



## Evidence of mid-Holocene climate instability from variations in carbon burial in Seneca Lake, New York

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### Abstract

The amounts and types of carbon delivered to the sediments Seneca Lake, New York, have varied since the middle Holocene. Concentrations of  $\text{CaCO}_3$  first fluctuate between 14 and 6% around 7 ka before decreasing erratically until about 5 ka and then remain 2% in younger sediments. Because the amount of calcite that precipitates in hard-water lakes is related to summertime thermal stratification, the carbonate fluctuations suggest that cyclic strengthening and weakening of seasonality at intervals of about three centuries accompanied the end of the Holocene Hypsithermal in northeast North America. Organic C/total N values record short, decade-long intervals of enhanced delivery of land-plant material during episodes of wetter climate that are independent of the temperature variations. Higher organic  $\delta^{13}\text{C}$  values indicate that recent fertilization of lake waters from soil disturbance and land-derived runoff has increased aquatic productivity.

### Introduction

Evidence for a variable Holocene climate is widespread (e.g., Overpeck (1996)). In particular, sediment records from North American lakes provide a continental perspective of local and regional responses to climate variations. A brief interlude of post-Younger-Dryas cold climate (the Preboreal Oscillation, 9.6  $^{14}\text{C}$  ka) is evident in lake sediments from the Great Lakes region (Anderson et al. 1997; Yu and Eicher 1998). This period was closely followed by an early-middle Holocene period of warmth and altered precipitation from  $\sim 9$  to 5  $^{14}\text{C}$  ka that is variously called the 'Altithermal', the 'Atlantic Warm Period', the 'Little Climatic Optimum', and the 'Hypsithermal' (Cronin 1999). Because the latter term is one of long standing (e.g., Deevey and Flint (1957)), I will use it in this contribution. The Hypsithermal is recorded as a period of warm and dry climate in much of central North America (Krishnamurthy et al. 1995; Schwalbe et al. 1995; Dean et al. 1996; Haskell et al. 1996; Hassan et al. 1997), but as a time of warm and wet climate in the eastern Great Lakes area (Dwyer et

al. 1996; Silliman et al. 1996). It is succeeded by period of warm and dry climate from 4.8 to 2  $^{14}\text{C}$  ka that is evident in lake sediment records from the central Great Lakes region (Yu et al. 1997). These changes are local and regional examples of the global pattern of Holocene climate instability evident in ice cores (e.g., Meese et al. (1994), Alley et al. (1997)).

Past environmental changes that have occurred within a lake and in its surrounding catchment commonly appear as distinctive differences in the compositions of sediments that were deposited at successive times. Climate changes are a major environmental variable. Lakes in temperate latitudes can be especially sensitive to climate changes because their seasonal stratification and primary production respond strongly to annual cycles. In particular, the calcite that precipitates from the surface waters of hard-water lakes offers a potentially valuable, high-resolution sedimentary record of environmental changes and particularly of those caused by climate changes (Kelts and Talbot 1990; Anderson et al. 1997; Hodell et al. 1998; Mullins 1998).

Summertime calcite precipitation events (whittings)

are well-known in the Laurentian Great Lakes (Strong and Eadie 1978; Hodell et al. 1998), which reside in carbonate-rich catchments. Precipitation of calcite occurs when the solubility product of  $\text{CaCO}_3$  is exceeded (i.e., the water is supersaturated with respect to calcite) and nucleation sites for crystal formation are available. Calcite has retrograde solubility – it becomes less soluble in warmer water. Furthermore, primary productivity affects solubility by removing  $\text{CO}_2(\text{aq})$ , increasing pH, and shifting carbonate equilibria towards  $\text{CO}_3^{2-}$ , thereby favoring calcite precipitation (Thompson et al. 1997). The combination of warmer surface waters and longer duration of primary production magnifies Great Lakes whiting events in years when summer thermal stratification is better developed (Schelske and Hodell 1991; Hodell et al. 1998).

Holocene records from the Great Lakes region show that the calcite contents of lake sediments have varied systematically since the end of the last glacial period. Concentrations are highest in sediments deposited during the mid-Holocene Hypsithermal in sediments of Lake Ontario (Silliman et al. 1996), Seneca Lake (Anderson et al. 1997), and Cayuga Lake (Mullins 1998). This pattern has been interpreted to be a result of warmer summers, which induced earlier seasonal stratification and lengthened the time of photosynthetic algal and bacterial removal of  $\text{CO}_2(\text{aq})$  from the surface waters (Mullins 1998). Greater amounts of calcite consequently precipitated and are recorded as higher concentrations in the sediments that accumulated during this period of warmer climate.

I report here measurements of  $\text{CaCO}_3$  in closely spaced samples in a sediment core from Seneca Lake, New York, that reveal strongly developed cycles in burial of carbonate carbon during the transition from mid-Holocene warm climate to modern climate.

### Setting and samples

Seneca Lake is the largest of the Finger Lakes of New York State and is part of the Great Lakes watershed. The morphology of the Finger Lakes results from deepening of existing valleys by the Laurentide ice sheet during the latest Pleistocene age, which explains why the lakes are narrow and long and why some, such as Seneca, have bottom depths that are below sealevel. The narrow and deep basins provide excellent sites for recovery of undisturbed sediment records

of environmental changes that have occurred since present-day lake levels were established at approximately 13.9 ka (Mullins et al. 1996).

A 5.4 m piston core (4 cm O.D.) was obtained at a water depth of 164 m in the southern part of Seneca Lake in April, 1994. An important factor in choosing this core site was that the water depth was sufficiently great to minimize sediment disturbance from water turbulence. A second factor was that sedimentation rates were anticipated to be high because the site is located on a submerged ridge created by sediment delivery from two major creeks on the west side of the lake (Figure 1). The combination of these two factors predicted good resolution of the sedimentary record. The recovered sediment is an olive-gray silty clay that grades into an olive-gray, brownish-black color 3 m below the water/sediment interface. The laminations observed by Anderson et al. (1997) in the northern part of Seneca Lake were not evident in this core. The top 20 cm of the core was divided into 1-cm sections, the 20–50 cm portion was divided into 2-cm sections, and the remainder of the core was divided into 3-cm sections. A total of 197 sediment samples was obtained.

Samples from plants similar to the flora present around Seneca Lake were collected in and around Ann Arbor, Michigan, to characterize the bulk properties of the land-derived organic matter that might be delivered to the lake. Senescent leaves and needles were picked from trees prior to their dropping in the fall. These materials are representative of the ground litter that could be washed into the lake. The leaves and needles were dried at 60 °C and ground to a coarse powder for elemental and carbon isotopic determinations.

### Analytical methods

Concentrations of  $\text{CaCO}_3$  were measured on freeze-dried sediment samples using the carbonate bomb technique of Müller and Gastner (1971). This procedure involves dissolution of carbonate minerals with cold 3 N HCl to release a volume of  $\text{CO}_2$  that is proportional to the  $\text{CaCO}_3$  content. The insoluble residue concentrates organic matter and non-carbonate minerals and is recovered for subsequent analyses. Carbonate concentrations were calculated assuming all of the inorganic carbon is present as  $\text{CaCO}_3$ .

Total organic carbon (TOC) concentrations of the carbonate-free sediment residues and the dried floral

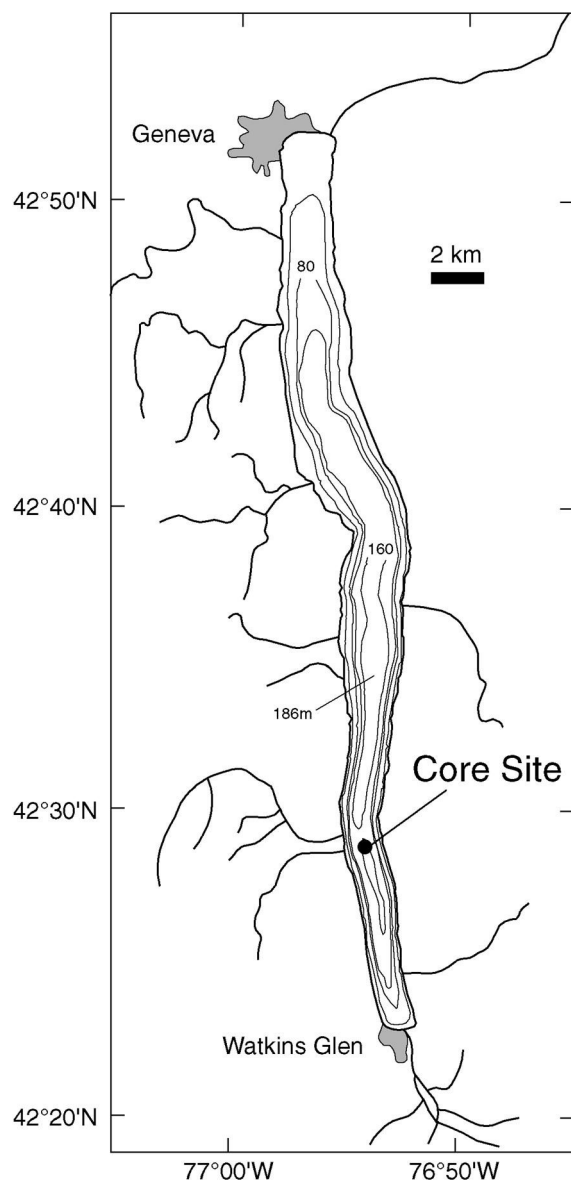


Figure 1. Locations of the 164 m core site and the 186 m maximum depth in Seneca Lake, New York. Bathymetry is shown in meters. The lake drains via the north end.

samples were measured by high-temperature combustion using a Carlo Erba 1108 CHNS analyzer. TOC concentrations are expressed on a whole-sediment basis using the measured percentages of calcium carbonate. Atomic organic C/total N ratios were calculated from the results of the CHNS analyses.

Organic  $\delta^{13}\text{C}$  values were determined on a subset of 47 carbonate-free sediment samples and on the floral samples. The  $^{13}\text{C}/^{12}\text{C}$  ratios of organic carbon

were measured in the Stable Isotope Laboratory at The University of Michigan with a Finnigan Delta S mass spectrometer after combustion of samples at  $800^\circ\text{C}$ . NBS standards are routinely and frequently used to calibrate the instrument. Analytical uncertainty is  $< 0.1\text{‰}$ , and  $\delta^{13}\text{C}$  values are reported relative to the PDB standard.

## Results and discussion

### *Changes in burial of calcium carbonate*

$\text{CaCO}_3$  concentrations are low, hovering around 2%, in the upper 3 m before increasing to values that fluctuate between 6 and 14% at the bottom of the sediment core (Figure 2). Actual age determinations have not been made on this core, yet the approximate age of this major change in sediment carbonate content can be estimated by comparison with nearby dated cores. In cores from Lake Ontario, Cayuga Lake, and the northern part of Seneca Lake, the elevated carbonate concentrations that correspond to the Holocene Hypsithermal decline at the end of this period of warm climate (Silliman et al. 1996; Anderson et al. 1997; Mullins 1998). The time of this change has been determined to be 5.5 ka in three  $^{14}\text{C}$ -dated cores from northern Seneca Lake (Anderson et al. 1997). Because of the relatively short 12-year retention time of the lake (Michel and Kraemer 1995) and because annual overturn homogenizes lake waters (Wing et al. 1995), the changes in conditions that caused the reduction in carbonate precipitation in the northern end of the lake are likely to have occurred simultaneously in the southern end. Therefore, the radiocarbon age of 5.5 ka established by Anderson et al. (1997) can be assigned to the part of the core between 4 and 5 m where  $\text{CaCO}_3$  concentrations first drop to  $\sim 5\%$ . This age estimate yields an approximate sedimentation rate of  $0.8\text{ m ky}^{-1}$  and a basal radiocarbon age of about 6.7 ka for the 5.4 m core. The core therefore provides a paleoclimate record starting in the late Hypsithermal and continuing to modern time.

The closely spaced measurements of  $\text{CaCO}_3$  concentrations from this core yield novel evidence of climate instability during the Holocene Hypsithermal and its termination. The concentrations fluctuate strongly and regularly in the lower 2 m of the core (Figure 2). The spacing of these variations is approximately three centuries, based on the estimated sedi-

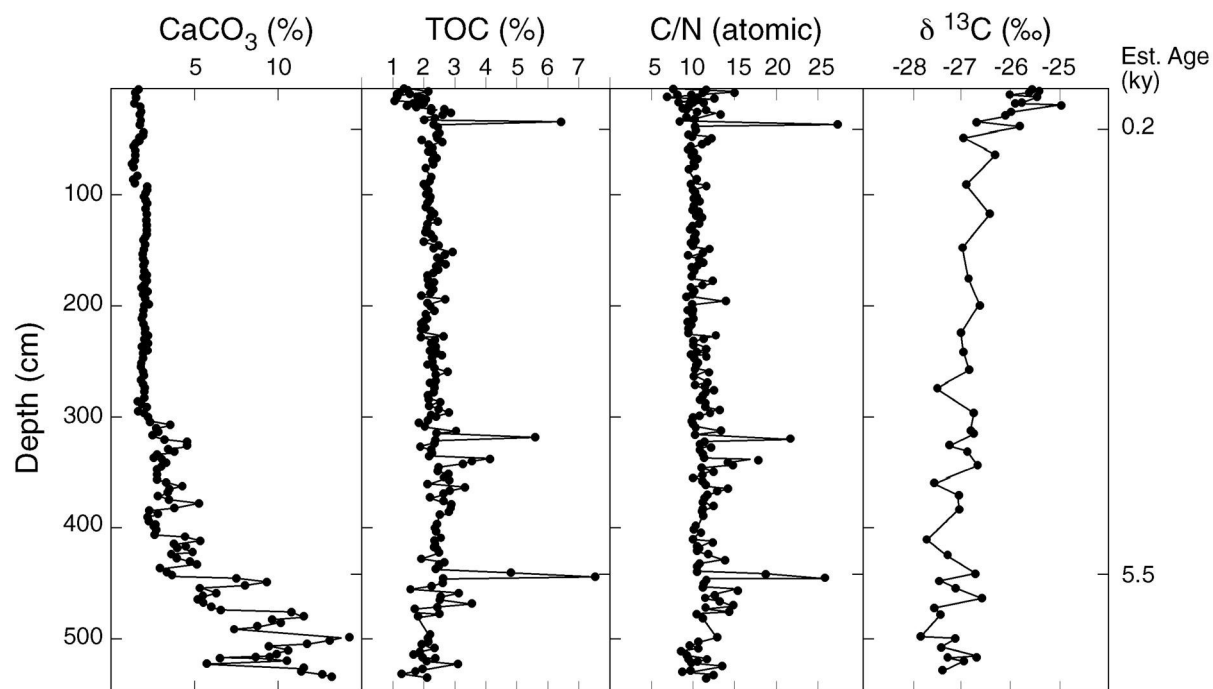


Figure 2. Concentrations of  $\text{CaCO}_3$ , organic carbon (TOC), atomic organic C/total N values, and organic  $\delta^{13}\text{C}$  values in sediment of Seneca Lake. Radiocarbon ages of 5.5 and 0.2 ka are estimated by comparison to similar changes in sediment contents found in  $^{14}\text{C}$ -dated cores from nearby locations. Sedimentation rate is estimated to average approximately 0.8 m/ky. Strongly developed fluctuations in  $\text{CaCO}_3$  concentrations indicate century-scale cycles in summer temperatures between 7 and 5 ka. Peaks in C/N values indicate episodes of elevated wash-in of land-plant organic matter and hence periods of extreme precipitation.

mentation rate of  $0.8 \text{ m ky}^{-1}$ . Lower-resolution  $\text{CaCO}_3$  records from nearby locations (Silliman et al. 1996; Anderson et al. 1997; Mullins 1998) contain hints that similar variations in concentrations continue back to 9 ka. If formation of calcite in the surface lake waters is influenced principally by summer temperatures and duration of thermal stratification (e.g., Hodell et al. (1998), Mullins (1998)), then these fluctuations suggest important variations in seasonality during the early-to-middle Holocene in this part of North America.

Factors in addition to precipitation of calcite can cause changes in concentrations of this sediment component. A very likely paleoclimatic factor would be changes in amounts of rainfall. Periods of greater rainfall can increase delivery of the clastic sediment components that dilute the calcite concentrations. Episodes of massive flooding is evident in the Holocene in the American Southwest (Ely et al. 1993), in the Mississippi drainage basin (Brown et al. 1999), in New England (Brown et al. 2000), and in the nearby Susquehanna River catchment (Cronin et al. 2000). Because the catchment of Seneca Lake

could have been also influenced by episodes of elevated precipitation, I explored for independent evidence of increased wash-in of land-derived sediment components.

#### *Changes in delivery of land-derived organic matter*

Periods of increased runoff would simultaneously deliver magnified pulses of clastic sediment components, organic matter derived from land plants, and nitrates and phosphates washed out of soil to the lake. The proportions of sediment organic matter that originate from land and from within a lake can be distinguished by the characteristic difference between the C/N ratios of vascular land plants and algae (Table 1). Increased delivery of land-plant organic matter would be recorded as elevations of C/N values in the sediment (e.g., Kaushal and Binford (1999)). Several large C/N spikes in fact appear in the core record (Figure 2), but only the one between 437–443 cm corresponds to one of the six periods of diminished  $\text{CaCO}_3$  concentration below 3 m core depth. Therefore, the fluctuations in calcite concentration do

Table 1. Atomic C/N ratios and  $\delta^{13}\text{C}$  values of some representative sources of organic matter to lake sediments in the Great Lakes system. Plankton data are from Meyers (1994)

Organic matter source	Location	C/N	$\delta^{13}\text{C}$
Yellow poplar leaves	Ann Arbor, Michigan	33	-29.1
Eastern cottonwood leaves	Ann Arbor, Michigan	26	-26.9
	Grosse Ile, Michigan	31	-30.5
White oak leaves	Ann Arbor, Michigan	22	-29.0
	Grosse Ile, Michigan	21	-25.1
Red oak leaves	Ann Arbor, Michigan	29	-29.8
	Grosse Ile, Michigan	31	-28.7
	Bancroft, Ontario	22	-28.9
American beech leaves	Grosse Ile, Michigan	17	-28.3
	Pinckney, Michigan	24	-31.0
Sugar maple	Bancroft, Ontario	32	-28.2
	Ann Arbor, Michigan	31	-27.8
	Ann Arbor, Michigan	32	-26.8
Mixed plankton	Lake Michigan	7	-26.8

not appear to result from variations in precipitation and consequent greater and lesser amounts of clastic dilution of the carbonate.

The large C/N spikes obvious in Figure 2 nonetheless appear to be valid indicators of episodes of increased wash-in of land-plant material that were probably associated with short-lived periods of massive flooding. The well developed spike at 437–443 cm, for example, corresponds to a thin layer of leaves and twigs that was noted in the core (M.R. Wing, personal correspondence). Moreover, elevated TOC concentrations correlate with higher C/N values (Figure 3), suggesting that washed-in land-plant material contributes at least partially to enhancements in organic carbon concentrations. Smaller elevations of C/N ratios exist throughout the core; they may indicate that other short intervals of increased rainfall occurred throughout the Holocene in this part of North America. By analogy to independent evidence of wet periods in Chesapeake Bay, which receives the runoff from the Susquehanna River, these intervals may have spanned less than two decades (Cronin et al. 2000). However, the 2–3 cm sample intervals cannot give such temporal resolution at an average sedimentation rate of  $0.8 \text{ m ky}^{-1}$  in the Seneca Lake core. In addition, the absence of laminations suggests that bioturbation of the sediments occurred, which would have dispersed contributions of land-derived organic matter over several core intervals, as evident in some peaks in C/N values (Figure 2). The fact that the C/N excursions are still present despite sediment mixing suggests that very large amounts of land-derived

organic matter must have been delivered during the postulated periods of wetter climate.

#### Changes in algal production of organic matter

Organic  $\delta^{13}\text{C}$  values are affected by rates of algal production in lakes (Hollander and MacKenzie 1991; Keeley and Sandquist 1992; Bernasconi et al. 1997; Brenner et al. 1999), which is controlled by availability of dissolved nutrients. Runoff of soil-derived nitrates and phosphates enhances aquatic productivity, which selectively removes  $^{12}\text{C}$ -rich dissolved inorganic carbon and leads to less negative  $\delta^{13}\text{C}$  values in the organic matter produced from the remaining inorganic carbon. Part of the history of anthropogenic additions of nutrients to the Great Lakes is recorded in such a change in the  $\delta^{13}\text{C}$  values of organic matter in the sediments of Lakes Erie and Ontario (Schelske and Hodell 1991, 1995; Hodell and Schelske 1998). The isotopic shift in the upper 35 cm of the core (Figure 2) to  $\delta^{13}\text{C}$  values that are  $\sim 1\%$  less negative than in plankton from oligotrophic Lake Michigan (Table 1) and in deeper sediment indicates recovery of modern sediment by the piston core. The watershed

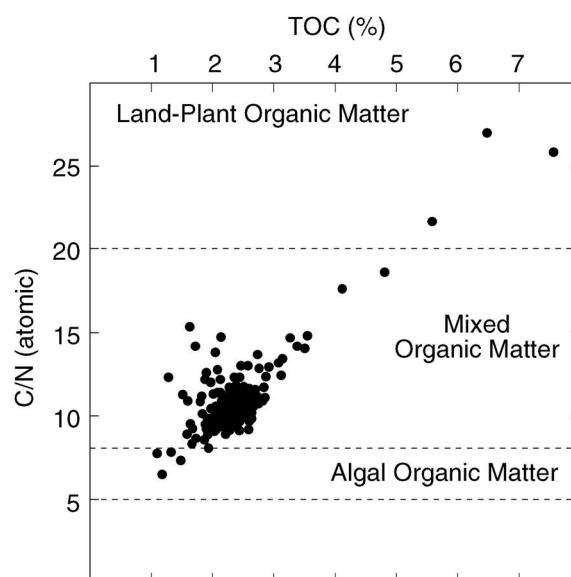


Figure 3. Relation between atomic C/N values and total organic carbon (TOC) concentrations in sediment of Seneca Lake. Elevations in C/N values and TOC concentrations record wash-in of land-plant organic matter and soil nutrients, the latter stimulating aquatic production of organic matter.

of Seneca Lake changed from an undisturbed forest to clear-cut farm fields shortly after the completion of the Erie Canal in 1825. This environmental change accelerated release of soil nutrients and their delivery to the lake. Subsequent expansion of human and livestock populations further increased nutrient deliveries to the lake system, enhancing algal growth and progressively decreasing the availability of dissolved  $^{12}\text{C}$ . These changes in watershed conditions are mirrored in the progressively less negative  $\delta^{13}\text{C}$  values of organic matter in the younger lake sediments (Figure 2). With the exception of one core interval in which the elevated C/N value indicates a large proportion of land-derived organic matter (Figure 2), a systematic shift to less-negative  $\delta^{13}\text{C}$  values is present in the upper 35 cm of Seneca Lake sediment (Figure 4). This isotopic shift indicates a general enhancement in recent aquatic productivity that would not be evident from the isotopic compositions of land and algal organic matter (Table 1) without the impact of enhanced productivity on the dissolved inorganic carbon reservoir.

Other similarly well-developed organic carbon isotopic excursions that would reflect prehistoric nutrient additions to Seneca Lake do not appear deeper in the sediment record. The absence of such excursions and the lack of correspondence between C/N peaks and changes in  $\text{CaCO}_3$  concentrations again suggests that variations in rainfall are probably not the principal cause for the  $\text{CaCO}_3$  fluctuations in lower part of the core. Instead, century-scale temperature variations between 7 and 5 ka emerge as the strongest probable cause for these fluctuations.

#### *Modern changes in accumulation of carbon*

The increase in modern aquatic productivity evident in the  $\delta^{13}\text{C}$  data should result in greater delivery of both inorganic and organic carbon to the lake bottom (Schelske and Hodell 1995; Thompson et al. 1997; Hodell et al. 1998; Mullins 1998; Teranes and McKenzie 1999). Concentrations of  $\text{CaCO}_3$  do not change significantly over the top 3 m of sediment (Figure 2), which contrasts with increases since 1940 documented by Mullins (1998) in nearby Cayuga Lake and by Hodell et al. (1998) in Lake Ontario. Interestingly, TOC concentrations decrease in the same interval of upper sediments in which  $\delta^{13}\text{C}$  values record elevated productivity (Figure 2). This disparity suggests that greater delivery of clastic sediment components has

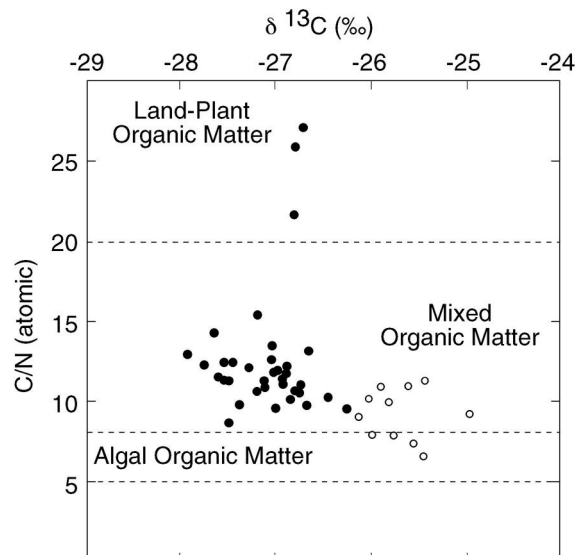


Figure 4. Relation between atomic C/N values and organic  $\delta^{13}\text{C}$  values in sediment of Seneca Lake. Representative ranges of C/N values of organic matter from algae and land plants are shown. High C/N values identify intervals of elevated wash-in of land-plant organic matter. Open symbols represent samples in the upper 35 cm of the sediment core in which C/N values are low and  $\delta^{13}\text{C}$  values are high. These samples represent modern and near-modern conditions of elevated aquatic productivity.

accompanied the increased wash-in of nutrients that has magnified aquatic production in recent times. The clastic components evidently have diluted the proportions of both  $\text{CaCO}_3$  and TOC in the sediments and have consequently concealed the actual increases in their rates of accumulation. Without accurate determinations of sediment ages, the mass accumulation rates needed to quantify the magnitude of these changes cannot be determined. Nonetheless, the approximately halving of the TOC concentrations in the upper sediments (Figure 2) suggests that delivery of both  $\text{CaCO}_3$  and clastic sediment components has increased by at least a factor of two in modern times.

#### **Summary and conclusions**

Study of closely spaced samples from a 5.4-m core of sediment from Seneca Lake reveals evidence of two types of mid-Holocene climate instability in the eastern Great Lakes region: 1. Well-developed fluctuations in calcite concentrations in sediments that were

deposited between 7 and 5 ka represent cyclic alternations of periods of warmer and cooler summers in northeastern North America that lasted two-to-three centuries. 2. Spikes in organic C/N values indicate short events of elevated wash-in of land-derived organic matter that appear to record episodes of markedly wetter climate that probably lasted for no more than a few decades.

In addition, modern and near-modern delivery of lake-derived organic matter and calcite has been magnified by anthropogenic impacts, which have also increased delivery of the clastic sediments that dilute the biogenic sedimentary components.

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