}_3$  that is dissolved in the hypolimnion is small compared to the amount dissolved at the sediment-water interface and in the sediments. I will now examine the OC and  $\text{CaCO}_3$  contents in several cores to see if there are any patterns in changes of these two components with time.

#### $\text{CaCO}_3$ and organic carbon in cores of sediment in Minnesota lakes

Values of %  $\text{CaCO}_3$  and % OC versus sub-bottom depth for Williams and Shingobee Lakes are plotted in Figure 5. Values of percent loss on ignition at 550°C (LOI-550) and percent  $\text{CaCO}_3$  calculated from percent loss on ignition at 1000°C also are plotted to show the good agreement between the two methods of determining  $\text{CaCO}_3$  (coulometry and LOI-1000), and that, to a reasonable approximation, total organic matter measured as LOI-550 is about twice the OC content. Five pollen zones were recognized by Locke (1995; see also Schwalb et al., 1995, and Locke & Schwalb, 1997): a late-glacial/early-Holocene spruce (*Picea*) zone; an early Holocene zone dominated by jack pine (*Pinus banksiana*) and red pine (*Pinus resinosa*); a mid-Holocene prairie period dominated by oak (*Quercus*), sagebrush (*Artemisia*), and grasses (Gramineae); a hard-



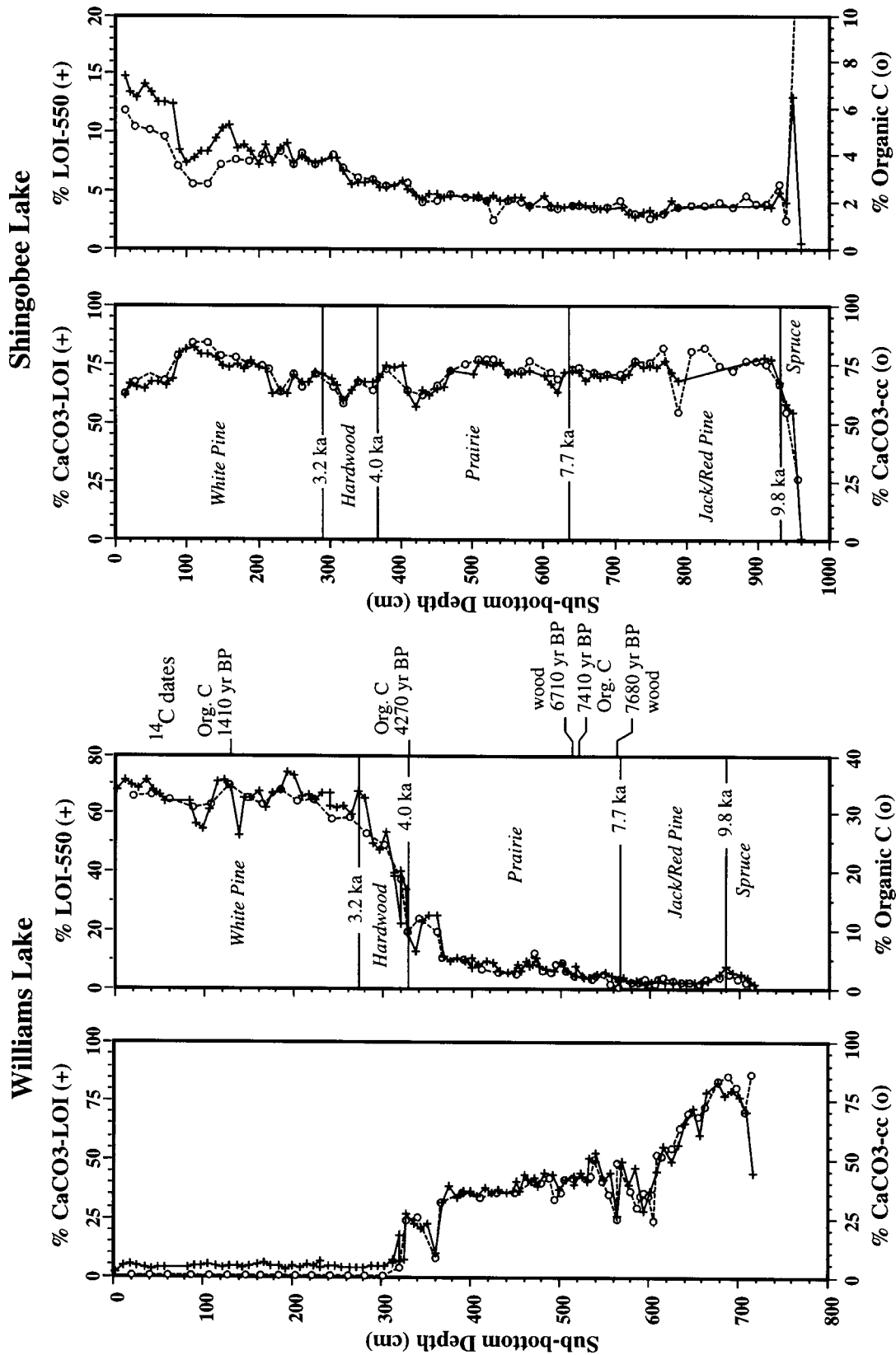


Figure 5. Profiles of % CaCO<sub>3</sub>, % organic carbon, and % LOI-550 versus depth in sediments in cores from Williams and Shingobee Lakes. Percentages of CaCO<sub>3</sub> were calculated from loss on ignition (LOI) between 550 and 1000°C (Schwalb et al., 1995), and from carbonate carbon (cc) determined by coulometry. Pollen zones and ages (in radiocarbon ka) assigned to pollen-zone boundaries (horizontal lines) are from Schwalb et al. (1995) and Locke and Schwalb (1997).

wood zone with oak and ironwood (*Ostrya*) pollen; and a late Holocene white pine (*Pinus strobus*) zone. The pollen zones in these two cores are essentially the same as those recognized from cores of sediments from other lakes in northwest Minnesota where the zones have been dated by radiocarbon. The ages shown at the boundaries of pollen zones in Figure 5 are in radiocarbon years before present assigned by Locke (1995). The five radiocarbon dates obtained from sediments in Williams Lake agree reasonably well with the ages assigned to the pollen zones (Figure 5). The radiocarbon dates are uncalibrated in order to compare with uncalibrated radiocarbon dates reported in the literature for other sites.

The most striking feature of the plots in Figure 5 is the abrupt cross-over from carbonate-carbon burial to organic-carbon burial in Williams Lake about 4,000 years ago. The sediments deposited in both Williams and Shingobee Lakes during the early Holocene had similar characteristics with about 80%  $\text{CaCO}_3$  and only a few percent OC. Carbon- and oxygen-isotope data from ostracodes (Schwalb et al., 1995) and marl (Schwalb & Dean, in preparation) show that values of both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in sediments from Williams Lake increased by about 8‰ between 9,000 and 4,000 years ago whereas those in sediment from Shingobee Lake remained at low early Holocene values throughout the Holocene. This suggests that the hydrology of Williams Lake became progressively more closed during the early Holocene but Shingobee Lake remained hydrologically open with little difference in water or sediment characteristics. As Williams Lake became more closed, the amount of OC buried in the sediments increased, slowly at first and then more rapidly at the end of the prairie period (Dean & Schwalb, 1997). Carbonate decreased progressively throughout the early Holocene. The rapid decline in  $\text{CaCO}_3$  between 660 and 600 cm sub-bottom is matched by a rapid decline in abundance of ostracode valves (Schwalb et al., 1995). Ostracode valves are scarce above 600 cm sub-bottom and are absent above 500 cm. Once the content of OC in the sediments reached about 12% at 310 cm sub-bottom,  $\text{CaCO}_3$  was eliminated from the sediments entirely (Figure 5).

Elk Lake in Itasca State Park (Figure 2) was not classified by Dean and Gorham (1976) as a high-carbonate group 3 lake because profundal surface sediments in their survey contained only 20%  $\text{CaCO}_3$  (Table 1). Elk Lake drains into Lake Itasca and, therefore, the two lakes have virtually identical water chemistries (Table 1). The surface sediments in Lake Itasca and, in fact, most of the surface sediments in Elk

Lake, contain more than 30%  $\text{CaCO}_3$  (Figure 3A). As discussed under surface sediments, the low content of  $\text{CaCO}_3$  in the deepest part of Elk Lake (30 m) is due to greater dissolution of  $\text{CaCO}_3$  in the anoxic hypolimnion and sediments. The  $\text{CaCO}_3$  content of profundal sediments in Elk Lake reported by Dean and Gorham (1976) was 20% (Table 1), but analyses of sediments in a more recent frozen box core from the deepest part of Elk Lake (Figure 7C) show that the  $\text{CaCO}_3$  contents in surface sediments are closer to 10% (the point labeled 'Elk (surf)' in Figure 4). During the first 5,000 years of the life of Elk Lake, as calibrated by annual laminations (varves; Anderson et al., 1993), the  $\text{CaCO}_3$  content of sediments fluctuated mostly between 40 and 50% (Figure 6A), and that of OC between 2 and 4% (Figure 6B). At about 4.0 ka, the  $\text{CaCO}_3$  content of the sediments was about 50% and that of OC was about 3% (Figure 6; Figure 7A; point labeled 'Elk (4 ka)' in Figure 4). At that time the OC content of sediments in the deepest part of Elk Lake began to increase rapidly (Figure 6B), and that of  $\text{CaCO}_3$  began to decrease (Figure 6A). The increase in OC in sediments of Elk Lake beginning about 4 ka was not so dramatic as that in sediments in Williams Lake at the same time (Figure 5B), but still represents a significant change. Because of the precise varve calibration and measured bulk densities (Dean, 1993), I was able to calculate mass accumulation rates (MAR) for each component in Elk Lake sediments. The changes in MARs of  $\text{CaCO}_3$  and OC (dashed lines in Figure 6) are not as large as changes in percentages of these two components, but, as I showed for surface sediments, it is the relative increase in OC that is the key to  $\text{CaCO}_3$  dissolution. I do not know whether the changes in OC and  $\text{CaCO}_3$  burial in both Williams and Elk Lakes is coincidental and due to internal lake processes, or the result of external forcing, such as the return of cooler, moister conditions and reforestation following the prairie period. Results of analyses of sediments in additional cores presently being conducted may help to resolve this question.

### Discussion: Eutrophication and biogeochemical dynamics in lakes

#### *Eutrophication and the carbon cycle*

Between 4 ka and European settlement (ca. AD 1850), the OC content of sediments deposited in the deepest part of Elk Lake increased from 3–7%, and that of  $\text{CaCO}_3$  decreased from 50–40% (Figure 7A; point

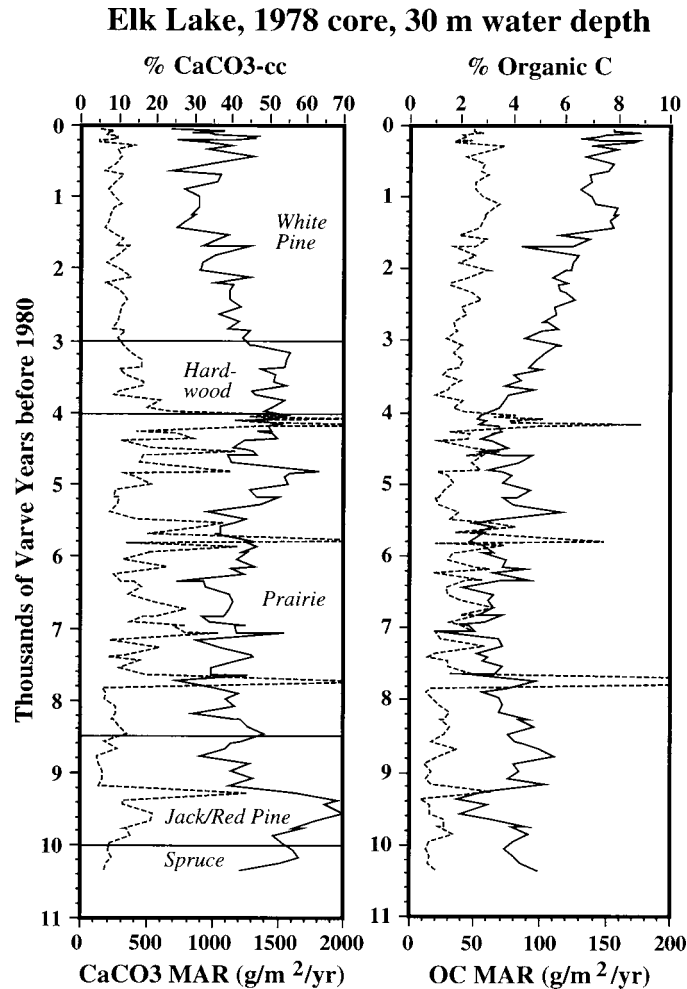


Figure 6. Profiles of percentages (solid lines) and mass accumulation rates (MAR) (dashed lines) of  $\text{CaCO}_3$  and organic carbon versus depth in sediments in a core from Elk Lake (data of Dean, 1993). Pollen zones (horizontal lines) are from Whitlock et al. (1993).

labeled 'Elk (AD1850)' in Figure 4). Again, this change was the result of natural eutrophication. However, since AD 1850, the OC content of sediments deposited in the deepest part of Elk Lake increased from 7–10%, and that of  $\text{CaCO}_3$  decreased dramatically from 40–10% (Figure 7B and C; point labeled 'Elk (surf)' in Figure 4). This was the result of cultural eutrophication, related at least initially to logging activities in Itasca State Park between 1903 and 1919. At that time the level of Elk Lake was raised to float logs into Lake Itasca and down the Mississippi River (Hansen et al., 1974). If the concentration organic matter continues to increase in the profundal sediments of Elk Lake, and the trend of decreasing  $\text{CaCO}_3$  shown in Figures 4 and 7 continues, I would expect that  $\text{CaCO}_3$

will be completely eliminated in the profundal sediments of Elk Lake just as it was in Williams Lake 4000 years ago. The changes in contents of OC and  $\text{CaCO}_3$  in the upper meter of sediment in Shingobee Lake probably also are the result of cultural eutrophication (Figure 5). In this interval, OC content increases from 7–15% and  $\text{CaCO}_3$  content decreases from 85–60%. The ranges of OC and  $\text{CaCO}_3$  contents in surface sediment in Shingobee Lake are extreme (Figure 3A; line in Figure 4), and this variation is related entirely to variable dissolution of  $\text{CaCO}_3$  in the sediments (Dean & Bradbury, 1997). In spite of this variation in carbon content of surface sediments, the average (point labeled 'Shingobee (surf. av.)' in Figure 4) still represents a significant change from sediments

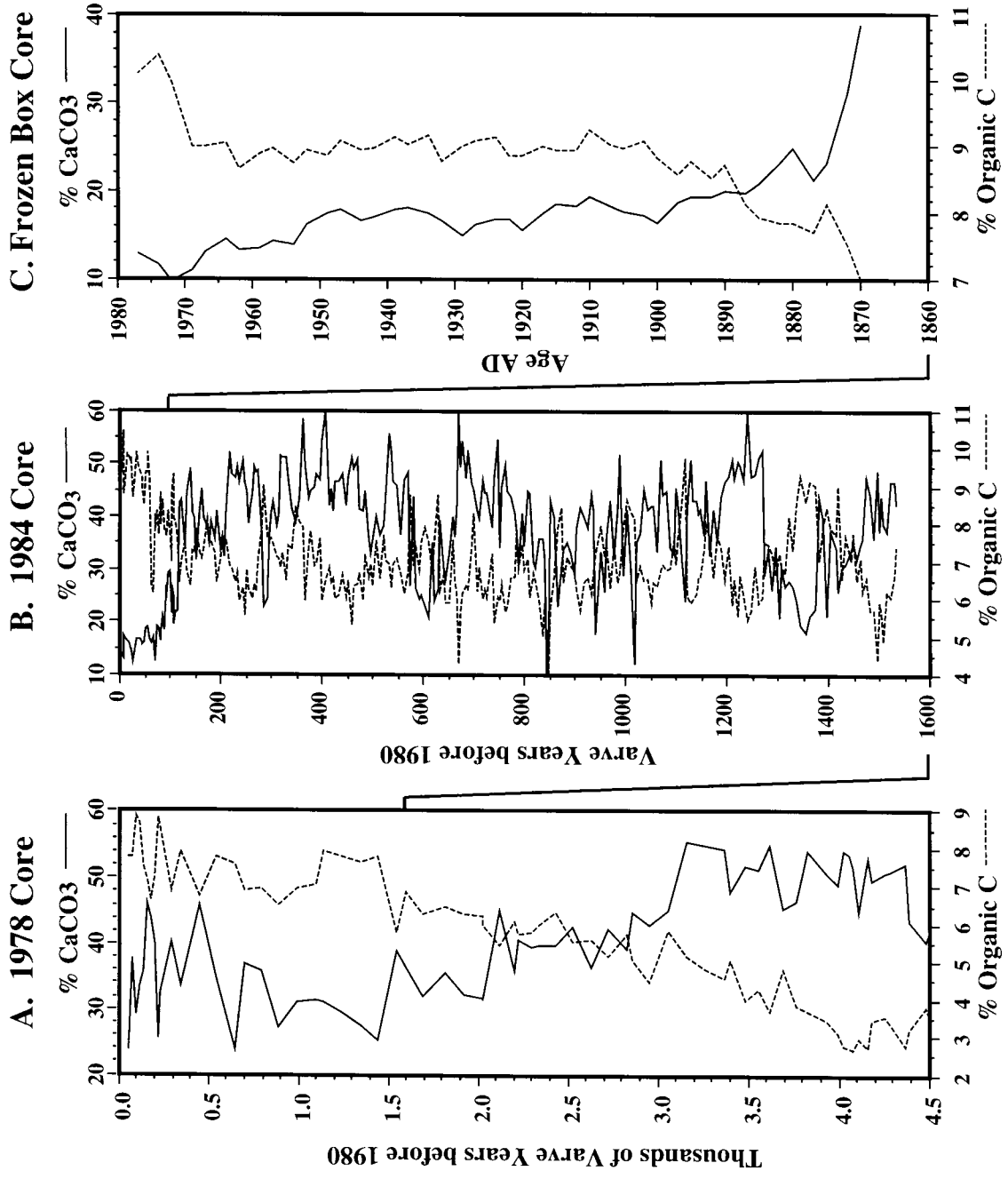


Figure 7. Profiles of % CaCO<sub>3</sub> and % organic carbon in sediments deposited in Elk Lake over three time intervals: (A) last 4 ky (data of Dean, 1993); (B) last 1550 years (data of Dean et al., 1994), and (C) since AD 1870 (Dean unpublished data).

deposited during most of the Holocene (Figure 5; point and lines labeled 'Shingobee (Holocene range)' in Figure 4).

Based on cores from central Minnesota lakes for which there are basal radiocarbon dates, 10–12 m of Holocene profundal sediment is fairly typical (H. E. Wright, Jr., personal communication, 1997). At 10 m deposited in 10,000 years, an average Holocene sedimentation rate in a central Minnesota lake is about 1 mm yr<sup>-1</sup>. The average Holocene sedimentation rate in 164 mid-latitude (40–50° N) Holocene lakes in eastern North America (including Minnesota) is 81 cm kyr<sup>-1</sup> (0.8 mm yr<sup>-1</sup>) (Webb & Webb, 1988). Webb and Webb also note that sediments deposited during the last 330 years accumulated at rates that were four to five times faster than Holocene rates. Post-settlement sediments in Minnesota lakes (i.e., those deposited during the last 150 years) were deposited at rates up to ten times higher because these sediments typically are 50–100 cm thick, and up to 150 cm thick, in urban and agricultural areas, and 40–50 cm thick in forested regions of northeastern Minnesota (based on the increase in ragweed pollen (Bradbury, 1975) and <sup>210</sup>Pb dating; D. R. Engstrom, personal communication, 1997). Therefore, the top meter of sediment in Shingobee Lake most likely was deposited during the last 150 years.

Another potential Williams-Shingobee pair of lakes are Green and Spectacle Lakes on the Anoka sand plain of east-central Minnesota (Figure 2). Dean and Gorham (1976) classified Green Lake as a high-carbonate group 3 lake based on a CaCO<sub>3</sub> content of 31% (Table 1). They classified Spectacle Lake as a high-organic group 3 lake based on an organic content of > 30% (loss on ignition; 21% OC, Table 1). Short (ca. 4 m) cores from Green and Spectacle Lakes (Figure 8) show considerable changes that probably are the result of cultural eutrophication although no dates have been obtained for these two cores. In Green Lake, this change is manifested as a marked increase in OC from 7% at 80 cm to 14% at 20 cm, and a marked decrease in CaCO<sub>3</sub> from 80% at 150 cm to 30% at 20 cm (Figures 4 and 8A). The OC content at the top of the Green Lake core is even higher than the 10.6% measured by Dean and Gorham (1976; Table 1; arrow on % OC scale in Figure 8A). The top of the Spectacle Lake core contains about 21% OC, the same as measured by Dean and Gorham (Table 1; arrow in Figure 8B), but the OC content is > 35% below 60 cm. Dean and Gorham reported 3% CaCO<sub>3</sub> in their surface-sediment sample from Spectacle Lake (Table 1), but that was measured by loss on ignition. Measurements of inorganic carbon by coulo-

meter show that the sediments in Spectacle Lake are indeed carbonate-free. Because the sediment in Spectacle Lake consists of essentially two components (organic matter plus detrital clastic material), the decrease in OC at the top of the Spectacle Lake core is the result of dilution by increased detrital clastic material, almost certainly due to increased erosion following land clearing in the late 1800s.

Collecting long cores of the entire Holocene from Green and Spectacle Lakes is planned for 1998. I anticipate that the trends in OC and CaCO<sub>3</sub> in earlier Holocene sediments in Green Lake will be similar to those in Shingobee Lake, that is OC should decrease with depth and CaCO<sub>3</sub> should remain constant at between 70 and 80%. I anticipate that trends in OC and CaCO<sub>3</sub> in earlier Holocene sediments in Spectacle Lake will be similar to those in Williams Lake (Figures 5A and B), and that at some depth there will be a marked decrease in OC and a marked increase in CaCO<sub>3</sub>. If that OC-CaCO<sub>3</sub> cross-over occurs in sediments deposited at about 4 ka, this would be one further piece of evidence that the dynamics of the carbon cycle in lakes of central Minnesota changed profoundly after the mid-Holocene prairie period.

#### *Influences of the carbon cycle on the biogeochemical dynamics of other elements*

Sediment-trap studies in Elk Lake (Nuhfer et al., 1993) and detailed analyses of sediments deposited over the last 1500 years in Elk Lake (Dean et al., 1994) show that the carbon cycle in a lake and lake sediments can

*Table 2.* Major components in Elk Lake sediments from a single sample from about 5.7 ka varve years, and averaged for the the last 2.0 ky and for the period from 10.36 to 8.47 ka. Values in parentheses following values of organic matter + H<sub>2</sub>O are percent organic carbon. Leaders (—) indicate insufficient data.

Component	Percent		
	last 2.0 ky	5.7 ka	10.36–8.47 ka
CaCO <sub>3</sub>	40.	38.	70.
Org. Matter + H <sub>2</sub> O (OC)	21.(7.5)	7.1 (2.7)	17. (4.0)
SiO <sub>2</sub>	18.	39.	—
Al <sub>2</sub> O <sub>3</sub>	0.8	6.4	2.9
Fe <sub>2</sub> O <sub>3</sub>	16.	3.1	5.7
PO <sub>4</sub>	3.1	0.7	—
MnO	1.4	0.2	2.6
MgO	0.8	3.2	1.3
Total S	0.3	0.2	1.3
K <sub>2</sub> O	0.2	1.2	—
Na <sub>2</sub> O	0.1	0.9	0.2
Total	101.7	100.0	—

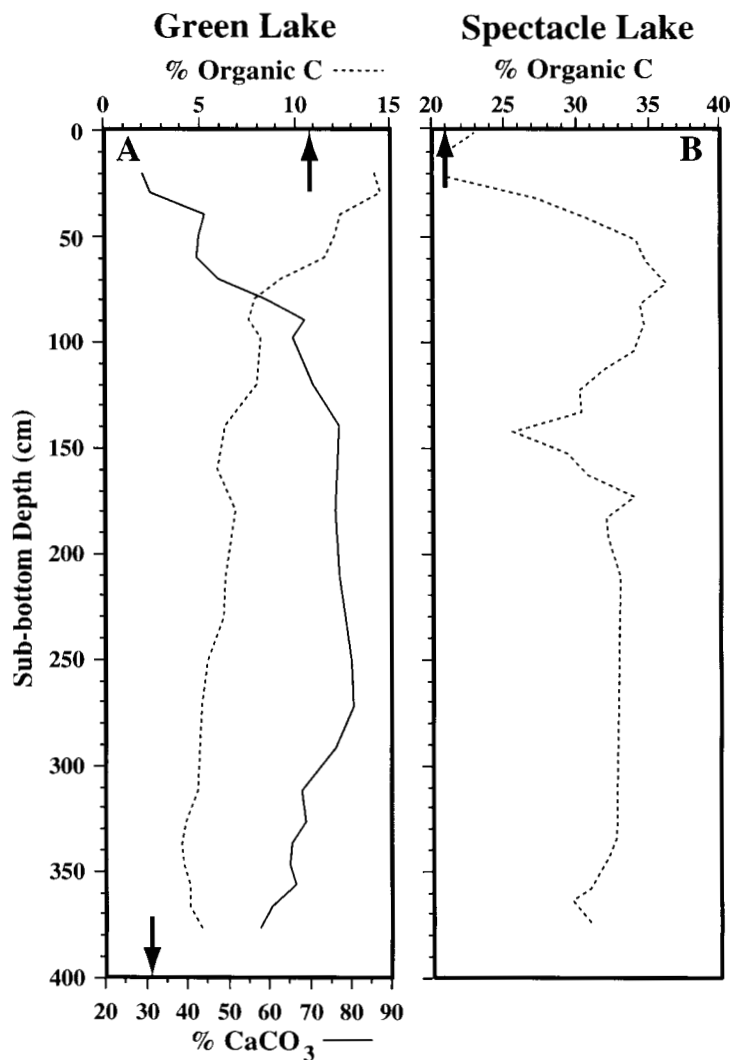


Figure 8. Profiles of % CaCO<sub>3</sub> and % organic carbon in sediments from Green Lake, and % organic carbon in sediments from Spectacle Lake. Arrows indicate the values of % CaCO<sub>3</sub> and % organic carbon in profundal surface sediments from the same lakes reported by Dean and Gorham (1976).

have a profound influence on the biogeochemical cycles of other elements. More than 90% of the components in sediments deposited in Elk Lake over the last 2,000 years were produced in the lake (Table 2). These include biogenic silica (diatoms), organic matter, CaCO<sub>3</sub>, and several iron and manganese minerals, with very little detrital clastic material. Sediment deposited 5,700 years ago (Table 2) reflects the maximum influx of detrital clastic material into Elk Lake (Dean, 1993). Identified iron and manganese compounds are ferric hydroxide, manganese oxyhydroxides, rhodochrosite (MnCO<sub>3</sub>), and an iron-manganese phosphate

mineral tentatively identified as rockbridgeite (Nuhfer et al., 1993).

Immediately after spring turn-over, the iron and manganese concentrations throughout the water column in Elk Lake are < 3 μg L<sup>-1</sup> (parts per billion). During summer stratification, concentrations of iron and manganese increase in the hypolimnion reaching low part per million levels prior to fall over-turn at which time they are major cations. There are marked concentration gradients of these two ions in the hypolimnion, decreasing away from the sediments, indicating that the iron and manganese are derived from dissolution of

### Elk Lake Deep Trap, 1983-1984

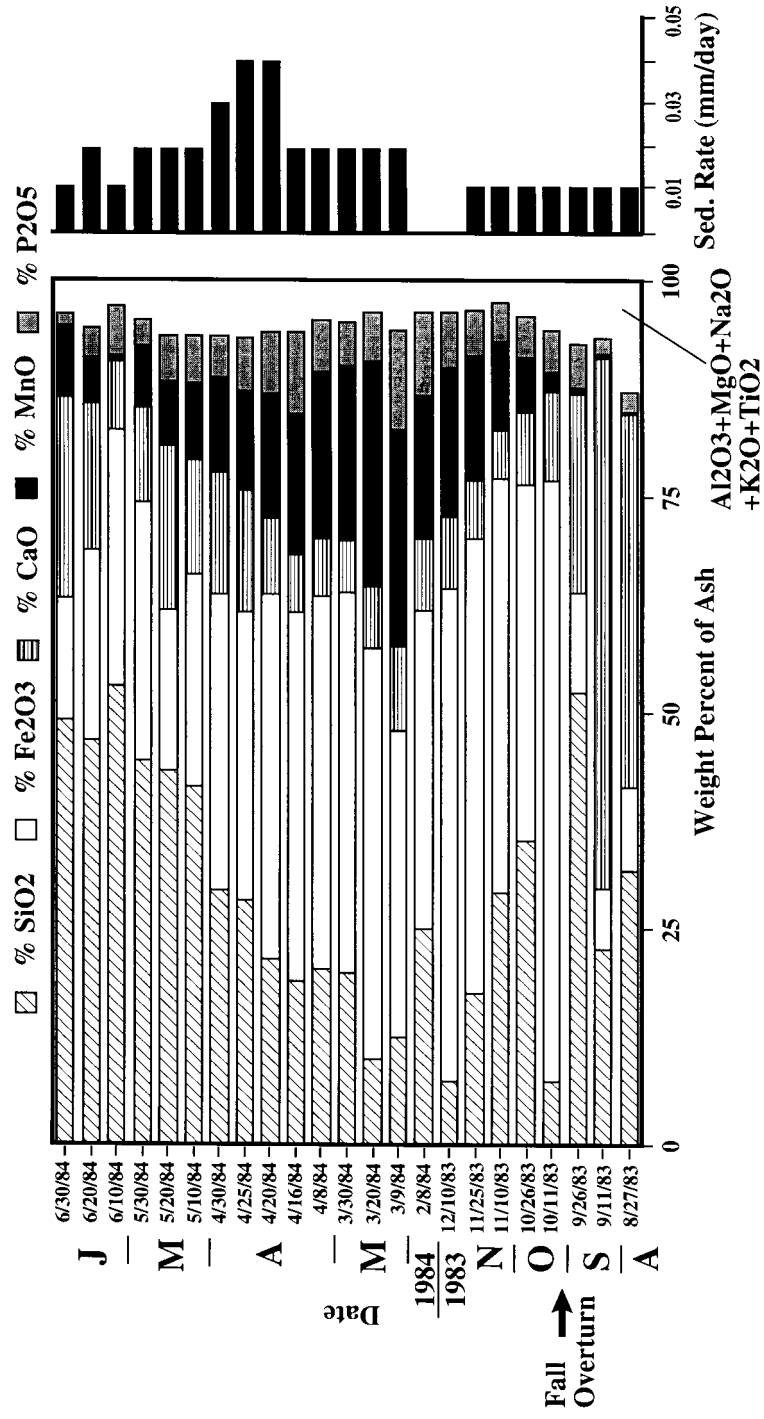


Figure 9. Concentrations of major-element oxides in ashed sediment samples from a sediment trap deployed in the hypolimnion of Elk Lake from August, 1983 to July, 1984. Also shown are sedimentation rates for two-week periods determined for the same sediment trap.

iron and manganese minerals in the sediments. At fall over-turn when iron- and manganese-rich, anoxic hypolimnetic waters mix with well oxygenated epilimnetic waters, there is massive precipitation of ferric hydroxide that is manifested as a bright orange floc in sediment traps and high iron concentrations in the sediment collected in the traps (Figure 9). When varves in sediment cores are examined under the microscope, ferric hydroxide appears as a orange gel-like layer overlying the white  $\text{CaCO}_3$  layer deposited during late summer (Figure 9; Dean & Megard, 1993). The ferric hydroxide layer in varves often has a thin black band at the base (Anderson, 1993) suggesting that manganese oxyhydroxides may precipitate out before the ferric hydroxide. Iron and manganese continue to accumulate in sediment trap during the winter months when sedimentation rates are extremely low (Figure 9). Silica accumulates in the traps mainly in the spring and fall (Figure 9) coincident with spring and fall diatom blooms.

These biogeochemical events are illustrated diagrammatically in Figure 10 for the periods of summer stratification and fall overturn. Algal photosynthesis during summer in the epilimnion consumes  $\text{CO}_2$ , produces organic matter, and increases pH triggering calcite precipitation (Dean & Megard, 1993). Some (most?) of the organic matter produced in the epilimnion decomposes in the hypolimnion imposing a high biological oxygen demand on the hypolimnion, which becomes anoxic at some point during the summer depending upon how high that demand is. Decomposition of organic matter also produces  $\text{CO}_2$  and lowers the pH dissolving some of the  $\text{CaCO}_3$  produced in the epilimnion. The iron and manganese minerals formed as described above (Figure 10B) under oxic conditions in the epilimnion are unstable under anoxic conditions in the hypolimnion and sediment pore waters. Some portions of the previously formed iron and manganese minerals dissolve releasing iron, manganese, and phosphorus to the hypolimnion. The amounts of organic matter,  $\text{CaCO}_3$ , and iron and manganese minerals that are ultimately buried in the sediments, therefore, are functions of how much is produced in the epilimnion and how much is destroyed in the hypolimnion and sediments. If the intensities of these processes change with time, these changes should be recorded in the sediments.

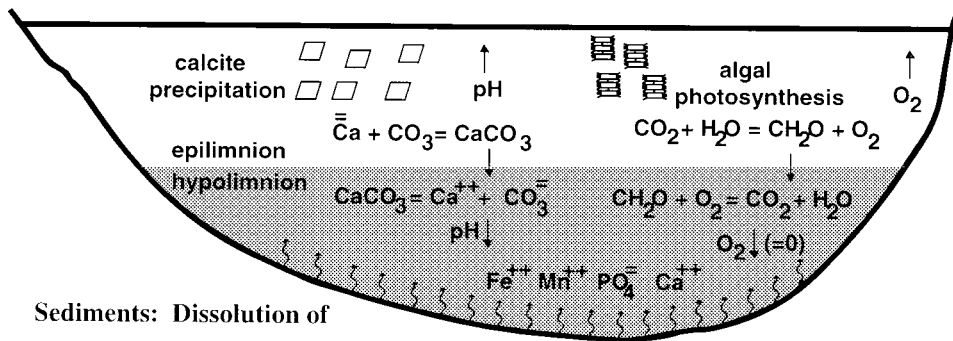
The marked increase in OC in Elk Lake that began at about 4 ka resulted in a decrease in  $\text{CaCO}_3$  (Figure 7). Using the model for summer stratification (Figure 10A) and setting it in motion through time, I interpret the changes in the carbon cycle in Elk Lake over the last 4000 years as indicating a gradual increase in

organic productivity that would also place a greater oxygen demand on the hypolimnion. As a result of greater oxygen consumption, the hypolimnion became anoxic earlier and remained anoxic longer with a lower pH. More  $\text{CaCO}_3$  may have been produced in the epilimnion because of the increased pH, but much more was dissolved in the corrosive hypolimnion and sediment pore waters. The net result of this 'carbon pump' was an increase in OC burial and a decrease in  $\text{CaCO}_3$  burial. If the hypolimnion was anoxic for a longer period of time, I would anticipate that more iron, manganese, and phosphorus would accumulate in the hypolimnion and more iron, manganese, and phosphorus would precipitate on mixing with the oxic epilimnion. If the rate of production in the epilimnion was greater than the rate of destruction in the sediments, then there should be a net increase in iron, manganese, and phosphorus in the sediments. This is exactly what happened in response to the OC increase beginning at 4 ka. Between 4 and 2 ka, the concentration of iron in the sediments in the deep core from Elk Lake increased from 5–20%; that of manganese increased from 0.5–2%; and that of phosphorus increased from 0.6–1.8% (Dean, 1993). The phosphorus increase has an interesting implication because it suggests that if phosphorus was not removed from the lake by precipitation as iron phosphate (rockbridgeite?), the rate of eutrophication may have been much greater. The rapid increase in iron and manganese beginning at 4 ka indicates that the supply of dissolved iron and manganese was not limiting. The ultimate source of iron and manganese probably is from groundwater entering the lake through porous littoral sediments. There is no direct evidence for this, but there are several iron-rich springs around the lake, and A. L. Baker (written communication, 1992) indicated that iron-rich waters from springs enter the hypolimnion as density currents during the summer because the cold (ca 7 °C) and ionically more concentrated (ca. 2x lake water; Megard et al., 1993) spring water is heavier than the epilimnetic water. During the prairie period, groundwater influx into Elk Lake may have been reduced and then reactivated when wetter conditions returned after 4 ka.

The detailed analyses of Elk Lake sediments deposited over the last 1500 years (Dean et al., 1994) show that there often is an antithetic relation between OC and  $\text{CaCO}_3$  (Figure 7B) indicating that the carbon pump was operating at short (decadal) time scales. This relation is better seen in smoothed plots of percentages of OC,  $\text{CaCO}_3$ , Fe, and P for the last 1500 years (Figure 11), which show several 400-year cycles that are best



### A. Period of Summer Stratification



Sediments: Dissolution of

$\text{FeOOH}$  (ferric hydroxide)

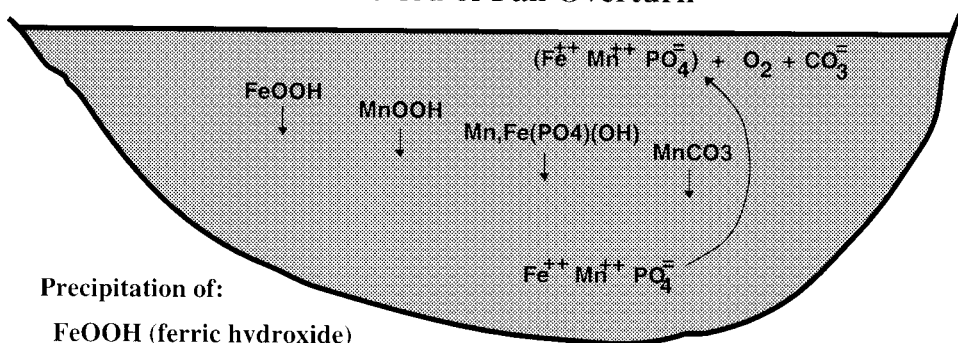
$\text{MnOOH}$  (manganese oxyhydroxides)

$\text{Mn,Fe(PO}_4\text{)(OH)}$  (iron phosphate = rockbridgeite?)

$\text{MnCO}_3$  (rhodochrosite)

$\text{CaCO}_3$  (calcite)

### B. Period of Fall Overturn



Precipitation of:

$\text{FeOOH}$  (ferric hydroxide)

$\text{MnOOH}$  (manganese oxyhydroxides)

$\text{Mn,Fe(PO}_4\text{)(OH)}$  (iron phosphate = rockbridgeite?)

$\text{MnCO}_3$  (rhodochrosite)

Figure 10. Biogeochemical processes inferred to be operating in Elk Lake, Minnesota during summer stratification (A) and fall overturn (B). See text for discussion of processes.

seen in the iron data. The cycle that includes the time interval between 1600 and 1200 years ago shows distinct maxima in amounts of OC, Fe, and P, and a distinct minimum in amount of  $\text{CaCO}_3$ . This appears to be a period when redox conditions in Elk Lake were particularly sensitive to the carbon pump.

### Conclusions

The accumulation rates of organic matter and  $\text{CaCO}_3$  in lake sediments are delicately balanced between the

rates that they are produced in the epilimnion and the rates that organic matter is decomposed and  $\text{CaCO}_3$  is dissolved in the hypolimnion and sediments. Today, lakes in Minnesota that are saturated with calcite during the summer months usually precipitate calcite in late summer in response to increasing pH during algal blooms. However, if the sediments of those lakes contain large amounts of organic matter (more than about 12% organic carbon), little if any  $\text{CaCO}_3$  is preserved in the sediments. In some lakes, the increase in sedimentary organic matter and dissolution of  $\text{CaCO}_3$  happened thousands of years ago in response

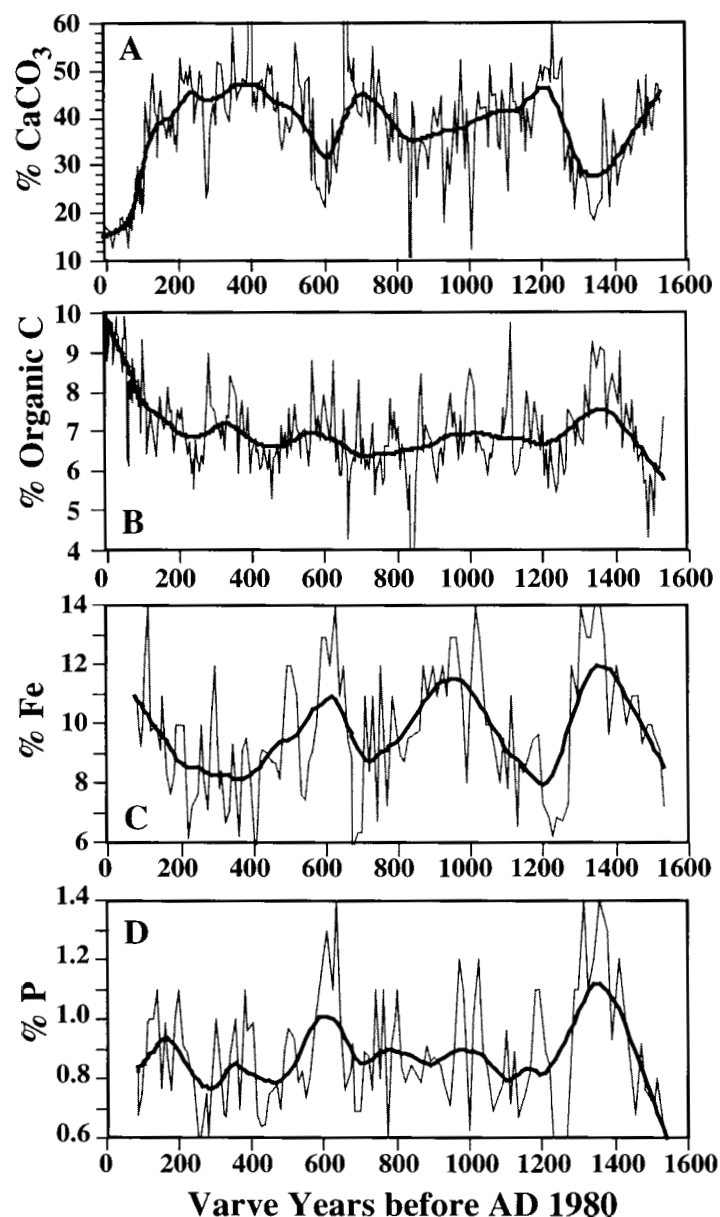


Figure 11. Raw data (thin lines) and smoothed profiles (15% weighted smoothing; heavy lines) of % CaCO<sub>3</sub> (A), % organic carbon (B), % Fe (C), and % P (D) in sediments deposited over the last 1550 years in Elk Lake (data of Dean et al., 1994).

to natural eutrophication. In other lakes, these processes happened, or are happening now, in response to cultural eutrophication. Although increased organic productivity due to eutrophication may increase the pH of the lake water and cause greater precipitation of CaCO<sub>3</sub>, the decomposition of the produced organic matter in the hypolimnion and sediments causes much greater dissolution of precipitated CaCO<sub>3</sub>.

In addition to the effect of organic productivity on CaCO<sub>3</sub> accumulation, it may also affect the biogeochemical cycles of other elements, particularly redox-sensitive elements. For example, increased productivity usually results in more prolonged hypolimnetic oxygen deficiency, which, in turn, may cause a build-up of elements such as iron and manganese in the hypolimnion. When oxygen-deficient hypolimnetic waters

mix with oxygenated epilimnetic waters during overturn, precipitation of oxidized iron and manganese minerals may occur and ultimately result in higher accumulation of iron and manganese in the sediments, assuming that iron and manganese are continuously replenished by ground water.

### Acknowledgments

This research was supported by the US Geological Survey Global Change and Climate History Program. I thank Kerry Kelts and Joe Rosenbaum for helpful reviews.

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