Historic calcite record from the Finger Lakes, New York: Impact of acid rain on a buffered terrane

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ABSTRACT

Most previous studies on the effects of acid rain have been conducted in areas with low acid-neutralizing, or buffering, capacity. In contrast, significantly less study has occurred in calcareous terrane that has high-buffering-capacity and that has traditionally been thought to be "insensitive" to the effects of acid rain. To address this fundamental inequity we have conducted a comprehensive study of near-surface (<1 m), historic age (<200 yr) sediments in the Finger Lakes of central New York State, a high buffering capacity area that has received significant quantities of acid rain. In particular, we have focused on authigenic calcite contained in historic bottom sediment as well as water-column geochemistry between 1972 and 1999.

Results indicate that the open-water precipitation of calcite ("whitings") returned to 7 of the 11 Finger Lakes during historic time following an ~4500 ^{14}C yr hiatus. Only those lakes with calcite in the near-surface sediment have calcareous soils and/or limestone outcrops in their drainage basins and summer surface waters that are supersaturated with respect to calcite. Water-column data indicate that the saturation state of summer surface waters has increased in at least seven Finger Lakes between 1972 and 1999 and that calcium loading to lakes lacking calcite has also increased over the same time interval.

We hypothesize that acid rain has increased carbonate weathering in the Finger Lakes region, leading to an increase in supersaturation of summer surface waters with respect to calcite. The precipitation of calcite in summer is triggered by evaporation, temperature increase, and/or photosynthetic removal of carbon dioxide. This new "chemical weathering" hypothesis contrasts with, but is not mutually exclusive of, the traditional "cultural-eutrophication" model that suggests that increased nutrient loading, biological productivity, and CO_2 removal are the primary causal mechanisms for historic calcite precipitation. Stable carbon isotope and water-column geochemical data from the Finger Lakes indicate decreasing levels of primary production since at least the 1960s, and there are statistically significant correlations between CO_2, SO_2, and NO_x emissions and calcite content of bottom sediments.

Historic calcite precipitation in the Finger Lakes began as early as the 1820s, suggesting that naturally acidic rain falling on freshly deforested and tilled landscapes increased chemical weathering and brought these lakes to supersaturation. There was also a rapid increase in calcite precipitation beginning in ca. 1940 (coincident with increased industrialization and acidic rainfall associated with World War II) that continued into the 1990s. During the mid- to late 1990s, calcite precipitation decreased in the Finger Lakes following the introduction of zebra mussels. Unlike regions with low acid-neutralizing-capacity where acid rain results in the "acidification" of lakes, acidic deposition across well-buffered terrane may result in the "alkalization" of lakes.

Keywords: acid rain, Finger Lakes, calcite precipitation, buffered terranes, alkalization.

INTRODUCTION

During the second half of the twentieth century, acidic deposition ("acid rain") became widely recognized as a critical, global environmental issue that has had detrimental effects on aquatic and terrestrial environments in North America, Europe, and Asia. Acidic deposition is defined as the "transfer of strong acids and acid-forming substances from the atmosphere to the surface of the Earth" (Driscoll et al., 2001). These acids are derived primarily via the gaseous and particulate emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from power plants and other fossil-fuel–burning industries and activities (Driscoll et al., 2001). Effects of acidic precipitation in North America were first recognized in the 1960s at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire (Likens et al., 1972), an igneous and metamorphic terrane having low acid-neutralizing capacity.

Sulfur dioxide emissions in the United States became subject to control in 1970 with implementation of the Federal Clean Air Act, which was supplemented in 1990 by the Acid Deposition Control Program, designed to further curb SO_2 emissions and initiate controls on NO_x emissions (Driscoll et al., 2001). Sulfur dioxide emissions during the twentieth century increased from ~9 Mt (million metric tons) in 1900 to a maximum of ~28.8 Mt in 1973, followed by a decline to ~17.8 Mt in 1998. In contrast, emissions of NO_x have in-
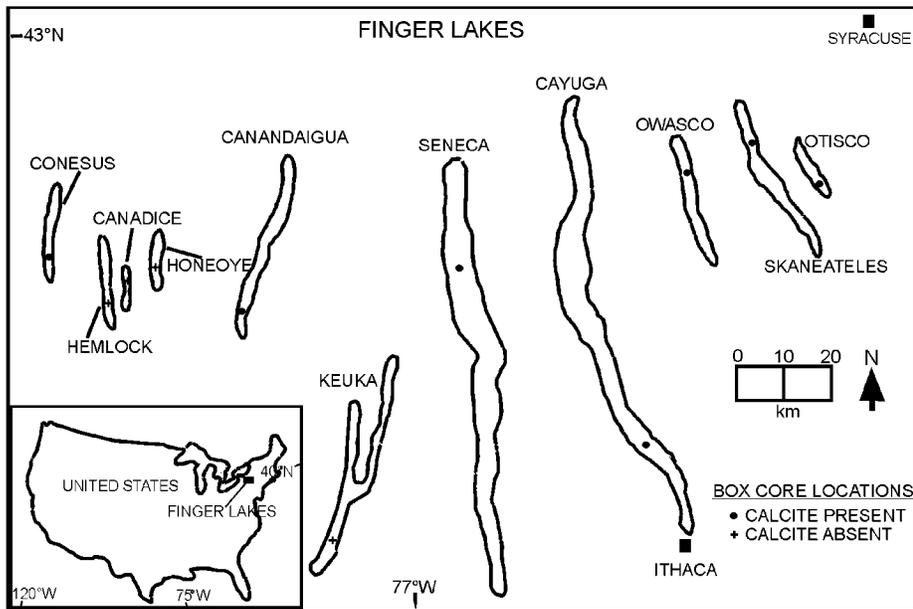
Figure 1. Index map of the Finger Lakes, illustrating location of box cores used in this study. Solid circles indicate calcite present; crosses indicate calcite absent.
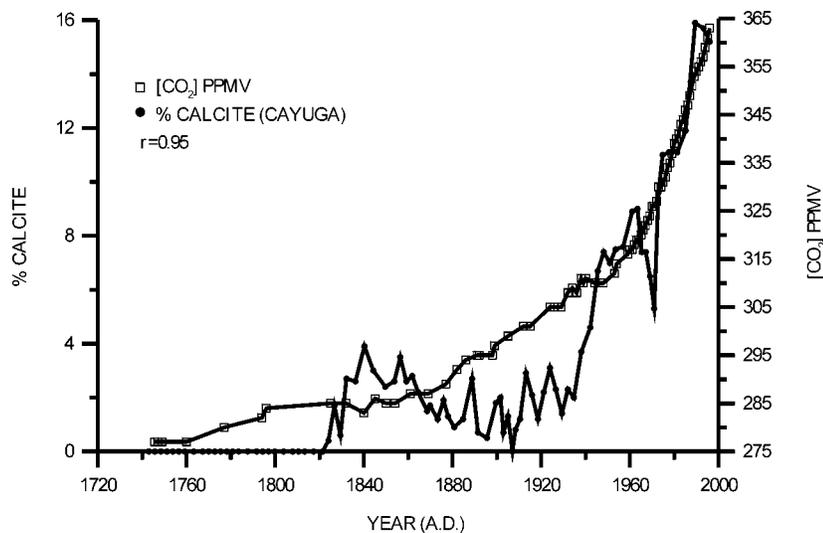

Figure 2. Temporal correlation between calcite content in Cayuga Lake and atmospheric carbon dioxide concentrations (from direct measurements and ice cores) over the past 200 yr (from Mullins, 1998a).

the Adirondack and Catskill Mountains of New York State as well as mountainous regions of New England, which have low acid-neutralizing capacity because of their elevation and the nature of their underlying bedrock. Regions with high acid-neutralizing capacity, such as calcareous terranes, have traditionally been viewed as "insensitive" to acidic deposition.

Does acid deposition significantly affect aquatic environments located in areas of relatively high acid-neutralizing capacity? To address this fundamental question, we have undertaken a comprehensive study of near-surface (<1 m), historic age (<200 yr) sediments in the 11 Finger Lakes of central New York State (Fig. 1). This present study is an outgrowth of previous work by Anderson et al. (1997) and Mullins (1998a, 1998b) on Holocene authigenic carbonates in Seneca and Cayuga Lakes, the two largest Finger Lakes (Fig. 1). They discovered that the open-water precipitation of calcite ("whitings") was both significant and widespread in these Finger Lakes during the early to middle Holocene when summer temperatures were 2–3 °C warmer than today (Ganopolski et al., 1998). However, calcite precipitation ceased by ca. 5500 ^{14}C yr B.P. in Seneca Lake (Anderson et al., 1997) and by ca. 3500 ^{14}C yr B.P. in Cayuga Lake (Mullins, 1998a, 1998b) during the transition from the relatively warm/wet Holocene Hypsithermal to the relatively cool/dry Neoglacial at ca. 4500 ^{14}C yr B.P. (Mullins and Halfman, 2001). Following at least a 3500 ^{14}C yr hiatus, calcite precipitation in Cayuga Lake returned during historic times, beginning slowly in the 1800s, followed by an exponential rise in about 1940 and extending through the 1990s (Mullins, 1998a, 1998b; Mullins et al., 2001).

Modern whiting events in the Finger Lakes have also been documented by direct observations and measurements in Otisco Lake (Effler and Johnson, 1987), Owasco Lake (Effler et al., 1987a), and Cayuga Lake (Effler et al., 2001). Such whitings have dramatic impacts on water clarity and quality and thus on the overall aquatic environment of the Finger Lakes. Mullins (1998a) further noted that the historic rise in calcite precipitation correlates extremely well ($r = 0.95$) with the anthropogenic rise of carbon dioxide in the atmosphere (Fig. 2), suggesting a linkage between industrialization and calcite precipitation in the Finger Lakes. On the basis of this suggested linkage, Mullins (1999) posed the hypothesis that historic calcite precipitation may be a consequence of acidic deposition and increased carbonate weathering on the buffered terrane surrounding the Finger Lakes.

creased from ~2.4 Mt in 1900 to ~21.8 Mt in 1990, where they have remained relatively constant to the present (Driscoll et al., 2001).

United States emissions of SO_2 and NO_x are greatest in the Midwest, particularly states in and around the Ohio Valley (Driscoll et al., 2001). Prevailing westerly winds transport SO_2 and NO_x emissions into the northeastern United States, where they are converted to sulfuric (H_2SO_4) and nitric (HNO_3) acids. Highest rates of acidic deposition have occurred over Pennsylvania and New York State (Stoddard

et al., 1999; Driscoll et al., 2001). Despite reduced SO_2 emissions in the United States since 1970, recovery from acidic deposition has been slower than expected, resulting in a continuing national environmental issue (Likens et al., 1996; Stoddard et al., 1999; Driscoll et al., 2001; Krajick, 2001).

Over the past 30 yr we have learned a great deal about acidic deposition and its effects on terrestrial and aquatic ecosystems. The vast majority of previous studies, however, have been conducted in acid-sensitive areas such as
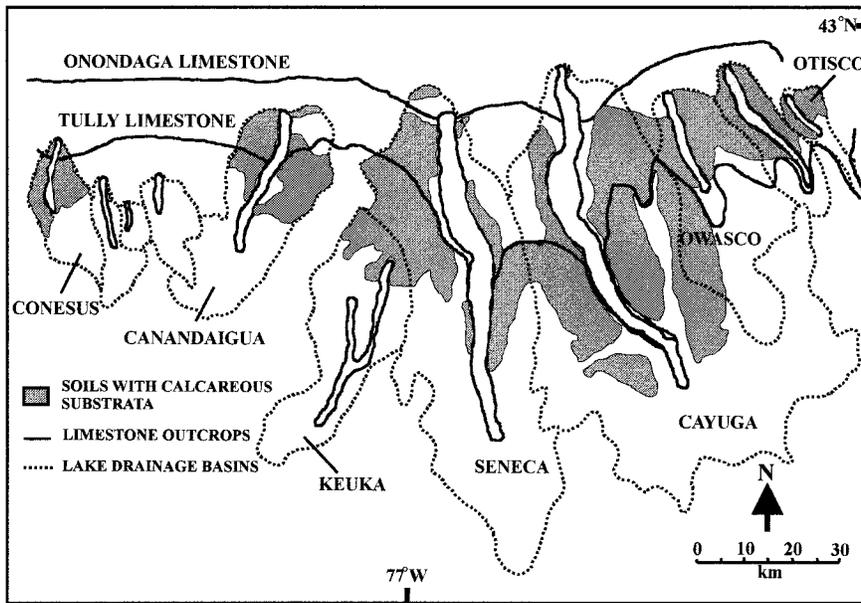
Figure 3. Surficial geology map of the Finger Lakes region (from Bloomfield, 1978), illustrating individual lake drainage basins, distribution of calcareous soil, and narrow outcrops of limestone; refer to Figure 1 for names of lakes.

SETTING

The Finger Lakes of central New York State consist of 11, elongate, north-south–oriented glacial lake basins that are traditionally divided into seven larger eastern Finger Lakes and four smaller western lakes (Fig. 1). All the Finger Lakes appear to have originated as preglacial stream valleys that were subsequently enlarged and overdeepened by a combination of ice and subglacial meltwater erosion during the Pleistocene (Mullins and Hinchey, 1989; Mullins et al., 1996). The basins of the modern Finger Lakes were last sculptured during the late Wisconsinan by a surge of the Laurentide ice sheet coincident with Heinrich event H-1 at ca. 14,500 ^{14}C yr B.P. (Mullins et al., 1996). These 11 lake basins have been eroded into Silurian to Devonian bedrock consisting of evaporite, limestone, calcareous shale, and siltstone. Authigenic carbonate within bedrock is common in the region and has a wide range of δ^{13}C values (–15.6‰ to +8.7‰), whereas calcite in host shale has much lower carbon isotopic values (–26.5‰ to −30.2‰; Dix and Mullins, 1987). Two prominent Devonian limestones form narrow outcrops in the Finger Lakes region, the younger Tully Limestone to the south and the older Onondaga Limestone in the north (Fig. 3). Surficial geology of the region is dominated by unconsolidated, calcareous glacial drift of variable thickness and localized bedrock outcrops (Muller and Cadwell, 1986). Calcareous soil is extensively, but not completely, distributed throughout the region, particularly in the eastern Finger Lakes (Bloomfield, 1978).

Limnologically, the Finger Lakes are highly diverse (Bloomfield, 1978). There is significant variation in lake-surface elevation (116 m to 334 m above sea level), maximum water depth (9 m to 186 m), length (5 km to 61 km), and drainage-basin area (32 km^2–1870 km^2; Mullins et al., 1996). The lakes also vary in their mixing (turnover) characteristics from warm monomictic, to dimictic, to polymictic (Bloomfield, 1978). In addition, the trophic state of the Finger Lakes is highly variable, ranging from oligotrophic Skaneateles Lake, to mesotrophic Cayuga Lake, to eutrophic Honeoye Lake (Bloomfield, 1978). Modern sediments in the lakes are a combination of allochthonous mineral matter and terrestrial organic matter as well as autochthonous production of aquatic organic matter, biogenic silica, and calcite. The thickest Holocene sediments are found in the deepest water depths owing to sediment focusing (Mullins et al., 1996).

The climate of the Finger Lakes is typical of its temperate, midlatitude, continental setting with long, snowy (lake-effect) winters and short, hot, humid summers. Mean monthly temperatures range from ~21 °C in July to ~–4 °C in January; mean annual precipitation is on the order of ~100 cm/yr, which is about equally distributed throughout the year (Bloomfield, 1978). The Finger Lakes are also located near the mean annual position of the polar-front jet stream and are thus dominated by prevailing westerly winds and storm tracks (Eichenlaub, 1979).

Two of the Finger Lakes (Hemlock and Canadice) are currently protected water resources for the city of Rochester and now have little, if any, cultural or agricultural development (Bloomfield, 1978). In contrast, many of the remaining Finger Lakes have extensive cultural and/or agricultural development within their watersheds; some, such as Canandaigua, Seneca, and Cayuga (Fig. 1), have small cities and/or power plants located along their shores. Thus, the significant diversity of the 11 Finger Lakes provides an ideal setting in which to evaluate the effects of acid deposition on aquatic environments in a highly buffered terrane.

Native Americans have inhabited the Finger Lakes region for at least the past 5000 yr (Galpin, 1941). However, it was not until the late 1700s and early 1800s that European immigrants began to settle the wilderness of the Finger Lakes region. Finding virgin forests and fertile soils, these settlers deforested the region such that by 1880, ~73% of the land had been transformed into an agricultural landscape (Siles, 1978). During the twentieth century the region was partially reforested as the number of farms has decreased (USDA, 1835–1992).

Previous research on the near-surface sediments of the Finger Lakes has been limited. Proctor (1978) studied the four small western Finger Lakes, focusing on metal loading as well as sediment-accumulation rates. Similarly, Hinchey (1986) examined trace element concentrations in the historic record of Otisco Lake and concluded that watershed development changed the chemical nature of near-surface sediments. A number of piston cores (up to 6 m long) have also been collected from Seneca and Cayuga Lakes. These relatively short sediment cores have allowed general description of Holocene and late glacial sediments (Ludlam, 1967; Woodrow et al., 1969; Wing et al., 1995; Mullins et al., 1996; Anderson et al., 1997; Halfman and Herrick, 1998). In addition, a 120-m-long drill core south of Canandaigua Lake has documented the entire sediment fill of the Finger Lake valleys (Wellner et al., 1996).

METHODS

Relatively short (<1 m) box cores were collected from deep-water areas of all 11 Finger Lakes during the summers of 1996 and 1998 by using a 7 m pontoon boat with a central moon pool and tripod as a research vessel. Box-core sediments were extruded vertically

in the field and sampled at 1 cm intervals for sedimentologic and isotopic analysis. Although only one box core was collected from each lake, previous study of multiple cores from Cayuga Lake showed that there is no significant lateral variability in the temporal record of calcite deposition (Mullins, 1998a, 1998b; Mullins et al., 2001).

Age control for each core is based on ^{137}Cs and ^{210}Pb data generated at Rensselaer Polytechnic Institute in Troy, New York, or the U.S. Geological Survey in Reston, Virginia. The upper 30 cm of each core was sampled every 2 cm for age analysis. Because ^{137}Cs is a fallout product of above-ground nuclear weapons tests, the initial occurrence and peak abundance of ^{137}Cs in a sediment profile correspond to ca. 1950 and 1963, respectively (Krishnaswamy et al., 1971). [210]Pb, which has a half-life of 22.26 yr, is supplied to lakes primarily via atmospheric fallout, where it is adsorbed onto sediment particles and deposited (Appleby and Oldfield, 1978). We used the constant-rate-of-supply dating method that utilizes "excess [210]Pb" activity (determined by subtracting supported ^{210}Pb from total ^{210}Pb activity), which is then plotted versus depth on a logarithmic scale (Appleby and Oldfield, 1978). An age model for each core was developed by using a combination of ^{137}Cs and ^{210}Pb data. After identifying ca. 1950 and 1963 via the ^{137}Cs results, regression lines were mathematically fitted to the ^{210}Pb data; the slope of the line was used to calculate sediment-accumulation rates and to extrapolate ages. Bioturbation is unlikely to result in "smoothing" of ages owing to high salinity (up to 30 parts per thousand) of pore waters in Seneca and Cayuga Lakes (Wing et al., 1995) or in the shallower Finger Lakes in which summer hypoxia occurs (Bloomfield, 1978; Callinan, 2001). Both of these situations inhibit bioturbation. X-radiographs of sediment cores from Seneca and Cayuga Lakes typically display millimeter-scale laminations, further suggesting a lack of bioturbation (Mullins et al., 1996).

Water content was determined by subtracting dry-sediment mass from wet-sediment mass and then calculating the percentage of water lost. Bulk density was determined by dividing wet-sediment mass by sediment volume, which was known from plastic cubes (~1 cm³) used for subsampling. Total organic matter (wt%) and total carbonate (wt%) content were determined primarily by loss-on-ignition (LOI) at 550 °C and 1000 °C, respectively (Dean, 1974). Because the LOI method can overestimate carbonate content by 3%–4% in clay-rich sediments (owing to water loss from clay minerals at 1000 °C; Dean,

1974), every fourth sample from each core was analyzed with a CM5012 carbon dioxide coulometer that determines inorganic carbon via acidification and titration techniques. The average difference between LOI and coulometer carbonate values for each core was then subtracted from all LOI values for that core. In addition, samples were analyzed by standard X-ray diffraction techniques (peak area) to quantify the amount of calcite versus dolomite present (Milliman et al., 1974). The dolomite fraction (usually <5%) was then subtracted from total carbonate values to determine the amount of calcite present in each sample.

Mass magnetic susceptibility of each sample was determined by measuring the magnetic field strength (SI units) with a Barrington MS-2 magnetic-susceptibility meter, dividing this value by sediment bulk density, and then dividing by 1000 (Gale and Hoare, 1991). Magnetic-susceptibility data were used as a proxy for the presence of detrital magnetic minerals, with the knowledge that bacterial diagenetic processes may also contribute to the susceptibility of lake sediment (Gale and Hoare, 1991).

Stable carbon isotope (δ^{13}C) analyses were conducted on fine-grained (<63 μm) carbonate in box cores recovered from Seneca, Cayuga, Owasco, and Otisco Lakes by using a Finnigan MAT 252 gas (isotope) ratio mass spectrometer directly coupled to a Kiel III carbonate preparation device. Prior to analysis, each sample was roasted in a vacuum tube furnace at 200 °C for 1 h to remove volatiles that might interfere with isotope analyses. Samples were then reacted with 103% orthophosphoric acid (H_3PO_4) at 50 °C for 30 s (prior to removal of noncondensibles) to avoid reaction of any trace amounts of detrital dolomite. Results are reported in standard per mil notation relative to the VPDB (Vienna Peedee belemnite) international standard:

$$\delta^{13}C = (R_{sample} - R_{standard}/R_{standard}) \times 1000, (1)$$

where $R = {}^{13}C/{}^{12}C$. (Note: δ^{18}O values were also determined, but are not reported in this paper; for oxygen data, see Lajewski, 1999). On the basis of replicate comparisons with internal and external laboratory standards, precision was determined to be better than ±0.1‰.

Surface-water samples from the Finger Lakes were collected monthly (May through October) between 1996 and 1999. Field measurements included Secchi Disk depths and vertical profiles of temperature, dissolved oxygen, pH, and conductivity taken with a Hydrolab Surveyor 4 instrument. Chemical anal-

yses of water samples, including alkalinity and elemental concentrations (such as Ca^{2+} and Mg^{2+}), followed standard USEPA guidelines as outlined in Callinan (2001; http://www.dec.state.ny.us/website/dow/fingerlakes/index.html). The degree of summer calcite saturation in the epilimnion (mixed surface waters) of each lake was determined via published geochemical data for 1973 (Bloomfield, 1978), as well as new data collected from 1996 to 1999 as part of this study. Degree of calcite saturation (Ω) values were calculated by using the equation

$$\Omega = (a_{Ca^{2+}})(a_{CO_3^{2-}})/K_{sp}, \quad (2)$$

where a is the ion activity and K_{sp} is the solubility product of calcite. Activities were quantified by using the WATEQ4F program of Drever (1997) with a constant value of pH = 8 and a temperature = 20 °C, based on new data as well as that in Bloomfield (1978). Ω values of >1 are indicative of supersaturation, whereas values of <1 indicate undersaturation with respect to calcite.

Historic agricultural land-use data were collected for each county in the Finger Lakes drainage district (USDA, 1835–1992). The amount of agricultural lime use was also determined for each county by using the same database for the period 1954–1987. Estimates of the amount of agricultural land (km²) and lime use (tons) were based on individual lake-watershed analysis using the U.S. Geological Survey Elmira topographic sheet. Data were available by county and were proportioned to each watershed depending upon what percentage of a county was contained in a given watershed.

Tables of all data used in this study are available in the GSA Data Repository.[1]

RESULTS

Spatial Distribution of Calcite

One of the most obvious and perhaps most significant results of our study is that calcite is present in the near-surface sediments of only seven of the eleven Finger Lakes (Fig. 1). Calcite is absent from historic sediments in three of the four small western Finger Lakes (Hemlock, Canadice, Honeoye), as well as Keuka Lake (Fig. 1). A comparison of Figures 1 and 3 reveals that the drainage basins of these four lakes have minimal amounts of

calcareous soils and lack limestone outcrops, a sharp contrast with the remaining seven Finger Lakes that do contain calcite in near-surface sediments.

Surface-water chemistry data from three of the lakes that lack calcite (Hemlock, Honeoye, Keuka) reveal that in 1972, all were undersaturated with respect to calcite (Fig. 4). Hemlock and Honeoye Lakes continue to be undersaturated as of 1999, whereas Keuka Lake surface waters appear to have reached supersaturation as of 1999 (Fig. 4). In contrast, surface waters of all seven Finger Lakes that contain calcite in historic sediment have been seasonally supersaturated with respect to calcite from at least 1972 to 1999 (Fig. 4). These data document that the degree of surface-water calcite saturation is a primary control of calcite precipitation in the Finger Lakes. Furthermore, these data indicate a direct linkage between drainage-basin calcareous soils and limestone outcrops and supersaturation of summer surface waters with respect to calcite. In addition, between 1972 and 1999, at least seven of the Finger Lakes increased in calcite saturation; one lake (Owasco) remained the same; and only two lakes (Conesus and Otisco) declined in their degree of surface-water calcite supersaturation (Fig. 4). Overall, these results strongly suggest that inorganic geochemical processes play a primary role in controlling the spatial (and perhaps temporal) distribution of calcite precipitation in the Finger Lakes.

Temporal Distribution of Calcite

Because of space limitations, our presentation on the temporal (nonseasonal) distribution of calcite in near-surface sediments of the Finger Lakes focuses only on those lakes (Cayuga, Owasco, Otisco) that have the highest calcite contents in the lake sediments and the greatest degree of summer surface-water supersaturation with respect to calcite. An example of ^{137}Cs and ^{210}Pb data used for age control is given for Cayuga Lake (Fig. 5); geochronologic and geochemical data for the remaining Finger Lakes can be found in the GSA Data Repository (see text footnote 1).

As previously reported (Mullins, 1998a, 1998b; Mullins et al., 2001), the calcite content of Cayuga Lake has increased during historic time (Fig. 6). Calcite content in Cayuga Lake sediments was zero from at least 1740 to 1825, implying an absence of open-water precipitation (whiting) events. However, calcite first appeared in Cayuga Lake sediments in ca. 1825; the low values (<5%) measured were relatively stable until ca. 1940, when a rapid increase began. Maximum values of
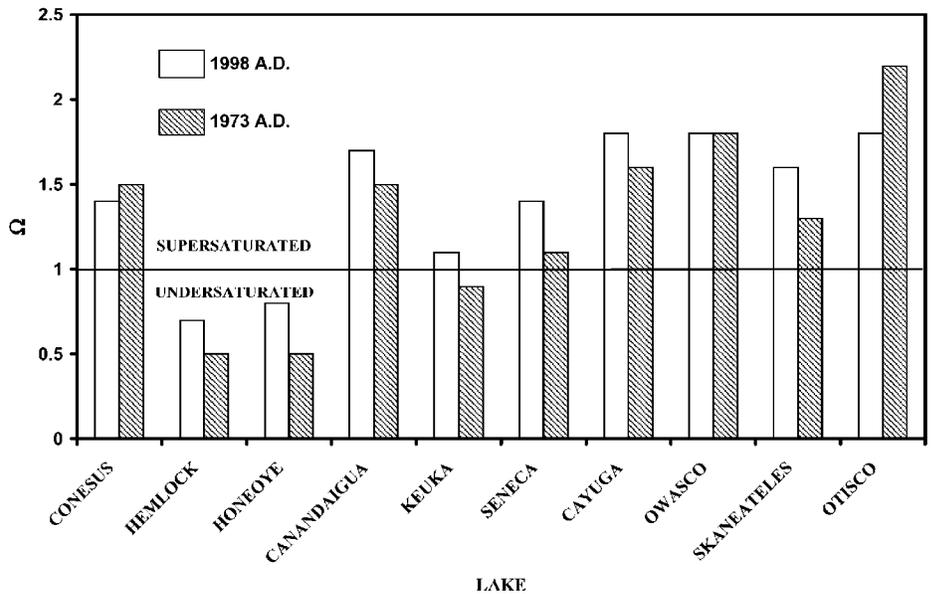

Figure 4. Degree of summer (20 °C) calcite saturation (Ω value) for the Finger Lakes in 1973 and 1998.
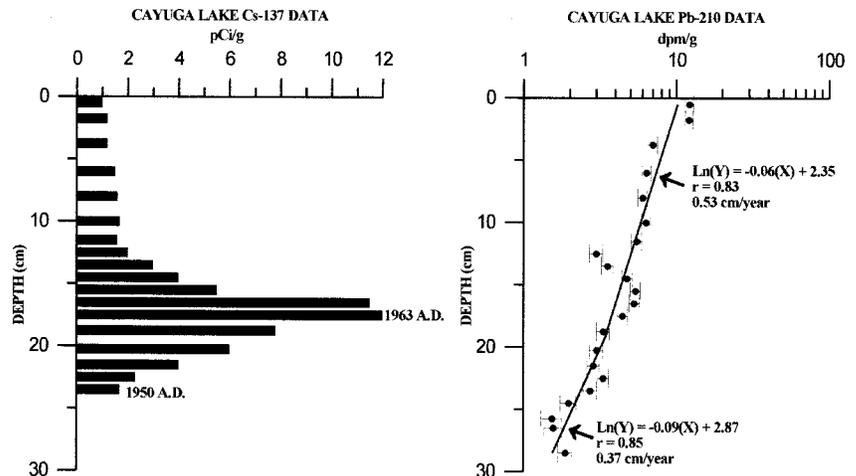

Figure 5. Example from Cayuga Lake of ^{137}Cs and ^{210}Pb concentrations used to date box cores from the Finger Lakes; see text for details on methods.

~16% were reached in the early 1990s (Fig. 6). Total organic matter (TOM) content of Cayuga sediments was relatively stable at ~9%–10% between 1740 and 1825; these concentrations were followed by a slight drop to ~8% (coincident with an increase in calcite) and a subsequent gradual rise to ~12% in the late 1990s (Fig. 6). Mass magnetic-susceptibility values for Cayuga Lake sediments are very low; a small increase occurred between ca. 1900 and 1980 (Fig. 6), suggesting a minor increase in the detrital flux of magnetic minerals to the basin during this interval, probably owing to watershed development.

A similar temporal trend for calcite is re-

corded in Owasco Lake sediments (Fig. 6). Calcite content was zero from at least 1690 to 1820. Calcite first appeared in the Owasco record in ca. 1825, but was maintained at relatively low (<7%) values until ca. 1940 when there was a rapid increase in calcite content, which reached a maximum value of ~18% in the early 1990s (Fig. 6). As with Cayuga Lake, calcite content in Owasco Lake showed a decline during the mid- to late 1990s (Fig. 6). Total organic matter content of Owasco Lake sediments was fairly constant at ~10% between 1690 and 1820; a decline to ~7% occurred between 1820 and 1860 (as calcite increased), and then the TOM content re-
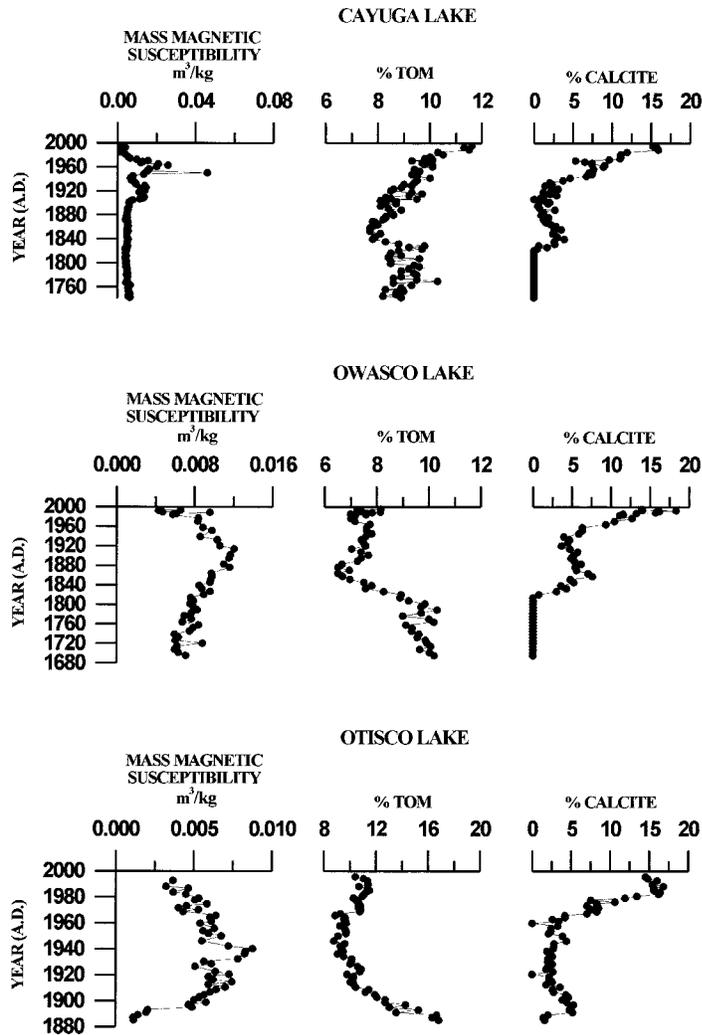
Figure 6. Sedimentology of Cayuga, Owasco, and Otisco Lake box cores, illustrating mass magnetic susceptibility, total organic matter (TOM), and total calcite vs. year (A.D.).

Stable Carbon Isotopes

Carbon isotope values of calcite have been widely used as a proxy for paleoproductivity in aquatic environments (McKenzie, 1985). The $\delta^{13}C$ values for calcite from Seneca, Cayuga, Owasco, and Otisco Lakes all show decreasing values (i.e., implying decreasing productivity) since at least the mid-1960s despite the fact that calcite contents for all these lakes rose substantially over this interval of time (Figs. 6–8). Cayuga Lake $\delta^{13}C_{calcite}$ values declined by ~0.8‰ between 1950 and the late 1990s and by ~1.0‰ since 1915 (Fig. 8). Owasco Lake $\delta^{13}C$ data show a subtle, general increase from the early 1800s until the early 1960s, when values began to decline. A decline of ~1.6‰ occurred from then until the late 1990s (Fig. 8). Similarly, $\delta^{13}C$ data for Otisco and Seneca Lakes further reveal declines of ~0.8‰ and 1.0‰, respectively, from the 1960s through the late 1990s (Fig. 8).

DISCUSSION

The open-water precipitation of calcite from the surface waters of modern hard-water lakes is a common and widespread phenomenon in the midlatitudes (Kelts and Talbot, 1990). The environmental controls of aqueous calcite precipitation, however, are not completely understood because they involve a complex interplay of physical, chemical, and biological processes. Some (e.g., Brunskill, 1969) have previously argued for strictly inorganic controls such as temperature, whereas others have noted the important role of biological processes (direct or indirect) in aquatic calcite precipitation (Thompson and Ferris, 1990; Schelske and Hodell, 1991; Thompson et al., 1997; Hodell et al., 1998). For nearby Lake Ontario, Hodell et al. (1998) have summarized the myriad of processes that can influence calcite precipitation. They argued that temperature is the "most obvious" control on calcite precipitation because increased temperature lowers the solubility of calcite (K_{sp}) and thus increases the degree of calcite saturation. Temperature may also indirectly control the rate of primary productivity, timing of water-column stratification, and the abundance of picoplankton (Hodell et al., 1998). In Fayetteville Green Lake, New York, picoplankton are known to precipitate calcite epicelluarly. The cyanobacterium *Synechococcus* sp. uses HCO_3 as a carbon source and releases OH^-, creating a high-pH microenvironment around its micrometer-sized cell (Thompson et al., 1997). The overall level of primary productivity in a lake can also trigger calcite precipitation by lowering concentrations of aqueous CO_2, which in turn increases
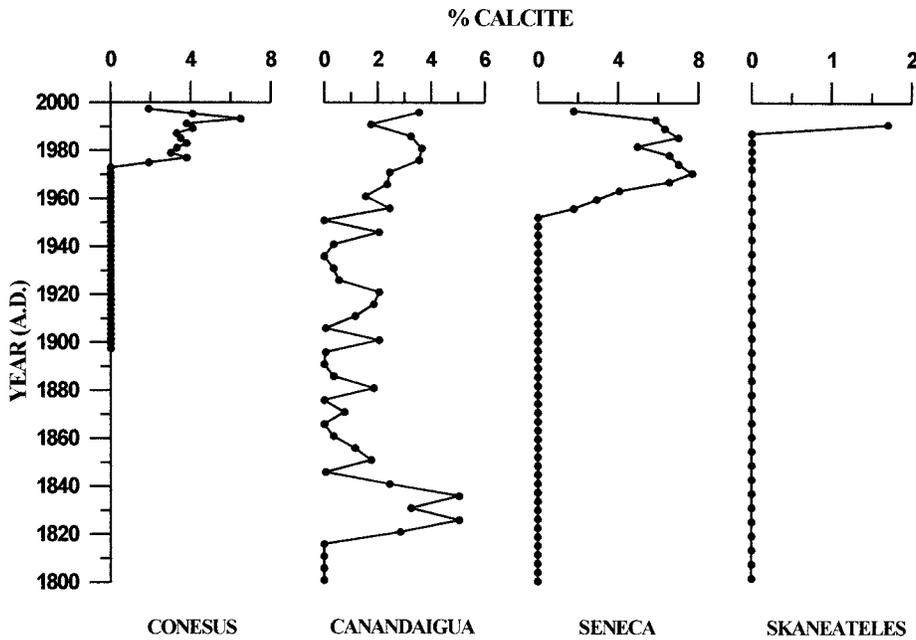
mained stable at 7%–8% into the late 1990s (Fig. 6). Mass magnetic-susceptibility values for Owasco Lake have also been very low, but showed a subtle increase between 1690 and 1915 followed by a subtle decrease into the 1990s (Fig. 6). These susceptibility data probably reflect minor changes in watershed disturbance due to agricultural activity that increased during the late 1700s and 1800s but declined during the twentieth century (Bloomfield, 1978). The very low, mass magnetic-susceptibility values in Cayuga and Owasco (as well as Otisco) Lakes suggest that historic sedimentation is largely autochthonous in nature (Gale and Hoare, 1991).

The box-core sediment results from Otisco Lake vary slightly from those in Cayuga and Owasco Lakes because relatively high sediment-accumulation rates (0.67 cm/yr since 1963) limit the temporal length of the recovered Otisco Lake record. Calcite, for example, is present throughout the recovered Otisco Lake record, which extends back only to ca. 1885 (Fig. 6). Calcite contents in Otisco Lake remained low (<5%) between 1885 and the early 1960s; this record was followed by a rapid increase to maximum values of ~17% in 1990 and a subsequent subtle decline during the 1990s (Fig. 6). TOM values in Otisco Lake decreased from ~17% to 12% between 1885 and 1910, followed by relatively stable TOM contents of ~9%–12% throughout the twentieth century (Fig. 6). Unlike with Cayuga and Owasco Lakes, TOM values are not strongly correlated ($r = 0.22$) with calcite contents. Mass magnetic-susceptibility values for Otisco Lake, however, are very low, displaying a broad increase from 1885 to 1940 followed by a broad decrease to the end of the twentieth century (Fig. 6), which again probably reflects subtle changes in watershed disturbance over time.

% CALCITE

Figure 7. Total calcite contained in Conesus, Canandaigua, Seneca, and Skaneateles Lake box cores vs. year (A.D.).
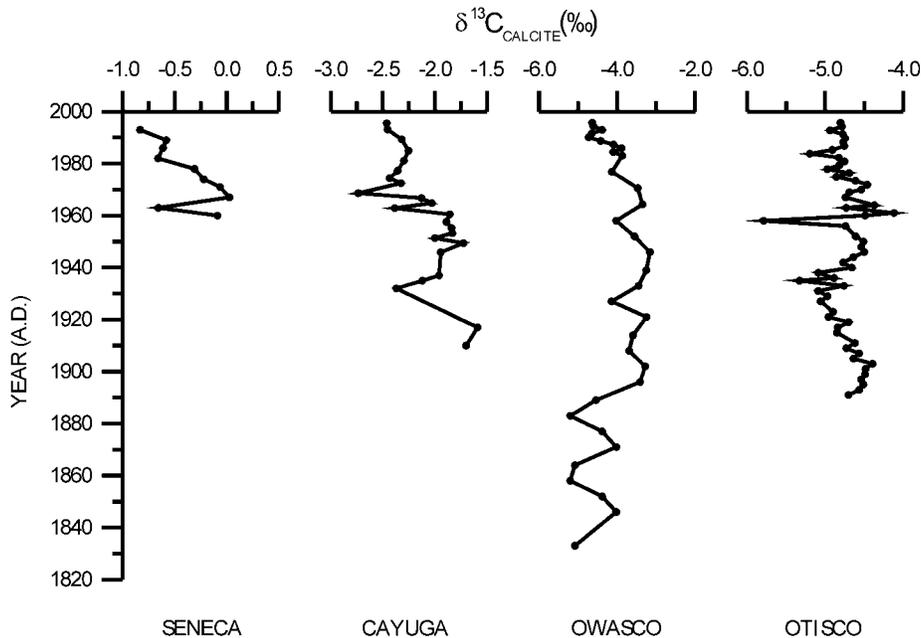
$$\delta^{13}C_{CALCITE}(\permil)$$

Figure 8. $\delta^{13}C$ data vs. year (A.D.) for box cores from Seneca, Cayuga, Owasco, and Otisco Lakes.

pH and results in higher carbonate ion concentrations (Kelts and Talbot, 1990; Hodell et al., 1998).

The Cultural-Eutrophication Hypothesis

Aqueous precipitation of calcite during historic times has typically been attributed to cultural eutrophication: the anthropogenic loading of nutrients (mainly phosphorous) to lakes via urbanization and agricultural activity (Schelske and Hodell, 1991; Hollander et al., 1992; Hodell et al., 1998; Teranes and McKenzie, 1999). In this model, increased nutrient loading yields greater concentrations of primary producers that remove CO_2 and drive carbonate equilibria toward calcite precipitation.

The conventional model for calcite precip-

itation premised upon cultural eutrophication does not appear to fit the Finger Lakes for a number of reasons. Simple distribution data indicate that some eutrophic (high-nutrient) Finger Lakes lack calcite whereas oligotrophic (low-nutrient) lakes contain calcite in near-surface sediments. Furthermore, summer water-column total phosphorous concentrations in eight of the eleven the Finger Lakes have either remained the same ($N = 2$) or decreased ($N = 6$) between 1972 and 1999 (Fig. 9), despite the fact that calcite concentrations in bottom sediments increased significantly over the same interval of time (Fig. 6). Only three lakes (Otisco, Honeoye, and Conesus) display increases in total water-column phosphorous (Fig. 9). For Owasco Lake, total phosphorous and chlorophyll-a concentrations (a proxy for primary production) decreased by 42% and 52%, respectively, between 1973 and 1985 (Effler et al., 1987b) before rebounding to present-day values. The decrease between 1973 and 1985 was likely an initial response to New York State's ban on phosphate detergents in 1973 (Bloomfield, 1978). Over the same time interval (1973–1985), calcite in bottom sediments of Owasco Lake increased from ~10% to 15% (Fig. 6).

Lower levels of primary productivity in the Finger Lakes are further supported by decreasing $\delta^{13}C_{calcite}$ values since the early 1960s (Fig. 8), while calcite contents continued to increase (Figs. 6 and 7). Because primary producers selectively remove ^{12}C from the aquatic dissolved-inorganic-carbon pool during photosynthesis, $\delta^{13}C$ values in precipitated calcite should increase with increasing primary production (McKenzie, 1985), which is opposite of the trend observed in the Finger Lakes (Fig. 8). Alternative explanations for decreased $\delta^{13}C_{calcite}$ values include increased input of isotopically light carbon from terrestrial soils and/or the atmosphere (because of the burning of fossil fuels). $\delta^{13}C_{calcite}$ values can also become more negative if aquatic primary production becomes dominated by chemoautotrophic or methanotrophic microbes (Hollander and Smith, 2001). However, a change to a dominance by these microbes appears to happen only after long-term eutrophication, for which there is no evidence in the Finger Lakes.

There are no data currently available from the Finger Lakes on the seasonal concentrations and isotopic composition of dissolved inorganic carbon (DIC). However, Thompson et al. (1997) have collected such data from nearby Fayetteville Green Lake, New York, between January and November 1990. They found that when DIC concentrations are relatively high (winter), $\delta^{13}C$ values are relatively
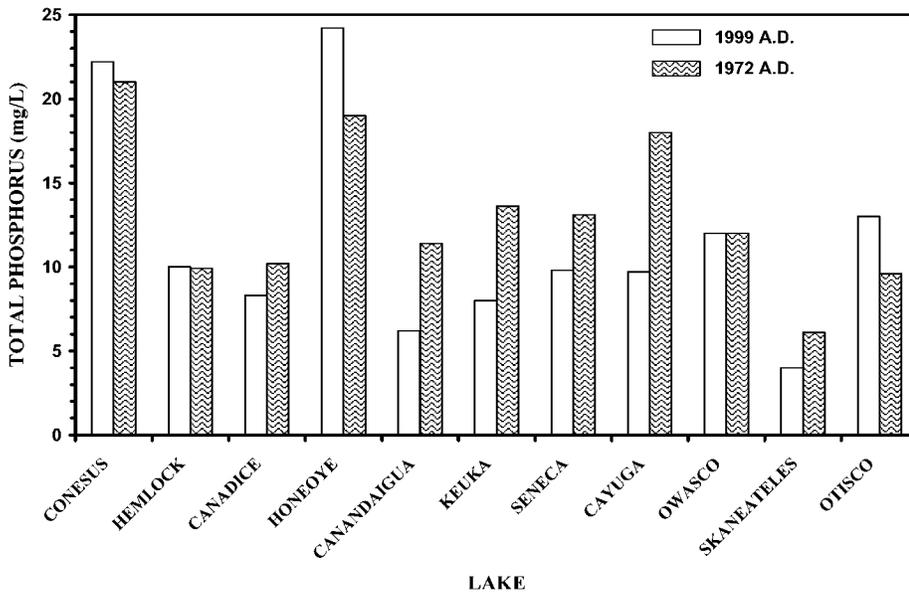
Figure 9. Total phosphorus concentrations in summer lake water for the Finger Lakes in 1972 (Bloomfield, 1978) and 1999.
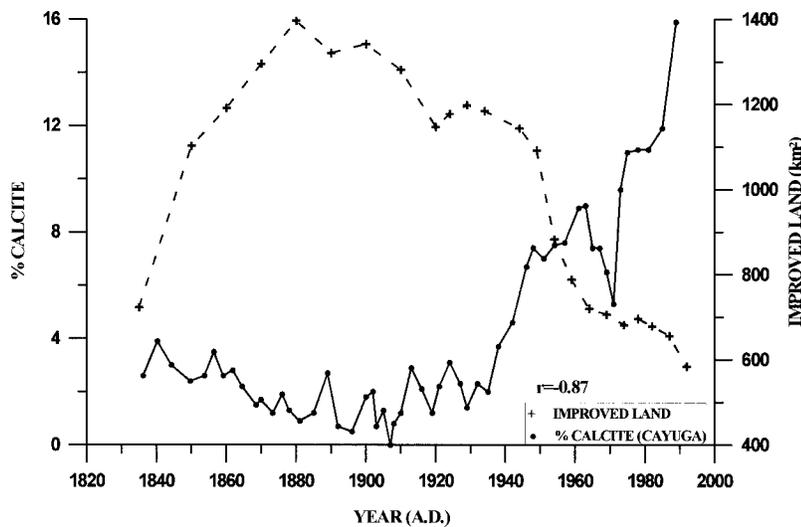

Figure 10. Changes in bottom-sediment calcite concentration and area of agricultural ("improved") land in watershed of Cayuga Lake between 1830 and 1998. Note strong inverse correlation ($r = -.87$), indicating that calcite content is not a primary function of land use.

low, and vice versa (summer). They also discovered that $\delta^{13}C_{calcite}$ values are ~4‰ higher than $\delta^{13}C$ values in ambient DIC owing to preferential uptake of ^{12}C by cyanobacteria that mediate calcite precipitation (Thompson et al., 1997). Overall, our carbon isotope interpretations for the Finger Lakes are supported by direct measurements of the trophic state of Cayuga Lake (Secchi Disk, total phosphorous, chlorophyll-a) that indicate a moderate decline in productivity between the

1960s and 1999 (Callinan, 2001). In addition, chlorophyll-a concentrations in Seneca Lake have declined by at least a factor of three during the 1990s (Halfman et al., 2001). We have also evaluated historic agricultural land use in the Finger Lakes as a test of the cultural-eutrophication hypothesis. Statistical analyses indicate a strong negative correlation between watershed agricultural land use and calcite content in bottom sediments of Cayuga Lake ($r = -0.87$; Fig. 10), Owasco Lake ($r =$

-0.84), and Otisco Lake ($r = -0.69$). Thus, based on all the evidence presented, we conclude that cultural eutrophication alone has not been the primary control on the return of calcite precipitation in the Finger Lakes following an ~4500 ^{14}C year hiatus.

The Carbonate-Weathering Hypothesis

If cultural eutrophication is not the primary driving force of historic calcite precipitation in the Finger Lakes, what is? Summer surface-water chemistry data between 1972 and 1999 indicate that calcite saturation states have largely increased ($N = 7$) or remained the same ($N = 1$) in the Finger Lakes (Fig. 4). The fact that calcite saturation is in part dependent upon the activities (concentrations) of Ca^{2+} and CO_3^{2-} suggests increased loading of calcium and carbonate (or bicarbonate) to the Finger Lakes over historic time. Mullins (1998a) noted a very strong correlation ($r = 0.95$) between the calcite content of Cayuga Lake sediments and the concentration of atmospheric CO_2 over the past 200 yr (Fig. 2), suggesting a link between industrialization and calcite precipitation. He later speculated that the anthropogenic rise of atmospheric CO_2 may be increasing the acidity of meteoric waters by forming carbonic acid,

$$CO_2 + H_2O = H_2CO_3, \qquad (3)$$
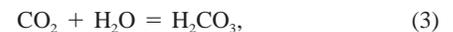
and, thus, increasing the chemical weathering of limestone and calcareous soil in the drainage basins of the Finger Lakes (Mullins, 1999). During the reaction between carbonic acid and calcite,

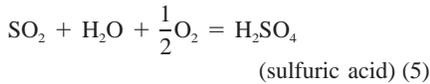$$H_2CO_3 + CaCO_3 = Ca^{2+} + 2HCO_3^-, \qquad (4)$$

dissolved calcium and bicarbonate ions are released from soils and bedrock and carried by surface and ground waters to lakes (Lawrence et al., 1995; Likens et al., 1996), where they can increase the saturation state of surface waters with respect to calcite.

Preindustrial levels of atmospheric CO_2 have been estimated from ice cores at ~280 ppmv versus today's concentration of ~370 ppmv (IPCC Working Group, 2001). At a CO_2 concentration of 280 ppmv, the pH of natural meteoric precipitation is slightly acidic (~5.6) (Likens and Bormann, 1995). Higher concentrations of atmospheric CO_2 (363 ppmv in 1998) would further lower the pH of meteoric precipitation (Berner, 1992), but only slightly (~5.5). Thus, it appears unlikely that the increase of atmospheric CO_2, alone, has resulted in increased loading of Ca^{2+} and CO_3^{2-} and

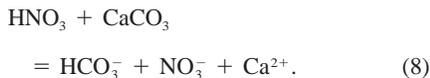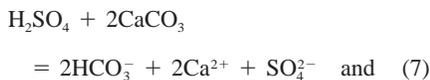thus the return of calcite precipitation to the Finger Lakes in historic time.

However, widespread burning of fossil fuels via industrialization releases not only CO_2 to the atmosphere but also SO_2 and NO_x (Driscoll et al., 2001). The hydrolysis of sulfur dioxide and nitrogen oxides produces strong acids,

$$SO_2 + H_2O + \frac{1}{2}O_2 = H_2SO_4$$

$$\text{(sulfuric acid) (5)}$$

and

$$2NO_x + H_2O = 2HNO_3 \text{ (nitric acid)} \quad (6)$$

which can significantly increase the acidity (pH = ~4.3) of the meteoric precipitation that falls in the northeastern United States and enhance its capacity to chemically weather limestone as well as calcareous soil (Peters et al., 1981; Park, 1987). These acids then participate in reactions that release calcium and bicarbonate to lakes:

$$H_2SO_4 + 2CaCO_3$$

$$= 2HCO_3^- + 2Ca^{2+} + SO_4^{2-} \quad \text{and} \quad (7)$$

$$HNO_3 + CaCO_3$$

$$= HCO_3^- + NO_3^- + Ca^{2+}. \quad (8)$$

In order to test the "carbonate weathering" hypothesis for the Finger Lakes, we statistically evaluated the relationships between SO_2 and NO_x emissions (USEPA, 1996; Driscoll et al., 2001) and the calcite content of Cayuga, Owasco, and Otisco Lakes sediments. Overall, SO_2 emissions increased ~250% between 1900 and implementation of the Clean Air Act in 1970 (with significant declines during the 1930s and 1950s), followed by an ~40% decline to 1995. Available data indicate that calcite content and SO_2 emissions are not strongly correlated, but are statistically significant, for Owasco Lake ($r = 0.24$; Fig. 11), Cayuga Lake ($r = 0.30$), and Otisco Lake ($r = 0.21$). The correlation between NO_x emissions and historic calcite content, however, is very strong for Owasco Lake ($r = 0.94$; Fig. 12), Cayuga Lake ($r = 0.94$), and Otisco Lake ($r = 0.88$). NO_x emissions have increased 700% from 1900 to 1995 (Likens et al., 1996; Driscoll et al., 2001).

Atmospheric increases during the twentieth century of CO_2, SO_2, and especially NO_x, have apparently increased the chemical-weathering potential of buffered terranes in the Finger Lakes region. This statement appears to be particularly true for agricultural areas in which calcareous soils are annually tilled and ex-
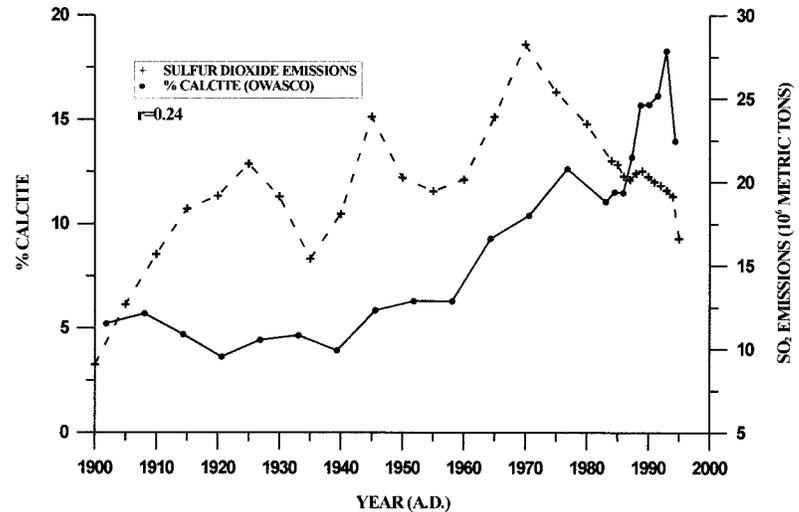

Figure 11. Changes in bottom-sediment calcite concentration and U.S. SO_2 emissions between 1900 and 1995. Note statistically significant, but not strong, correlation between these two variables.
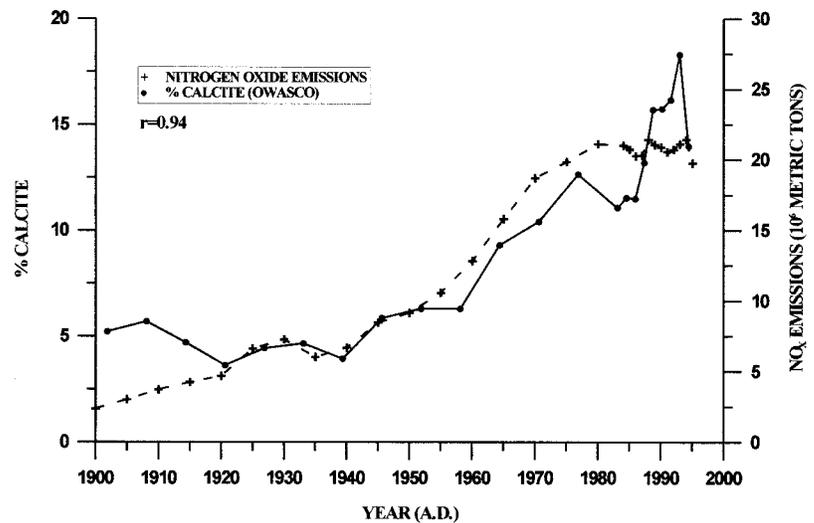

Figure 12. Changes in bottom-sediment calcite concentration and U.S. NO_x emissions between 1900 and 1995. Note robust statistical correlation ($r = 0.94$), suggesting that nitric acid is the most important acid in increasing chemical weathering in the Finger Lakes region.

posed along with limestone boulders. Evidence can be seen in a 1973 Finger Lakes data set (Bloomfield, 1978) of calcium concentrations in lake waters versus percent agricultural activity in their drainage basins ($r = 0.93$; Fig. 13). Note that the seven Finger Lakes that contain calcite in near-surface sediments all cluster in the upper right-hand corner of Figure 13, indicating both high dissolved calcium concentrations and high percentages of tilled land surfaces. This relationship is not due to liming practices, because liming is limited on

naturally buffered soils, and there are very poor statistical correlations between historic records of lime use and calcite in bottom sediments of Cayuga Lake ($r = 0.05$), Owasco Lake ($r = -0.11$), and Otisco Lake ($r = -.05$). Such a relationship could also be explained by the formation of organic acids by agricultural activity and the release of Ca^{2+}. This possibility seems unlikely, though, considering the strong ($r = -.87$) negative statistical correlation between agricultural land area and bottom-sediment calcite (Fig. 10).

We suppose that acidic deposition on the buffered terrane of the Finger Lakes region is responsible for increased carbonate weathering, the loading of Ca^{2+} and HCO_3^- to the lakes ("alkalization"), and ultimately the historic return of calcite precipitation in 7 of the 11 Finger Lakes (Fig. 14). Surface waters flowing into the south end of Cayuga Lake are known to be supersaturated with respect to calcite, particularly at low flow velocities (D. Bouldin, Cornell University, 1999, personal commun.). Precipitation of calcite in the surface waters of the Finger Lakes can be triggered during summer months by evaporation, photosynthetic drawdown of CO_2, rising temperatures (Mann et al., 1998; IPCC Working Group, 2001), and/or increased populations of picoplankton (Thompson and Ferris, 1990; Thompson et al., 1997; Hodell et al., 1998). Mullins (1998a, 1998b) previously argued that widespread calcite precipitation in the Finger Lakes during the early to middle Holocene was due to warmer summer temperatures (2–3 °C) of the Hypsithermal when regional lake levels were relatively high (Dwyer et al., 1996; Mullins, 1998b). Because the rate of chemical weathering is temperature as well as moisture dependent (Drever, 1997), warmer/wetter summers likely increased carbonate weathering during the early to middle Holocene. Calcite precipitation ceased in the Finger Lakes by ca. 4500 ^{14}C yr B.P. during the transition from the relatively warm/wet Holocene Hypsithermal to the cool/dry Neoglacial (Mullins and Halfman, 2001), concurrent with a decrease in lake levels and chemical weathering.

If our hypothesis is correct, then there should be evidence for increased loading of Ca^{2+} and HCO_3^- in the Finger Lakes during historic times, especially for those lakes that are not supersaturated and do not precipitate calcite. Reliable comparative data from 1972 (Bloomfield, 1978) and 1999 exist only for calcium. The Ca^{2+} concentration in summer surface waters of noncalcite-precipitating Finger Lakes increased from the early 1970s to the late 1990s; Hemlock Lake shows the least change (3%), and Canadice Lake shows the greatest change (27%) (Fig. 15). In contrast, six of the seven calcite-precipitating Finger Lakes display significant decreases in summer surface-water Ca^{2+} concentrations from 1972 to 1999; with a range of −2% for Cayuga and Canandaigua Lakes to a maximum of −17% for Otisco Lake (Fig. 15). This decrease in summer surface-water Ca^{2+} concentrations likely reflects the removal of Ca^{2+} ions via increased precipitation of calcite during whiting events or, alternatively, the dissolution of dolomite in the drainage basin, which would
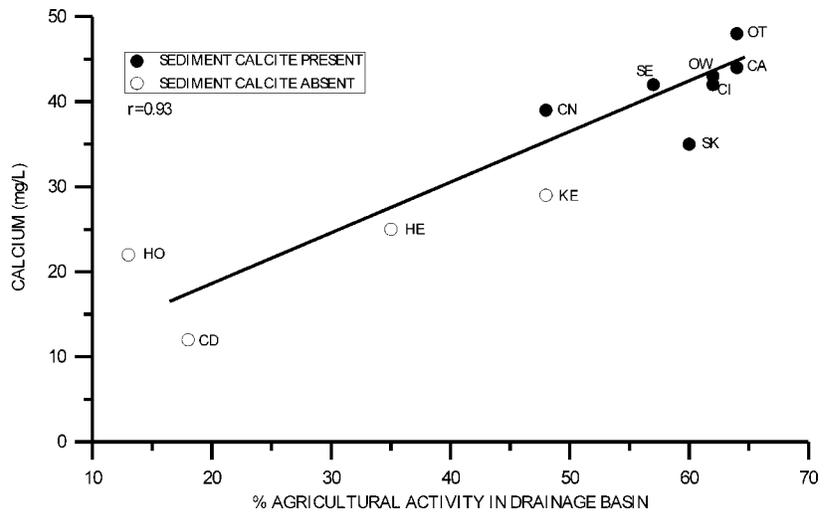

Figure 13. Percent agricultural activity in Finger Lake drainage basins vs. calcium concentrations in surface waters. Note cluster of the seven Finger Lakes with calcite in sediment in the upper right-hand corner of graph; abreviations are OT—Otisco; CA—Cayuga; OW—Owasco; CI—Canandaigua; SE—Seneca; SK—Skaneateles; CN—Conesus. Other lakes: KE—Keuka; HE—Hemlock; CD—Canadice; HO—Honeoye.
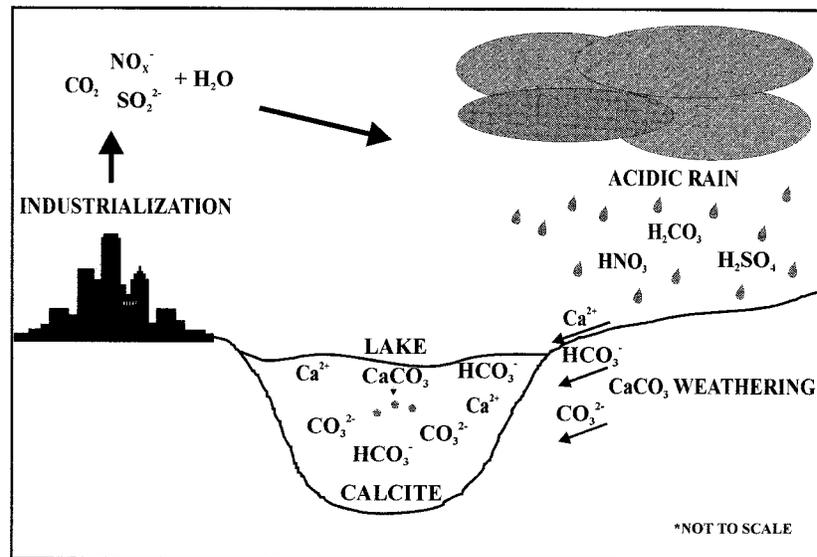

Figure 14. Schematic cartoon illustrating the "carbonate-weathering" hypothesis for the historic return of calcite precipitation in the Finger Lakes. Industrial emissions transport CO_2, SO_2, and NO_x to the troposphere, where they are hydrolyzed into carbonic, sulfuric, and nitric acids, which then rain down on the calcareous terrane, enhancing chemical weathering and the release of calcium, bicarbonate, and carbonate to streams, the loading of these ions ("alkalization") in regional lakes, and ultimately, the precipitation of calcite ("whitings").

load Mg^{2+} to the lakes. This latter interpretation appears unlikely, though, because a comparison of Mg^{2+} data from all 11 Finger Lakes shows that the concentration of Mg^{2+} has decreased between 1972 and 1999 (Callinan,

2001). Reduced Mg^{2+} concentrations may be due to a decline in acidic rainfall during this time interval, especially in the form of sulfuric acid. Skaneateles Lake is the only anomaly in the Ca^{2+} data set in that it does have some
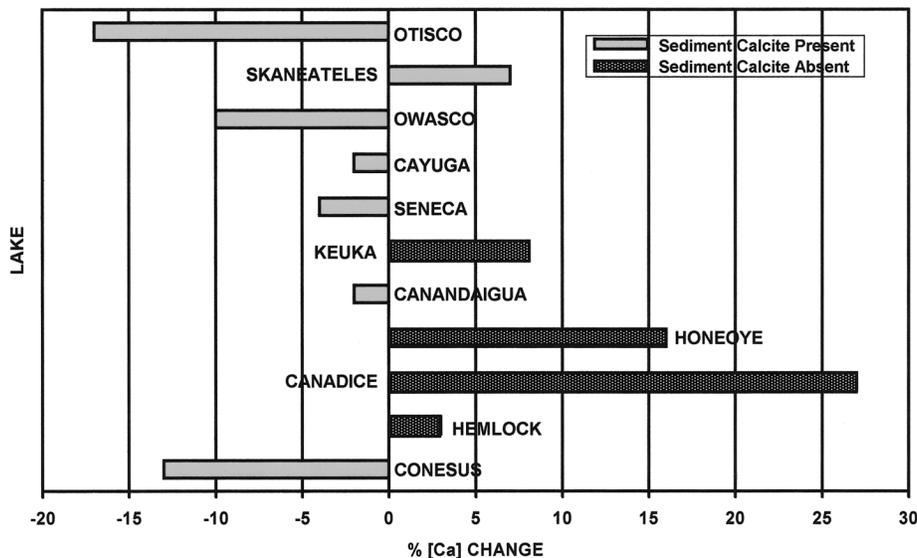
Figure 15. Change in the concentration of calcium in the waters of the Finger Lakes between 1972 (Bloomfield, 1978) and 1999. Note that with the exception of Skaneateles Lake, the Finger Lakes lacking calcite in near-surface sediments display increases in calcium dissolved in their waters, whereas lakes with calcite show decreases in dissolved-calcium concentrations.

calcite present in near-surface sediments (~2%; Fig. 7) yet displays a 7% increase in Ca^{2+} concentrations during the latter one third of the twentieth century (Fig. 15).

The onset of historic calcite precipitation in Cayuga and Owasco Lakes (as well as Canandaigua) during the early 1820s predates the industrial revolution of the mid- to late 1800s. Whitings in these Finger Lakes, however, did begin shortly after European settlers deforested the region during the late 1700s and early 1800s. This occurrence suggests that naturally acidic rain falling on newly exposed and tilled calcareous soils (or, alternatively, the production of agricultural organic acids) was sufficient to leach Ca^{2+}, CO_3^{2-}, and HCO_3^- from their drainage basins and bring the summer surface waters of these lakes to supersaturation with respect to calcite. The strong correlation ($r = 0.93$) between Ca^{2+} concentrations in lake waters and the percentage of tilled land surfaces in their drainage basins (Fig. 13) supports this view that tilling of calcareous soils continuously exposes fresh carbonate minerals and enhances chemical weathering and alkalization of these lakes.

Although calcite precipitation in some of the Finger Lakes started in the early 1820s, it was not until ca. 1940 that the amount of calcite in bottom sediments began to increase rapidly. This proliferation was likely a response to higher levels of acidic deposition coincident with increased industrialization be-

ginning with World War II. This interpretation is supported by paleolimnological studies by Cumming et al. (1992) in the Adirondack Mountains of New York, who found that lakes there began to acidify near the start of the twentieth century (ca. 1900), but did not further acidify significantly until between 1930 and 1950.

Despite the rapid increase in the calcite content of Finger Lake bottom sediments since ca. 1940, most of the lakes that contain calcite display decreasing concentrations at the tops of the box cores (i.e., in sediment deposited in the mid- to late 1990s). This most recent decrease in calcite content is, in most of the lakes, within the range of observed interannual variability and thus could be due to a number of factors previously discussed. This recent decline in calcite, however, is also coincident with the invasion of zebra mussels (an exotic species) into the Finger Lakes beginning in the early 1990s (Halfman et al., 2001). Zebra mussels, which are extremely prolific, may be affecting calcite precipitation in the Finger Lakes by decreasing standing crops of primary producers via filter feeding and/or by lowering the calcite saturation state of lake waters by extracting Ca^{2+} and CO_3^{2-} to form their calcite shells. For Seneca Lake, the calcite content of near-surface sediments has declined from 6% to 2% during the 1990s (Fig. 7). Preliminary budget analyses indicate that zebra mussels annually remove ~200 Mt

of calcium from the water column of Seneca Lake, which is equivalent to ~5% of the annual calcium flux to the lake floor (Halfman et al., 2001).

CONCLUSIONS

Open-water precipitation of calcite (whitings) has returned to 7 of the 11 Finger Lakes during historic times following an ~4500 ^{14}C yr hiatus. The primary control of this precipitation is the saturation of summer surface waters with respect to calcite. Saturation state has been controlled by increased carbonate weathering in individual Finger Lake drainage basins containing calcareous soil and/or limestone by acidic rain during historic time. Calcite precipitation during summer months, however, can be triggered by evaporation, higher summer surface-water temperatures, picoplankton concentrations, and/or photosynthetic removal of CO_2 and pH increase.

Historic calcite precipitation began as early as the 1820s in the Finger Lakes, following regional deforestation. A marked increase in calcite precipitation occurred in ca. 1940 coincident with increased industrialization associated with World War II. Of the industrial pollutants responsible for acid rain, nitrogen oxides—which react with water to form nitric acid—appear to have been most important in increasing carbonate weathering and the transport of calcium and bicarbonate ions to the lakes. Unlike regions with low acid-neutralizing capacity where acid rain results in "acidification" of lakes (such as in the Adirondacks), acidic deposition across well-buffered terrane may result in the "alkalization" of lakes.

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