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Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates

Philip A. Meyers[1] & Elisabeth Lallier-Vergès[2]
[1]*Department of Geological Sciences and Center for Great Lakes and Aquatic Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, USA*
[2]*URA 724 - FW 09 CNRS. Laboratoire de Géologie de la Matière Organique, Université d'Orléans, F-45067 Orléans Cedex 2, France*

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Abstract

Identification of the sources of organic matter in sedimentary records provides important paleolimnologic information. As the types and abundances of plant life in and around lakes change, the composition and amount of organic matter delivered to lake sediments changes. Despite the extensive early diagenetic losses of organic matter in general and of some of its important biomarker compounds in particular, bulk identifiers of organic matter sources appear to undergo minimal alteration after sedimentation. Age-related changes in the elemental, isotopic, and petrographic compositions of bulk sedimentary organic matter therefore preserve evidence of past environmental changes.

We review different bulk organic matter proxies of climate change in tropical and temperate sedimentary records ranging in age from 10–500 ka. Times of wetter climate result in enhanced algal productivity in lakes as a consequence of greater wash-in of soil nutrients, and these periods are recorded as elevated Rock-Eval hydrogen indices, lowered organic C/N ratios, less negative organic δ^{13}C values, and increased organic carbon mass accumulation rates. Lowering of lake water levels, which typically depresses algal productivity, can also cause an apparent increase in organic carbon mass accumulation rates through suspension of sediments from lake margins and redeposition in deeper basins. Alternations between C_3 and C_4 watershed plants accompany climate changes such as glacial/interglacial transitions and wet/dry cycles, and these changes in land-plant types are evident in δ^{13}C values of organic matter in lake sediments. Changes in climate-driven hydrologic balances of lakes are recorded in δD values of sedimentary organic matter. Visual microscopic examination of organic matter detritus is particularly useful in identifying changes in bulk organic matter delivery to lake sediments and therefore is important as an indicator of climate changes.

Key words: carbon isotopes, nitrogen isotopes, hydrogen isotopes, Rock-Eval analyses, C/N ratios, pollen, organic carbon mass accumulation rates, organic petrography

Introduction

Organic matter constitutes a minor but important fraction of lake sediments. It originates from the complex mixture of lipids, carbohydrates, proteins, and other biochemicals produced by organisms that have lived in the lake and its watershed. As an accumulation of 'geochemical fossils', the organic matter content of lake sediments provides information that is important to interpretations of lacustrine paleoenvironments, histories of climate change, and the effects of humans on local and regional ecosystems.

The primary source of organic matter to lake sediments is from the particulate detritus of plants; only a few percent come from animals. Plants can be divided into two geochemically distinctive groups on the basis of their biochemical compositions: (1) nonvascular plants that contain little or no carbon-rich cellulose and lignin, such as phytoplankton, and (2) vascular plants that contain large proportions of these fibrous tissues, such as grasses, shrubs, and trees. These latter types of plants exist on land near lakes and in the shallow parts of lakes as bottom-rooted, emergent vegetation. The relative contributions from these two plant groups to lake sedimentary records are influenced strongly by lake morphology, watershed topography and climate, and the relative abundances of lake and watershed plants. Organic matter in lake sediments covers the spectrum of being predominantly algal in some lakes to being largely land-derived in others.

During deposition in the lake bottom, organic matter is subject to microbial reworking, with the result that much of its original molecular composition becomes altered. Humic substances, a general term that includes a range of difficult-to-characterize forms of organic matter, are diagenetically created from the biochemical starting materials. Humic substances constitute up to 60–70% of the organic matter in young lacustrine sediments, and this percentage rises to over 90% in older sediments (Ishiwatari, 1985). Because identifiable molecular fossils become minor constituents of lake sediments, the characteristics of bulk organic matter are generally more representative of paleoenvironmental conditions.

Studies of organic matter composition in the sediments of lakes from the different parts of the world have been used to help reconstruct records of regional and continental paleoclimates. A record of the sources of sedimentary organic matter is provided in its elemental, isotopic, petrological and molecular compositions. An important component of paleolimnologic investigations is to identify the sources of organic matter in sediments deposited at different times in the past. A critical question in view of the known decreases that occur to the quantity of sedimenting organic matter is ‘How accurately does the type of organic matter in sediments reflect the original sources?’. Despite the extensive early diagenetic losses of organic matter in general and of some of its important biomarker compounds in particular, bulk parameters appear to remain reliable indicators of organic matter sources.

In this paper, we summarize the information provided by bulk organic matter parameters, describe some examples of lacustrine organic matter sedimentary records, and consider their paleoenvironmental significance. Further details about organic matter in sedimentary records are given in the published reports that we cite and in more comprehensive publications such as Engel & Macko (1993), Killops & Killops (1993), and Tyson (1995).

Indicators of organic matter sources

Lacustrine accumulations of sedimentary organic matter reflect both the types and amounts of materials from primary sources and the extent of alteration and degradation of the starting material. Lake systems are diverse, and the sources and alterations of organic matter are geographically and temporally variable. Although the accumulation record of each individual lake is usually unique, studies of different lakes have produced generalizations about the factors that control and modify the organic matter contents of lacustrine sediments.

Losses of organic matter can be extensive during transport and incorporation in lake sediments (e.g, Meyers & Eadie, 1993; Bernasconi et al., 1997). Despite the very real potential for diagenetic biasing of the initial source character of organic matter, a number of the parameters that describe compositions of bulk organic matter provide relatively reliable evidence of its original sources. Elemental, isotopic, and petrographic compositions preserve records of the biologic origins of the organic matter that has been deposited in the sediments of lakes over time.

Source information preserved in C/N ratios of sedimentary organic matter

Origin of sedimentary organic matter from aquatic as opposed to land sources can be distinguished by the characteristic C/N ratio compositions of algae and vascular plants (Figure 1). C/N values of some typical plants that contribute organic matter to lake sediments and examples of C/N ratios of lake sediments are given in Table 1. Phytoplankton have low C/N ratios, commonly between 4 and 10, whereas vascular land plants, which are cellulose-rich and protein-poor, have C/N ratios of 20 and greater. Lakes for which the contribution of organic matter from vascular plants is small relative to water-column production, exemplified by Walker Lake and Lake Michigan, have lower C/N ratios in their sediments than lakes receiving important amounts of vascular plant debris, such as Mangrove Lake and Lake Bosumtwi (Table 1). Ratios of 13–14 for surface sediments of the latter two lakes suggest a subequal mixture of algal and vascular plant contributions, which is expected for most lakes.

Partial degradation of organic matter during early diagenesis can modify elemental compositions and hence C/N ratios of organic matter in sediments. C/N ratios of fresh wood samples, for example, are generally higher than those of wood that has been buried in sediments (Meyers et al., 1995). This change reflects selective degradation of carbon-rich sugars and lipids in the buried wood. In contrast, the C/N ratios of algal-

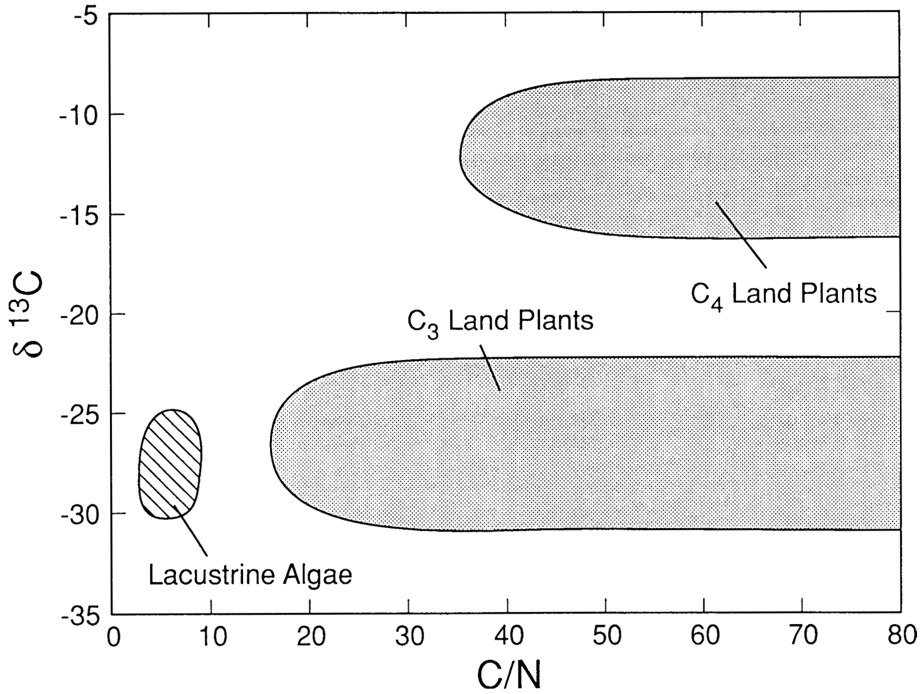

Figure 1. Representative elemental and carbon isotopic compositions of organic matter from lacustrine algae, C_3 land plants, and C_4 land plants that use CO_2 as their source of carbon during photosynthesis. Deviations from these generalized patterns occur and provide paleolimnologic information. Atomic C/N ratios and organic $\delta^{13}C$ values for individual plant samples in the general groupings are given in Table 1.

derived organic matter often increase during sinking and early sedimentation as nitrogen-rich proteins are selectively degraded. This trend is well-developed in lakes having high productivity, such as eutrophic Aydat Lake in France. An increase in the C/N ratio throughout the upper 40 cm of sediment (Sarazin et al., 1992) indicates active microbial denitrification of organic matter. In oligotrophic lakes, C/N ratios commonly decrease with depth in sediments as organic matter degrades. Anaerobic utilization of organic carbon yields CO_2 and CH_4, which escape from the sediments as TOC concentrations decrease. Nitrogenous matter yields NH_4^+, which is absorbed by clay minerals and thereby retained in the sediments, much as in the seafloor (Müller, 1977; Lallier-Vergès & Albéric, 1990), and therefore prevents a decrease in total nitrogen that is equivalent to the TOC decrease. An anologous decrease in C/N ratios has been observed in soils (Sollins et al., 1984), where it also involves the microbial immobilization of nitrogenous material accompanied by the remineralization of carbon. These changes in the elemental composition of sedimentary organic matter are not commonly large enough, however, to erase the large C/N differences (Table 1, Figure 1) between the organic matter derived from vascular land plants and non-vascular algae. For example, vascular plant debris isolated from sediment having a bulk C/N of 15 retained the C/N values between 30 and 40 that are characteristic of cellulosic plants (Ertel & Hedges, 1985).

Comparison of the organic matter C/N ratios of plankton, sediment trap contents, and surficial sediment in Lake Michigan suggests that these bulk parameters retain source information despite large decreases in the total amount of organic matter during sinking (Figure 2). Although organic carbon concentrations diminish by a factor of ten between plankton and the lake bottom, little difference is evident between the initial and final C/N ratios. Considerable variation is evident, however, in the C/N values of the sinking organic matter. These changes in organic matter elemental composition agree with observed changes in biomarker compositions that show selective losses of algal components in the upper water column and apparent lateral input of algal organic matter at greater depths (Meyers & Eadie, 1993). The changes evidently reflect different biogeochemical processes at different water depths.

Table 1. Representative atomic C/N ratios and organic δ^{13}C values (‰ PDB) of different types of primary organic matter sources to sediments of lakes, and some examples of the C/N and δ^{13}C signatures of bulk organic matter in modern lake sediments

Organic Matter Source	Location	C/N	δ^{13}C	Reference
C_3 Land Plants				
willow leaves	Walker Lake, Nevada	38	–26.7	Meyers (1990)
poplar leaves	Walker Lake, Nevada	62	–27.9	Meyers (1990)
cottonwood leaves	Grosse Ile, Michigan	31	–30.5	Meyers (unpublished)
yellow poplar leaves	Ann Arbor, Michigan	33	–29.1	Meyers (unpublished)
white oak leaves	Ann Arbor, Michigan	22	–29.0	Meyers (unpublished)
red oak leaves	Ann Arbor, Michigan	29	–29.8	Meyers (unpublished)
American beech leaves	Grosse Ile, Michigan	17	–28.3	Meyers (unpublished)
European beech leaves	Ann Arbor, Michigan	17	–30.2	Meyers (unpublished)
pinyon pine needles	Walker Lake, Nevada	42	–24.8	Meyers (1990)
white spruce needles	Ann Arbor, Michigan	42	–25.1	Meyers et al. (1995)
white pine needles	Ann Arbor, Michigan	42	–25.2	Meyers (unpublished)
red pine needles	Ann Arbor, Michigan	39	–27.1	Meyers (unpublished)
palm fronds	Lake Bosumtwi, Ghana	91	–25.5	Talbot and Johanessen (1992)
C_4 Land Plants				
salt grass	Walker Lake, Nevada	160	–14.1	Meyers (1990)
tumbleweed	Walker Lake, Nevada	68	–12.5	Meyers (1990)
blood grass	Lake Bosumtwi, Ghana	42	–11.1	Talbot and Johanessen (1992)
wild millet	Lake Bosumtwi, Ghana	156	–10.8	Talbot and Johanessen (1992)
Soil Organic Matter				
Lake Baikal watershed	Siberia, Russia	20	–23.4	Prokopenko et al. (1993)
Willamette valley	Oregon, USA	13	–26.2	Prahl et al. (1994)
peat bog	Washington, USA	17	–28.7	Ertel and Hedges (1984)
Lake Algae				
mixed plankton	Lake Baikal, Russia	9	–30.9	Prokopenko et al. (1993)
mixed plankton	Walker Lake, Nevada	8	–28.8	Meyers (1990)
mixed plankton	Pyramid Lake, Nevada	6	–28.3	Meyers (1994)
mixed plankton	Lake Michigan	7	–26.8	Meyers (1994)
Lake Surface Sediments				
Lake Biwa	Honshu, Japan	6	–25.3	Meyers and Horie (1993)
Lake Michigan	North America	8	–26.3	Rea et al. (1980)
Walker Lake	Nevada, USA	8	–24.2	Meyers (1990)
Pyramid Lake	Nevada, USA	9	–26.9	Tenzer et al. (1997)
Lake Baikal	Russia, Siberia	11	–29.9	Qiu et al. (1993)
Coburn Pond	Maine, USA	12	–28.4	Ho and Meyers (1994)
Lake Baikal	Siberia, Russia	13	–27.4	Prokopenko et al. (1993)
Lake Bosumtwi	Ghana, Africa	14	–26.4	Talbot and Johannessen (1992)

Source and paleoproductivity information from carbon stable isotopic compositions

Most photosynthetic plants incorporate carbon into organic matter using the C_3 Calvin pathway, which preferentially takes up ^{12}C with an isotopic discrimination that averages –20 ‰ from the ^{13}C/^{12}C ratio of the inorganic carbon source (cf. O'Leary, 1988). Some plants use the C_4 Hatch-Slack pathway, and others, mostly desert plants and succulents, utilize the CAM (crassulacean acid metabolism) pathway. The isotope discrimination in the C_4 pathway is –4 to –6 ‰, whereas that in the CAM pathway can vary from –4 to –20 ‰. Organic matter produced from atmospheric CO_2 (δ^{13}C = –7 ‰) by land plants using the C_3 pathway consequently has an average d^{13}C (PDB) value of ca. –28 ‰ and by those using the C_4 pathway ca. –14 ‰ (cf. O'Leary, 1988).

Lake-derived organic matter that is produced by phytoplankton (C_3 algae) using dissolved CO_2 in isotopic equilibrium with the atmosphere is usually isotopically indistinguishable from organic matter

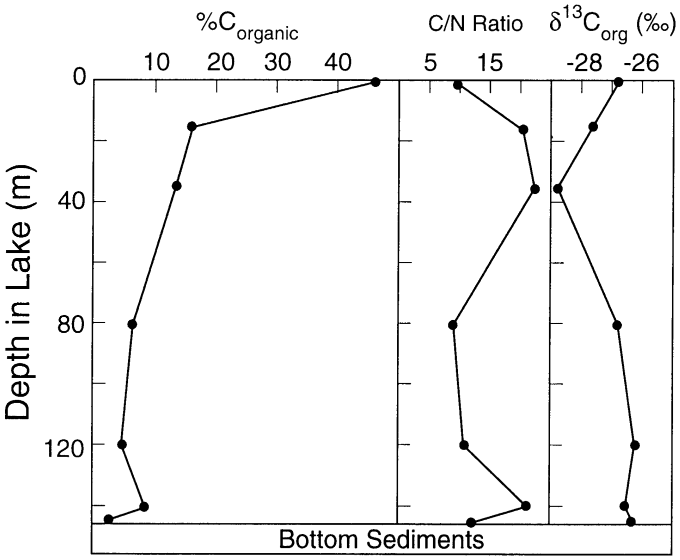

Figure 2. Organic carbon concentrations, atomic C/N ratios, and carbon isotopic signatures in phytoplankton, sediment traps at five depths, and surficial sediments in Lake Michigan. Organic carbon concentrations decrease by a factor of ten, but C/N and isotopic ratios are virtually unchanged between phytoplankton and sediment values. From Meyers and Eadie (1993).

produced by C_3 plants in the surrounding watershed (Table 1). Algal organic matter, moreover, typically has a distinctly different carbon isotopic composition than material produced by C_4 plants growing either on land or the lake bottom (Figure 1). However, this generalization about carbon isotopic source signatures erodes when the availability of dissolved CO_2 is limited and algae begin to use dissolved HCO_3^- ($\delta^{13}C = 1$ ‰) as their source of carbon. Situations where HCO_3^- becomes important include periods of high photosynthetic uptake of dissolved inorganic carbon during which the availability of CO_2 becomes diminished (Keeley & Sandquist, 1992; Hollander & McKenzie, 1991; Bernasconi et al., 1997) and in waters where the ratio of HCO_3^- to CO_2 is kept elevated by an alkaline pH (e.g., Hassan et al., 1997). In such cases, $\delta^{13}C$ values of algal organic matter can increase to reach as high as –9 ‰, which is in the range of C_4 plants (Figure 1). The possibility of this type of biasing of the isotopic source signature is a potent reminder that multiple indicators of organic matter origin should be employed in paleolimnologic studies.

Microbial reworking of organic matter during early diagenesis can potentially modify its bulk carbon isotopic content because organic matter is a mixture of different types of compounds that have different isotopic contents. Comparison of the organic $\delta^{13}C$ values of plankton, sediment trap contents, and surficial sediment in Lake Michigan reveals an interesting pattern of isotopic variation that accompanies a large decrease in the total amount of organic matter during sinking (Figure 2). The initial and final carbon isotopic ratios remain similar at ca. –26 to –27 ‰, yet values decrease to ca. –29 ‰ in the upper water column where organic carbon decreases are greatest. The location of these changes in organic matter isotopic composition correspond to changes in compositions of biomarker molecules that show selective losses of algal components in the upper water column (Meyers & Eadie, 1993). The isotopic changes apparently reflect progressive diagenetic losses of algal organic matter and eventual survival of the most resistant organic matter fractions. The overall diagenetic isotope shift, however, is minimal. This conclusion is supported by the virtually identical profiles of organic matter $\delta^{13}C$ values found in two sediment cores that were collected 6 yrs apart from the same location in Lake Ontario by Hodell & Schelske (1998). Post-depositional diagenesis diminished the mass of organic matter but did not significantly alter its isotopic composition during the 6 yrs that sediments resided in the lake bottom.

Because diagenetic isotope effects are typically minimal, differences between $\delta^{13}C$ values of sediments deposited at different times provide information about paleoenvironmental changes. The recent histories of cultural eutrophication of Lakes Ontario and Erie are recorded by 2 ‰ shifts towards less negative organic carbon δ^{13}C values between sediments deposited in the mid 1800's and sediments deposited from 1970–1980 (Schelske & Hodell, 1991, 1995). This isotopic excursion has been reversed in more modern sediments in these lakes as productivity has declined (Schelske & Hodell, 1995; Hodell & Schelske, 1998). Two periods of Holocene desiccation of Walker Lake, Nevada, created shifts in the overall carbon isotopic contents of this saline lake and are recorded as organic matter δ^{13}C values that are 3 ‰ less negative in sediment horizons deposited at 5 and 2 ka (Benson et al., 1991). The organic matter in the dry-period sediments is a combination of material synthesized by C_3 algae when the lake waters were concentrated by evaporation and consequently isotopically heavier and of material produced by C_4 salt grasses that colonized salt marshes on the former lake bed. A further illustration of the paleolimnological potential of organic δ^{13}C values is provided by Rau (1978), who finds that the organic δ^{13}C values of algae from Findley Lake, Washington, are as negative as –47 ‰. Extensive respiration of organic matter in this lake and its surrounding watershed produces isotopically light dissolved CO_2, which is then utilized by the algae to yield organic matter that is even more depleted in ^{13}C. Excursions to very negative organic δ^{13}C values in sedimentary records can therefore reveal periods of similar reutilization of organic carbon in the histories of lacustrine systems.

Source and paleoproductivity evidence from nitrogen stable isotopic compositions

Important paleolimnological information about the origins of sediment organic matter can potentially be obtained from nitrogen isotopic compositions, yet δ^{15}N values remain to be routinely applied to paleolimnological studies. Identification of organic matter sources is based on the difference between the isotopic contents of the inorganic nitrogen reservoirs available to aquatic plants and land plants. Dissolved nitrate has a mean isotope ratio of +7 to +10 ‰, whereas atmospheric molecular nitrogen has a δ^{15}N of about 0 ‰ (cf. Peters et al., 1978). This difference is preserved in the isotopic contents of plankton (δ^{15}N of +8 ‰) and C_3 land plants (δ^{15}N of +1 ‰) and has been used to trace coastal marine food chain relationships (Peterson et al., 1985). The dynamics of nitrogen recycling and of nitrogen isotope discrimination during biological uptake introduce considerable variability into these generalized numbers (Fogel & Cifuentes, 1993; Bernasconi et al., 1997; Hodell & Schelske, 1998). The consequent deviations from the expected δ^{15}N values can be seen both as challenges to their application as source indicators and as opportunities to learn more about the pathways of nitrogen utilization within a lacustrine system.

Investigations of the nitrogen isotope content of lake sediments indicate that the potential source information provided by the δ^{15}N values of organic matter appears to be preserved. For example, Pang and Nriagu (1976, 1977) found that sediments in areas of lakes Superior and Ontario receiving a large proportion of land-sourced organic matter have smaller δ^{15}N values than areas where aquatic organic matter is dominant (+3.7 vs. +4.9 ‰). Moreover, the potential isotopic biasing that could result from preferential degradation of relatively reactive forms of nitrogen-containing organic matter are minor or absent. Significant amounts of downcore degradation of nitrogenous matter relative to total organic matter occurs at all locations in these lakes, increasing the potential for diagenetic isotope shifts. Nevertheless, no differences are evident between δ^{15}N ratios in surface sediments and those at the bottoms of the half-meter cores. These results suggest that lake sediments integrate the range of δ^{15}N values in the organic matter delivered to them to give a reliable record of its dominant sources.

Records of environmental changes, therefore, can be provided by the δ^{15}N values of organic matter in lake sediments. Meyers et al. (1998) note a 2 ‰ shift towards higher δ^{15}N values that accompanied the lowering of the water level in Pyramid Lake, Nevada. This environmental change is a modern one caused by partial diversion of the Truckee River for agricultural use. Part of the isotopic increase probably reflects diminished input of isotopically light land-plant detritus carried by the river waters. The shift is therefore partially a source change – a change in the proportions of algal and land-plant contributions of organic matter to the lake sediments. An additional factor in the δ^{15}N shift, however, is decreased algal discrimination towards ^{14}N as fluvial replenishment of dissolved nitrate diminished after diversion of the river. Consequently, the shift also records lessened availability of dissolved nitrate to lake algae as lacustrine conditions changed.

Paleoprecipitation records from oxygen and hydrogen isotope contents of organic matter

One of the cornerstones of paleoclimatic reconstructions is the application of ^{18}O/^{16}O and D/H ratios in water, ice, and certain minerals as indicators of origins of paleoprecipitation. However, these isotopic ratios are not commonly determined in organic matter from sedimentary records. Various oxygen-rich compounds are commonly employed to oxidize organic matter to CO_2 prior to isotopic analysis, and the consequent introduction of additional oxygen has discouraged wide use of the $^{18}O/^{16}O$ ratios of organic matter in paleoclimatology. Some investigators, however, have found ways to circumvent this analytical limitation. Beuning et al. (1997), for example, isolated aquatic cellulose from the sediments of Lake Victoria, which they then pyrolyzed with a nickel catalyst to produce CO_2 that preserved the original $^{18}O/^{16}O$ ratios of organic matter produced within the waters of this lake. After correction for biological discrimination in favor of ^{16}O, the cellulose isotope results yield a reconstruction of lake-water $\delta^{18}O$ values over the past 13 ka that reflects a combination of precessional precipitation changes in East Africa and downcutting of the Lake Victoria outlet.

D/H ratios of sedimentary organic matter have also not been widely applied in paleolimnology, largely because not many laboratories are skilled in their use, yet they have considerable promise. Fractionation of hydrogen isotopes by land plants is complicated by a variety of environmental factors, including temperature, source and availability of water, and plant growth rates (Fogel & Cifuentes, 1993; White et al., 1994). Fewer variables affect the hydrogen isotope contents of algal organic matter, largely because water is unlimited to the growing plants and temperature changes are small in comparison to conditions on land. The δD values of organic matter in lake sediments can therefore provide important information about local hydrologic histories.

The basis of interpretation of δD records in organic matter is the demonstrable relationship between the δD value of water in which lake algae lived and the δD of the carbon-bound hydrogen in the algal cell walls. In practice, the D/H ratios of humin, the non-soluble humic matter fraction of sediment organic matter, are determined. The ratios are then interpreted in terms of past precipitation/evaporation balances and air mass trajectories. An example of the application of D/H ratios of sediment organic matter in paleolimnology is the study of Austin Lake, Michigan, by Krishnamurthy et al. (1995), which is discussed later in this paper.

Source evidence from Rock-Eval pyrolysis

Rock-Eval pyrolysis was initially developed to evaluate the hydrocarbon potential of petroleum source rocks (Espitalié et al., 1985a). Its use in studies of lake sediments is relatively recent and still not common, yet it has been shown to be of real value to paleolimnology. Rock-Eval pyrolysis consists of the progressive heating of sediment samples and measurement of the amounts of hydrocarbons that escape from the sediment at different temperatures. During heating from ~200–600 °C, three main signals, which correspond to gaseous hydrocarbons (S_0), volatile hydrocarbons (S_1), and hydrocarbon components produced due to thermal degradation of humic substances (S_2), are generated. The heating procedure for recent sediments differs from that used for petroleum source rocks by beginning at a lower temperature (200 vs. 300 °C) to improve discrimination of the S_1 and S_2 signals. Some systems also calculate the amount of CO_2 created during pyrolysis (S_3). The total organic carbon content (TOC) is determined as the sum of residual and pyrolysed organic carbon contents.

Two important parameters are derived from the pyrolysis results: (1) the Hydrogen Index (HI), which represents the hydrocarbon potential of the total organic matter expressed in mg HC g^{-1} C_{org}, and (2) the Oxygen Index (OI), which roughly represents the amount of oxygen in mg CO_2 g^{-1} C_{org}. The HI values are proxies for the H/C ratios of organic matter, whereas the OI values represent the O/C ratios (Espitalié et al., 1985a, 1985b). These parameters relate to the origin of the total organic matter (Peters, 1986) and are commonly plotted against each other in a Van Krevelen-type plot (Figure 3). In the HI-OI plot, which approximates the Van Krevelen plot of elemental H/C and O/C ratios, three main types of organic matter and their alteration routes during thermal maturation are identified. Type I organic matter is especially rich in hydrocarbon content and is derived from microbial biomass or the waxy coatings of land plants. Type II organic matter is moderately rich in hydrocarbons and originates from algae. Type III organic matter is poor in hydrocarbons but rich in carbohydrates; it typifies woody plant matter. Oxidation of organic matter affects both HI values and OI values. As hydrocarbon-rich organic matter (Type I or II) is oxidized, its hydrogen content decreases while its oxygen content increases, and it takes on the HI-OI characteristics of Type III organic matter. Because HI and OI values provide information about the geochemical quality of the bulk organic matter, they are often compared to the petrographical organic composition. Talbot and Livingstone (1989) provide a summary of the major types of organic matter delivered to lake sediments and their typical H/C ratios, HI values, and petrographic descriptions.

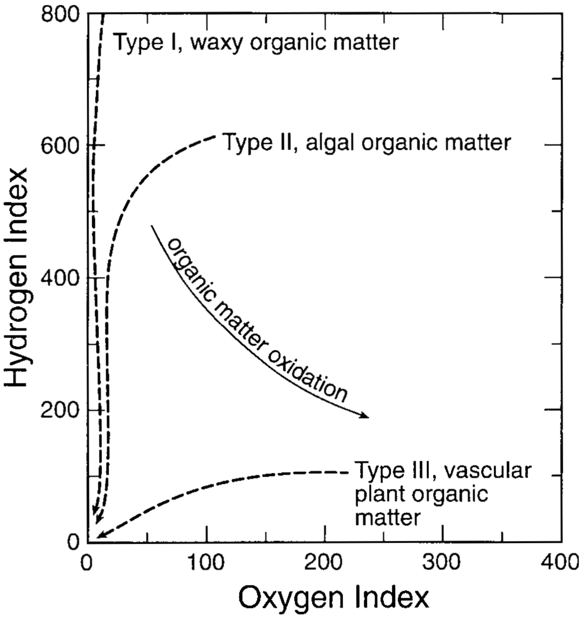

Figure 3. Rock-Eval Van Krevelen-type diagrams for sedimentary organic matter. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO_2 per gram TOC. Thermal alteration pathways of organic matter Types I, II, and III from source material to graphite are indicated by dashed lines, and the oxidation alteration pathway from hydrocarbon-rich Type I and Type II organic matter to hydrocarbon-poor material Type III is shown.

TOC concentrations and HI values often vary through lacustrine sedimentary sequences and indicate changes in organic deposition under different sedimentary conditions (e.g. Talbot & Livingstone, 1989; Hollander et al., 1992; Bertrand et al., 1992; Lallier-Vergès et al., 1993; Sifeddine et al., 1994a; Ariztegui et al., 1996a). A correspondence between TOC and HI values is often found (Figure 4). An increase in these parameters implies greater algal productivity. This pattern is also typical of marine sediments (Bertrand & Lallier-Vergès, 1993), where it represents plankton-derived organic matter rich in hydrocarbons diluting land-derived organic matter poor in hydrocarbons and also indicates the degree of preservation of algal organic matter. The correlation between the quantity and the geochemical nature of organic matter is often similarly evident in correlations between TOC concentrations and Rock-Eval S_2 values that indicate the addition of hydrocarbon-rich organic matter to a background of hydrocarbon-poor organic matter (Ramanampisoa & Disnar, 1994; Buillit et al., 1997).

Of particular interest to paleolimnological studies, variations in the HI values of sedimentary organic matter have been inferred to reflect changes in algal communities. Ariztegui et al. (1996b) note that sediments from Lago di Albano, Italy, with elevated HI values are associated with depositional intervals dominated by cyanobacteria production. Sediments having lower HI values correspond to periods during which diatom production was dominant.

Changes in TOC concentrations and HI values with depth in lake sediments can also result from diagenesis of organic matter. Non-oxidative degradation of organic matter in the sediments of Lac du Bouchet is evidenced by decreases in TOC concentrations, C/N ratios, HI values, and increases in OI values (Figure 4). Patience et al. (1996) noted that the downcore HI decrease closely resembles the TOC profile and is negatively correlated to the OI profile in these sediments, which have a constant organic supply in terms of composition and sedimentation rate.The similar decreases in HI values and in TOC concentrations appear to be the result of continued degradation of organic matter buried in the lake sediments as a result of of methanogenesis (Patience et al., 1995).

Source and paleoenvironmental information from organic petrography

Organic petrography is the microscopic analysis of particulate organic matter (Teichmüller, 1986). In sediments, it describes the different constituents of organic matter that remain after HCl and HF treatment to remove mineral particles. Their observation is made by transmitted light microscopy, and their quantification is achieved by visual estimations with charts, counting points, or image analysis. Sifeddine et al. (1994b) document discrepancies that may occur between these various counting methods and that may endanger absolute comparisons of data from different investigators. Relative trends within a given data set nonetheless remain valid, and these are particularly useful in estimating the relative proportions of organic matter from different sources in paleolimnologic records.

Organic petrography becomes important to establishing organic matter origins because organic components experience oxic and anoxic microbial processing before and after deposition. As a consequence, their metabolizable fraction has been strongly degraded, and the main part of sedimentary organic matter usually consists of the resistant fraction of the initially available organic matter. This resistant character is either inherited from the original, refractory biological tissues, or it is acquired as a result of bacterial de-

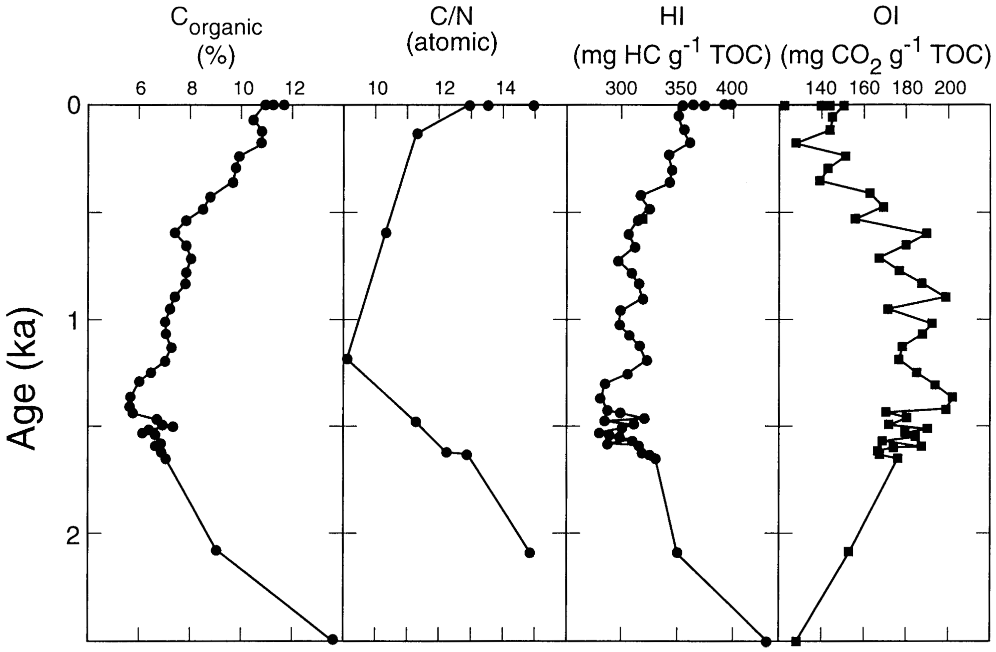

Figure 4. Comparison of TOC concentrations, organic matter atomic C/N ratios, and Rock-Eval hydrogen index (HI) and oxygen index (OI) values in sediments from Lac du Bouchet, France. High TOC concentrations positively correlate with higher C/N ratios and higher HI values and reflect improved preservation of organic matter. Inverse correlation between HI values and OI values indicates variable oxidation of organic matter and illustrates conversion of hydrocarbon-rich organic matter to hydrocarbon-poor material.

gradation. Visual examination can identify the origin of the resistant material.

Various degrees of preservation of organic matter particles can also be discerned from organic petrography, and each conveys useful evidence about paleolimnologic conditions. In some lake sediments, ligno-cellulosic debris may be present with a well-preserved morphology and texture and a translucent color. These particles indicate rapid transport from forest floors or paludal zones and quick burial in lake sediments, and they provide a well-preserved record of past assemblages of vascular plants in the watershed. In other cases, ligno-cellulosic particles may be gelified, or brown in color and be lacking in internal structures. These particles indicate partial degradation in subaqueous conditions like those encountered in peat-bogs (Sifeddine et al., 1995; Bourdon et al., 1997). In yet other situations, the particles may be pedogenetically altered and be present as reddish amorphous organic matter (AOM) particles. Abundant AOM particles and numerous fungi indicate incorporation of a large soil organic matter component in the lake sediments. In some lake sediments, ligno-cellulosic particles can be present as brown to opaque debris having a strongly oxidized character evident from infrared spectroscopy (Lallier-Vergès et al., 1993). Such particles indicate either a long transport time, a long contact with air, such as during cold periods, or a deep-soil erosional origin. Finally, carbonized ligno-cellulosic particles record either natural forest fires, fires produced by humans, or times of dry climate (Sifeddine et al., 1994a). The term 'charcoal' is often used to describe both the air-oxidized debris and the carbonized debris that is produced by forest fires. Because of the quite different paleoenvironmental implications of these two uses of this term, readers are cautioned to clarify the intended meaning from the context in which it appears.

Petrographical studies on lacustrine sedimentary records from different climatic, geomorphologic and geological settings have identified three main groups of organic constituents. These groupings reflect the type of organic matter, its origin, and its mode of transport to the sedimentary basin (Lallier-Vergès et al., 1993; Patience et al., 1994; Sifeddine et al., 1995):

- '*Autochthonous*' or '*aquatic*' organic particles are produced in the lake itself. They are mainly composed of the recognizable debris of algae and zooclasts and of greyish unstructured, amorphous organic flakes. Transmission electron microscopy of ultra-thin sections of unstructured organic matter from Lac du Bouchet revealed nanoscopic laminae, cell-walls and microbial structures (Patience et al., 1995). Both pyrolytic and ultrastructural studies show that the amorphous organic matter is a residual organic matter partly derived from microbial degradation of the micro-algal production (Derenne et al., 1992, 1993). This type of organic matter is essentially absent in environments dominated by vascular plants, such as mangrove swamps and soils.

- '*Allochthonous*' or '*terrestrial*' organic particles includes a variety of variably preserved ligno-cellulosic debris and pedogenetic organic material. In some specific environments as peat-bogs, however, ligno-cellulosic particles are paludal and therefore should be considered autochthonous. This is also true of lakes that have abundant emergent vegetation, such as Lake Tritrivakely in Madagascar (Sifeddine et al., 1995).
- The third organic fraction is composed of spores, pollen, and forest-fire debris brought to lakes by winds and rivers. It usually represents material having regional origins, except in the case of hydrologically isolated lakes such as maars and other closed lake systems in which it is of local origin. For lakes with riverine inputs, oxidized lignaceous debris can be derived from modern regional sources or from erosion of ancient sediments (Di Giovanni et al., 1997; Buillit et al., 1997)

The analysis of palynofacies, which has classically used organic petrography in the study of ancient organic-rich sediments, has been effectively applied to recent sediments. The strong likelihood of acid-soluble organic phases in modern sediments makes direct comparison of geochemical and petrographical results uncertain in the uppermost parts of the sedimentary column where diagenetic processes are most active. Optical study of sediments on smear slides, however, remains informative. Patience et al. (1996) petrographically studied the upper sediments from the Lac du Bouchet to investigate the impact of early degradation processes on the composition of sedimentary organic matter. The petrographical composition does not correlate with other bulk geochemical parameters, including Rock-Eval results, humic substance profiles, and C/N ratios. This lake has a low sedimentation rate (1 mm yr^{-1}), and organic matter is likely to have undergone substantial oxidation at the sediment/water interface. In the sediments of Annecy Lake, however, palynofacies analysis clearly shows the association of algal debris with greyish amorphous organic matter (Buillit et al., 1997). The proportion of algal debris decreases downcore relative to the amorphous organic matter. The petrographic compositions consequently reveal changes in origins of organic matter over time in the sedimentary records and indicate where diagenesis has modified traditional geochemical indicators of organic matter sources, such as C/N ratios or Rock-Eval HI values.

Dating of lake sedimentary records

Determination of the ages of sediment horizons is essential for paleolimnology, and it is particularly important to deciphering changes in the amount and type of organic matter in sediments. Moreover, calculation of the sediment mass accumulation rate, which is derived from the sediment age, density, and porosity of each horizon, is usually needed to fully explore the paleoenvironmental histories provided by lake sediments. A number of different approaches are commonly employed to determine the ages of samples obtained from different sub-bottom depths in sediment cores.

Varved sediments are especially informative. Lakes having varved, or annually laminated, sedimentary records are present at all latitudes (Overpeck, 1996). The laminations result from seasonal changes in rainfall or climate, and they reflect the absence of abundant benthic animal populations that would homogenize the sediments of the lakes through bioturbation. In some cases, variations in the thickness and composition of varves provides important paleoenvironmental information. For example, a period of increased Great Plains aridity between 8 and 3.8 ka is indicated by increased delivery of eolian quartz grains to Elk Lake, Minnesota, in the varved record of this lake (Dean et al., 1996; Dean, 1997). In general, the varves permit accurate, year-by-year dating of sedimentary records, as long as some portion of the varve sequence can be calibrated to an absolute age.

Most lakes do not have varved sediments, and the time-dependent decay of radioisotopes is therefore widely used to determine the ages of their sedimentary records. Lake sediments generally accumulate rapidly enough that their ages can be approximated from relatively short-lived radioisotopes. The two most common isotopes employed for this purpose are ^{210}Pb (half-life 22 yr) and ^{14}C (half-life 5730 yr). The times involved with very short-term sedimentary processes, such as seasonal events or sediment settling times, can be determined using ^{7}Be (half-life 53 d). Radiocarbon ages of sediments are usually determined from their organic carbon contents. Bulk organic matter in lake sediments typically contains some proportion of recycled detrital organic carbon, which commonly renders ^{14}C ages 1000 to 2000 yr older than actual sediment ages (e.g. Stuiver, 1975; Rea et al., 1980; Meyers & Horie, 1993). This problem is compounded in lakes with high concentrations of carbonate carbon (hardwater lakes). Dissolved inorganic carbon is retained and recycled in these lakes, making the radiocarbon age of the dissolved carbon greater than the actual age of the lake water. In the Great Lakes of North America, for example, the radiocarbon age of dissolved inorganic carbon is 250–450 yrs older than the true sediment age (Rea & Colman, 1994), and the radiocarbon age of organic matter dispersed in the sediments of these lakes can substantially misrepresent the actual depositional age of sediment layers (Silliman et al., 1996). Correction of sediment core ages for the ‘old’ carbon is difficult because it is unlikely that the proportion of detrital organic carbon in the bulk organic matter remains constant over time (e.g., Anderson et al., 1993). A very different possible complication results from the fact that sedimentary organic matter can support microbial growth after core recovery unless measures are taken to suppress microbial activity. Microbes living on core surfaces can add modern atmospheric carbon to the sediment carbon, thereby making the radiocarbon age younger than the actual sediment age (Colman et al., 1996). Because of these various possible ways in which bulk organic matter may yield erroneous radiocarbon ages, it is preferable to determine ages from twigs, leaves, or similar intact particles of organic matter or from the inorganic carbon contained in the carbonate shells of lake animals.

The ages of lake sediments can also be approximated from evidence of depositional events or horizons contained within sediment cores. Concentration maxima of long-lived radionuclides such as ^{137}Cs are one example. The major modern sources of ^{137}Cs are atomic bomb detonations and nuclear reactors. This radionuclide appears in sediment records starting ca. 1945 and has peaks during the maximum of bomb testing in 1963–64 and again in 1986 after the Chernobyl reactor accident (cf. Robbins & Edgington, 1975; Wieland et al., 1993). Clear-cutting of forested watersheds is typically accompanied by changes in land plant assemblages and increased erosion of forest soils. The types of pollen and of minerals delivered to lake sediments therefore change (e.g., Higgets et al., 1991). The proliferation of ragweed (*Ambrosia*) in North America as European settlements pushed westward during the 1800’s and cleared land for agriculture is a classic example of this change in watershed environment, and the first appearance of *Ambrosia* pollen in sedimentary records can be linked to the history of this land-use change. Some lakes contain layers of volcanic ash or tephra that can be related to dated volcanic eruptions. Event markers are usually best used to corroborate ages determined from radioactive decay, rather than as independent age determinants, because they cannot show that sediment records are uninterrupted. Teprochronology has nonetheless proved very useful in estimating sediment ages substantially older than the practical limit of radiocarbon dating (e.g., Meyers & Takemura, 1997).

Organic carbon accumulation rates and their use in paleolimnology

The concentration of total organic carbon (TOC) is a fundamental parameter for describing the abundance of organic matter in sediments. Weight loss on ignition (LOI) is also sometimes used to estimate how much organic matter is present in sediments. Typical organic matter contains approximately 50% organic carbon, so LOI values are equivalent to about twice the TOC values. Because variable amounts of volatile non-carbon sediment components can increase LOI values, measurement of the non-carbonate-carbon concentrations is generally preferred over LOI determinations to approximate how much organic matter is present.

TOC concentration is a bulk value that represents the fraction of organic matter that escaped remineralization during sedimentation. TOC concentrations are influenced by both initial biomass production and subsequent degree of degradation, so they integrate the different origins of organic matter, delivery routes, depositional processes, and consequent degrees of preservation. TOC concentrations are expressed in weight/weight ratios and are therefore influenced by other sediment components. TOC can be both diluted by clastic sediment particles and concentrated by dissolution of carbonate minerals. For this reason, mass accumulation rates (MARs) of organic carbon are better measures of delivery and preservation of organic matter than

TOC percentages. MARs are expressed as mass of TOC per unit of lake bottom area per unit of time, typically mg cm^{-2} yr^{-1}. Reliable sediment dating is obviously important to calculating meaningful MAR values.

Organic carbon MARs are especially useful to paleolimnology for identification of changes in delivery rates of organic matter to lakes. Often the proportions of lake-derived and land-derived organic matter can be estimated by organic petrography or C/N ratios, allowing calculation of MARs for autochthonous and allochthonous organic carbon.

Organic matter records of paleolimnological change

A number of descriptions of bulk organic matter contents of dated sediment cores exists in which changes in organic matter have been related to their paleolimnological histories. We have selected some examples that illustrate the effects of various environmental changes on the bulk organic properties.

Changes in lake level of Mono Lake, California

Mono Lake is a large, fairly deep lake located in the Great Basin Desert at the eastern edge of the Sierra Nevada Mountains in California. Because it is a terminal lake, water leaves the lake only by evaporation, making the waters saline. Large-scale agricultural diversion of the freshwater streams that replenish the water of the lake began in 1941. Since then, the water level has gradually lowered, the salt concentration of the lake water has doubled, and biological productivity has declined (Jellison et al., 1996).

Changes in the water level have also impacted the organic matter content of Mono Lake sediments. Concentrations of organic carbon in the sediments vary between 6 and 16% (Jellison et al., 1996), yet they generally increase after reaching a minimum ca. 1940 (Figure 5). The minimum follows the maximum historical water level, which existed from 1915–1925. Atomic C/N ratios do not similarly vary but instead hold between 7 and 8, except for higher values in sediments deposited ca. 1983 and 1943. The C/N ratios indicate that the type of organic matter delivered to the lake sediments has remained predominantly algal in origin (Figure 1). The 1983 C/N peak corresponds to the very strong 1982-1983 El Niño event with accompanying wet climate, and it coincides with the maximum organic carbon MAR. Enhanced wash-in of land-plant organic matter probably occurred at this time. The 1943 spike may record similar ENSO-related enhanced delivery of land-derived organic matter. Organic carbon MARs increase from ten-year-averaged values of 8.5 mg cm^{-2} yr^{-1} in 1940 to 14.5 mg cm^{-2} yr^{-1} in the early 1980’s (Figure 5). The increased rate of organic matter burial is curious, inasmuch as algal productivity declined over this period as a consequence of increased salinity (Jellison et al., 1996).

Several possible explanations exist for the progressive increase in organic matter accumulation as lake level lowered. First, the increase in lake water salinity could increase density stratification of the lake and thereby impede lake turnover. Hypolimnetic anoxia could gradually intensify and thereby improve preservation of organic matter. However, the depth at which the core was collected (35 m) has historically remained anoxic most of the year (Jellison et al., 1996), so a change in the oxygen content of the water is not likely to be important. A second possibility is that the rate of microbial metabolism of organic matter may have been depressed by the increased salinity. However, organic MARs fluctuate widely in sediments deposited well before lake level lowering (Figure 5), making salinity-depressed microbial activity an unlikely explanation for the increased burial of organic matter. A third possibility is that sedimentation rates at the coring site may have increased as lake level lowered. Diversion of river water to Pyamid Lake, Nevada, has caused lowering of lake water levels similar to the post-1940 situation in Mono Lake. Algal productivity similarly declined, yet organic matter burial increased (Meyers et al., 1998). The explanation for the increased rate of burial of organic matter as lake level decreased in Pyramid Lake is that fine-sized sediments formerly deposited along the lake margins have been progressively resuspended by wave turbulence as water levels dropped and were redeposited in deeper waters. Because finer-sized sediments typically carry higher concentrations of organic matter (Thompson & Eglinton, 1978; Tenzer et al., 1997), such sediment refocusing adds to the delivery of organic matter to the deep parts of the lake. The redistribution of sediments caused by recent lowering of lake water levels enhances organic MARs in the deep parts of the lake, even though the depressed algal productivity may result in diminished lake-wide organic matter burial.

Organic carbon concentrations and MARs are high in the sediments of Mono Lake in the years preceding the maximum lake level. During much of this time, lake levels were rising, and the core site was covered by

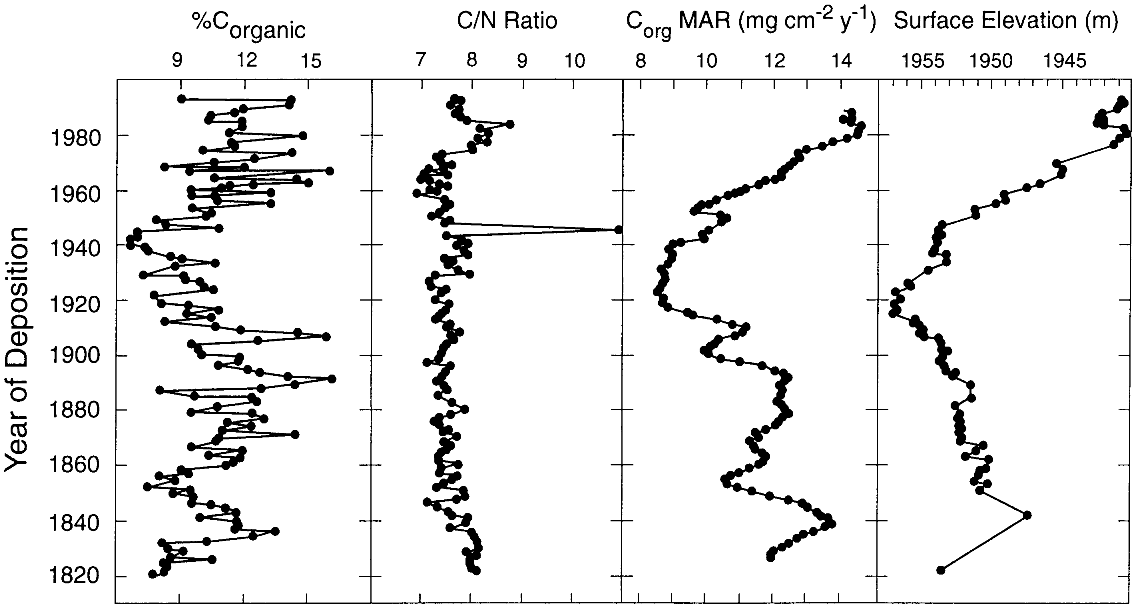

Figure 5. Changes in sediments of Mono Lake, California, over the last 170 yrs illustrate how changes in water depth, or local hydrologic balance, can affect accumulation of organic carbon in lake sediments. Atomic C/N ratios indicate that the source of the organic matter since 1820 has been predominantly from algal production within the lake. Large-scale diversion of watershed streams began ca. 1940, and lake water level has dropped 15 m since then. Decadal averages of organic carbon mass accumulation rates at the coring site have increased as water level dropped, largely because of progressive resuspension and relocation of fine-sized sediments to the deepest parts of the lake as water depths decreased. From Jellison et al. (1996).

progressively deeper water. It is likely that the fine-sized sediments that were refocused to this site by dropping lake levels since 1941 were instead dispersed over a larger portion of the lake bottom, altering the accumulation rate at this location in a pattern that mimics water depth (Figure 5).

Post-glacial paleoclimate record of Lake Baikal, Siberia

A paleolimnological record of the Pleistocene-Holocene glacial-postglacial climate transition in southeastern Siberia is provided by the organic carbon composition of a sediment core from the northern basin of Lake Baikal (Qiu et al., 1993). During this interval of time, montane glaciers retreated and modern forests became established in the catchment area. The change in sediment type from opal-poor glacial muds to a diatom ooze indicates that lake productivity increased at ca. 13 ka, and this conclusion is strengthened by an increase in sediment organic carbon concentrations (Figure 6). C/N values in postglacial blue clay muds vary between 15 and 50 (Figure 6). These variations record episodes in which contributions of vascular land plant material were large in proportion to the generally low algal production. In contrast, the ratios vary little from ca. 15 in the diatom ooze that has accumulated since 13 ka. The change in C/N ratios indicates that algal organic matter became a larger component of sediment organic matter after this transition. At the same time, organic carbon δ^{13}C values change from ca. –23 ‰ to ca. –28 ‰. Qiu et al. (1993) interpret the change in isotope ratios as a climate-driven change in watershed vegetation from cold-weather C_4 tundra grasses to the C_3 plants that have dominated the Holocene biomes of this region. This interpretation is supported by a shift in lignin biomarker composition that confirms that the vegetation around the lake changed from grasses and sedges to a gymnosperm/angiosperm forest at the same time that algal production increased at 13 ka (Orem et al., 1993).

The record of change in vegetation in the Lake Baikal catchment illustrates a special situation in which contributions of land-derived organic matter can be distinguished from lake-derived organic matter on the basis of δ^{13}C values. More typically, organic matter derived from lake algae and from watershed plants have the same δ^{13}C values (Figure 1) because both sources are C_3 plants that utilize CO_2.

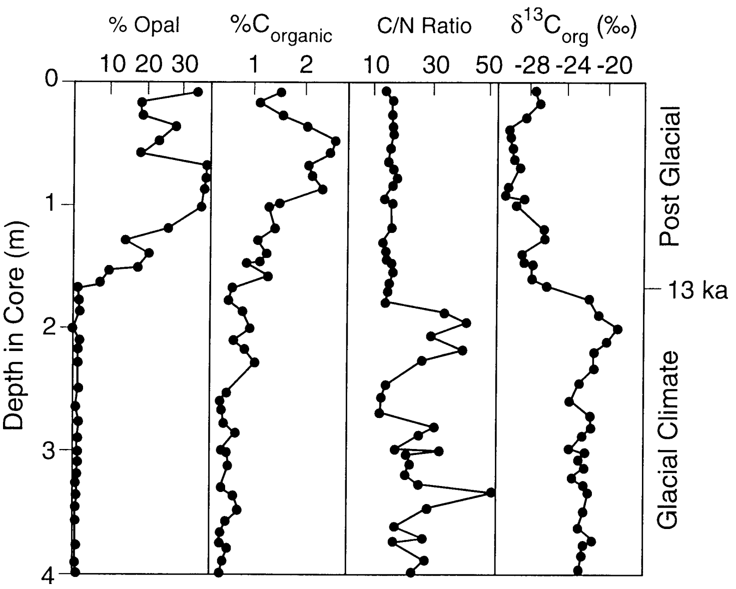

Figure 6. Evidence of organic matter source change from tundra vegetation to algal production at the glacial-postglacial boundary in sediment record from Lake Baikal, Siberia. Decreases in C/N ratios and in organic $\delta^{13}C$ values at the mud/diatom ooze transition record the transition from tundra to forests around Lake Baikal and an increase in algal productivity starting ca. 13 ka. Core data from Qiu et al. (1993); corrected sediment age from Colman et al. (1996).

Late Quaternary paleoclimate record of Lake Bosumtwi, Ghana

Lake Bosumtwi, which occupies a shallow meteorite impact crater in Ghana and is permanently anoxic, has a maximum depth of 78 m and is about 8 km in diameter. The sediments of this lake preserve an organic matter record of climate variations that have caused past fluctuations in lake water level. The downward sedimentary sequence consists of a laminated interval that corresponds to modern and near-modern climates of the past 3 ka, a sapropelic interval that corresponds to a period of higher lake level from 3–9 ka, an interval of laminated and shallow-water sediments that corresponds to the glacial maximum between 9 and 26 ka, and an interval of deep-water muds that ended at 26 ka. Organic carbon concentrations fluctuate between 1 and 23% through the sequence, but they usually remain between 5 and 10% (Figure 7). These are higher-than-average values, and they reflect enhanced preservation of organic matter because of anoxic lake bottom conditions.

In some intervals, organic matter C/N ratios vary between 15 and 35 in closely spaced sediment samples and record fluctuations in the proportions of land-derived and algal organic matter delivered to the lake sediments as climate conditions oscillated. The ratios are relatively high (15–20) throughout the core and indicate that contributions of land-derived organic matter to these sediments have been important throughout the period of time represented by this sedimentary record. Least variation is found in the sapropel layer (Figure 7), which represents a comparatively stable period of wetter climate and high lake level that existed between 9 and 3 ka (Talbot & Johannessen, 1992).

Because the C/N ratios show that a significant proportion of the sediment organic matter is from land plants, the sediment organic $\delta^{13}C$ values provide a record of climate-related changes in the types of land vegetation around Lake Bosumtwi (Talbot & Johannessen, 1992). The $\delta^{13}C$ values between –10 and –15 ‰ in the mixed clastic/carbonate laminated sediments (Figure 7) reflect contributions from C_4 savannah grasses that lived during the drier, low-lake-level conditions that existed during the last glacial maximum. In addition, four well-defined cycles exist in the $\delta^{13}C$ values. These approximate the cold-warm Dansgaard-Oeschger cycles known in ice cores and marine sediments and suggest that related dry-wet climate cycles impacted land vegetation on this part of tropical Africa. The $\delta^{13}C$ values in the laminated section contrast with the values that remain ca. –25 ‰ in the deep muds and in the upper sediment layers. These more negative values indicate

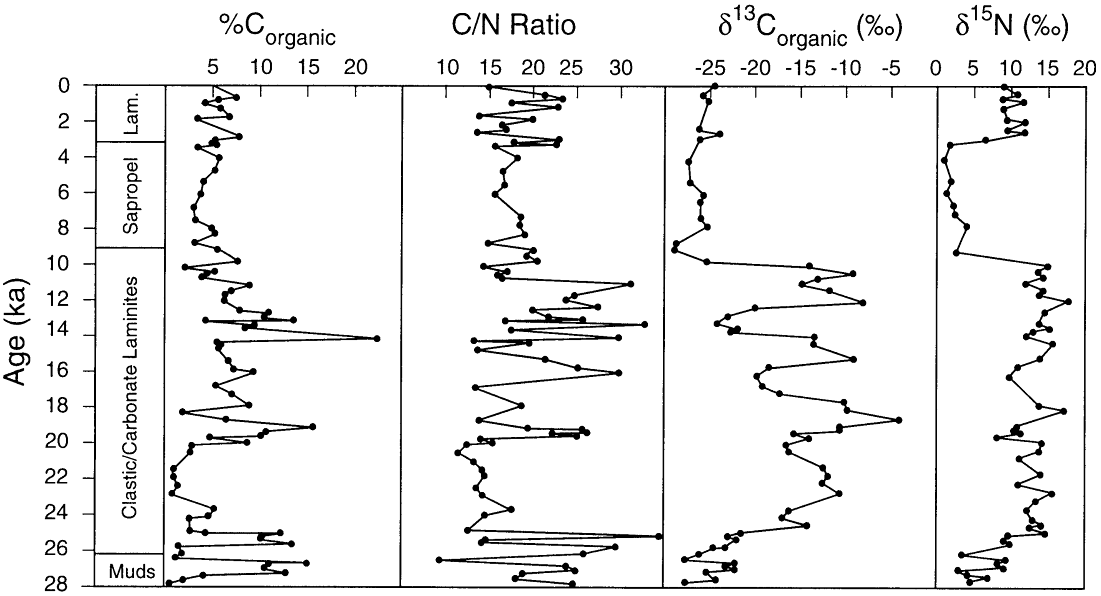

Figure 7. Organic carbon concentrations, atomic C/N ratios, and organic δ^{13}C and δ^{15}N signatures of sediments from Lake Bosumtwi, Ghana. Decreased C/N ratios and δ^{13}C and δ^{15}N values in the sapropel layer record a period of enhanced lake productivity and postulated wetter climate between 9 and 3 ka. Glacial-age savannah-forest fluctuations are evident in organic δ^{13}C values between 26 and 9 ka. From Talbot & Johannessen (1992).

delivery of organic matter from C_3 land plants that were present during tropical, wet periods of climate that existed prior to 26 ka and comprise the forests that have surrounded the lake from 9 ka up to the present.

Another factor that may contribute to the transitions from C_3 and C_4 plant dominance evident in the δ^{13}C record is the difference in atmospheric pCO$_2$ between glacial and interglacial times. Ehleringer et al. (1997) postulate that C_4 plants were favored during glacial periods because their uptake efficiency is impacted less than that of C_3 plants by the lower availability of atmospheric CO$_2$ that existed during these periods. In the case of Lake Bosumtwi, and also Lake Baikal, watershed vegetation appears to have been dominated by C_4 plants during the last glacial period, which is consistent with this hypothesis. The sediment records of both lakes, however, also provide evidence for drier regional climates, which is another factor that favors dominance of C_4 plants (O'Leary, 1988). Although resolution of which factor was more important is not possible, it is clear that the organic matter in the sedimentary records of these lakes documents that the types of land-plants were different during glacial times than during interglacial times in both catchments.

Organic δ^{15}N values reflect changes in aquatic nitrogen fixing and cycling as paleolimnologic conditions became altered in Lake Bosumtwi in response to climate changes. The isotopic values become more positive (ca. 13) in sediments deposited during the period of dry glacial-age climate between 26 and 9 ka (Figure 7). Talbot & Johannessen (1982) postulate that evaporative losses of isotopically light ammonium nitrogen from the relatively saline and alkaline lake waters occurred during these periods. The δ^{15}N excursions consequently reflect aquatic production of organic matter from a physically modified dissolved nitrogen reservoir. An alternative explanation is that the shift to more positive δ^{15}N values records depletion of dissolved nitrogen in the lake as a result of diminished wash-in of soil nutrients during this extended episode of dry climate. The excursions may therefore reflect biological drawdown of a limited dissolved nitrogen pool. In contrast, the δ^{15}N values are low (ca. 2) in the sapropel layer, which corresponds to a period of extremely stable stratification of Lake Bosumtwi between 9–3 ka (Talbot & Johannessen, 1992). Production of the lake-derived organic matter in this layer may have been dominated by the nitrogen-fixing cyanobacteria *Anabaena*. The δ^{15}N values of ca. 10 of sediments deposited since 3 ka document establishment of present-day lake conditions, under which wind mixing maintains a supply of dissolved nitrogen in the epilimnion that is adequate for algal growth.

Holocene paleoprecipitation record of Austin Lake, Michigan

The isotopic contents of sedimentary organic matter from Austin Lake, Michigan, record changes in the Holocene climate of Midwestern North America. The lake is a typical kettle lake, formed by melting of ice masses left during retreat of the Laurentide ice sheet. Because the main recharge of lake water is from direct precipitation and the principal manner of outflow is as groundwater, the hydrogen and oxygen isotopic compositions of the lake waters are virtually the same as local meteoric waters. Moreover, in the absence of any important fluvial or groundwater inflows, the main source of organic matter to the lake sediments is plant production within the lake (Krishnamurthy et al., 1995).

The sediments are rich in organic matter, averaging 30% TOC on a carbonate-free basis (Figure 8). Organic C/ total N ratios remain between 8 and 15 throughout the Holocene and suggest that algal inputs have dominated organic matter contributions to the sediments. The C/N ratios of humin, the insoluble fraction of sediment organic matter, are between 14 and 18 for most of the core and are greater than those of organic C/ total N. Two factors contribute to this difference. First, C/N ratios of the humin fraction typically are higher than of total sedimentary organic matter (Bourbonniere & Meyers, 1983). Second, the total nitrogen content of sediments includes inorganic nitrogen that is derived from the degradation of organic matter and is retained in the sediments by sorption onto clay minerals. The presence of this material systematically biases organic C/ total N ratios to lower values. This bias can become particularly important in sediments having low TOC concentrations (Müller, 1977; Meyers, 1997), which is not the case for Lake Austin. The difference between the two types of C/N ratios is greatest in sediments deposited during the last 2 ka. This pattern may reflect a change from dominance of algae to submerged macrophyes at that time, but it is unlikely to result from post-depositional diagenesis of organic matter, inasmuch as both types of C/N ratios change abruptly at the same sediment horizons (Figure 8).

Because the hydrogen contents of aquatic organic matter originate from lake waters, the δD values of the lake-derived organic matter can be used as a proxy record of the hydrologic balance of Austin Lake and also of the sources of meteoric water to the lake. Krishnamurthy et al. (1995) employ the δD values of the humin fraction of sediment organic matter, which is the fraction that is the most resistant to post-depositional alterations, to explore the hydrologic history of the lake. The δD values separate into four time intervals (Figure 8), which are interpreted to reflect changes in Midwestern North American Holocene climate. Especially prominant among the intervals is the period between 9–2 ka, during which δD values

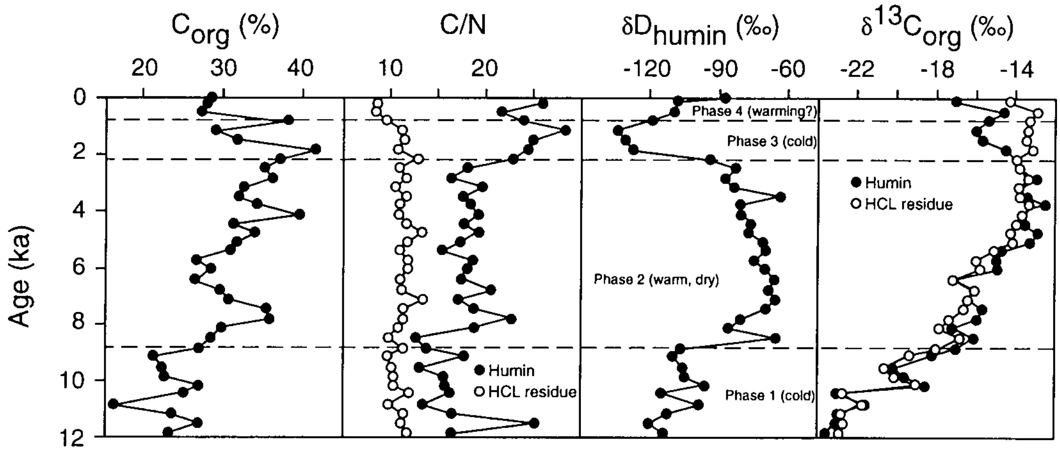

Figure 8. Record of postglacial climate change in hydrogen isotope contents of organic matter in sediments of Austin Lake, Michigan. Bulk C/N ratios indicate that most of the organic matter is from algal production and therefore humin δD values reflect lake water isotopic composition. Variations in δD values record changes in sources of meteoric water and in precipitation/evaporation ratios as local climate changed. The progressive upcore change to less negative $\delta^{13}C$ values may result from isotopic aging of the lake. From Krishnamurthy et al. (1995).

increase to ca. –75 ‰ from an earlier average of –110 ‰. This period generally corresponds to the mid-Holocene Hypsithermal time of warm, dry climate that has been recorded in lake sediments throughout the Great Plains and Rocky Mountain regions of North America (Dean et al., 1996). Krishnamurthy et al. (1995) postulate that the less negative δD values result from the evaporative distillation of the hydrogen isotopic contents of the lake waters that would occur in this type of climate. An alternative interpretation of the four isotopic intervals is that they represent changes in the air masses that deliver meteoric water to this part of North America. For example, if the proportion of precipitation from the Gulf of Mexico air mass (mean δD = –35 ‰) increased, then the organic matter δD values would become less negative. The possibility that the Austin Lake δD record may provide a history of Holocene changes in air mass trajectories is intriguing, inasmuch as sediment records from Lake Ontario (Silliman et al., 1996) and Owasco Lake in New York State (Dwyer et al., 1996) indicate wetter climates from 9–3 ka farther to the east. The location of the transition from drier to wetter mid-Holocene North American climates may possibly be identified by similar studies of lacustrine organic matter δD records.

A large shift in δ^{13}C values, from –23 to –14 ‰, occurs in both total organic matter and in its humin fraction in the postglacial sedimentary record of Austin Lake (Figure 8). Although elevated algal productivity can produce less negative δ^{13}C values, the magnitude of this change is too great to result from enhanced productivity alone. Another possible explanation for this curious pattern - that it records a shift in dominance of organic matter supply from C_3 vegetation in and around the lake at 12 ka to C_4 land-plants in modern times – is also unlikely. First, C/N ratios indicate that lake-derived production dominates organic matter delivery, and, second, land-plants in this region have been predominantly C_3 plants for most of the Holocene. Instead, the absence of important inflows and outflows in the Austin Lake hydrologic system may create a situation in which in-lake processes strongly influence the isotopic balance of carbon in the lake waters. Over time, removal of dissolved CO_2 by aquatic plants and burial of ^{12}C-enriched organic matter in sediments may have shifted the isotopic balance to one that is not in equilibrium with atmospheric CO_2. Utilization of bicarbonate carbon instead of CO_2 by lake plants would produce organic matter that is enriched in ^{13}C and leave a record of organic matter burial that would therefore have progressively less negative δ^{13}C values as the lake becomes more isotopically 'mature'. Similar shifts to less negative δ^{13}C values have been documented in the Holocene sedimentary records of other lakes. A change in the δ^{13}C values of ostracod valves (carbonates) from –7 to 0 ‰ has been documented in Williams Lake, Minnesota, as this kettle lake became hydrologically isolated from regional stream flow and water residence time increased (Schwalb et al., 1995). The δ^{13}C values of organic matter change from –25 ‰ in sediments deposited 5.3 ka to –11.7 ‰ in modern sediments of Swan Lake, Nebraska, as the species of dissolved inorganic carbon used by lake plants changed from CO_2 to HCO_3^- (Hassan et al., 1997). These examples illustrate potential interpretative pitfalls in using sedimentary δ^{13}C records without having additional evidence of changes in paleolimnological histories.

Holocene paleoclimate record in sediments of Elk Lake, Minnesota

Elk Lake is situated in north-central Minnesota and is part of the headwaters of the Mississippi River. The location of Elk Lake, in a forested region just east of the edge of the mid-continent prairie lands (the North American Great Plains), makes the sediments of this lake especially sensitive recorders of climate change. The lake fills a kettle created during recession of the Laurentide continental glaciers ca. 11 ka (Anderson, 1993). Its main sources of water are groundwater and direct precipitation. The lake is dimictic, and summer anoxia in the bottom waters of its central basin (30 m deep) results in a varved sedimentary record that is continuous to 10.4 ka. During this time, the lake-watershed ecosystem has gone through a progression of being first a postglacial lake (10.4–8.0 ka), then a prairie lake (8.0–3.8 ka), and finally a modern forest lake. These ecosystem changes are recorded in the lake sediments (Figure 9).

Diatom productivity evidently was elevated over earlier and subsequent periods during the prairie lake period. The flux of diatom frustules is markedly elevated in sediments deposited between 7.5 and 4 ka, and the mass accumulation rate of organic carbon doubles in this interval (Figure 9). Concentrations of $CaCO_3$ and organic carbon, which can both be indicators of increased algal productivity, do not increase because delivery of clastic sediment components increased and diluted these concentrations (Dean, 1993). Much of the increased clastic sedimentation was from eolian delivery, which magnified the thickness of the varve layers during the prairie period (Anderson,

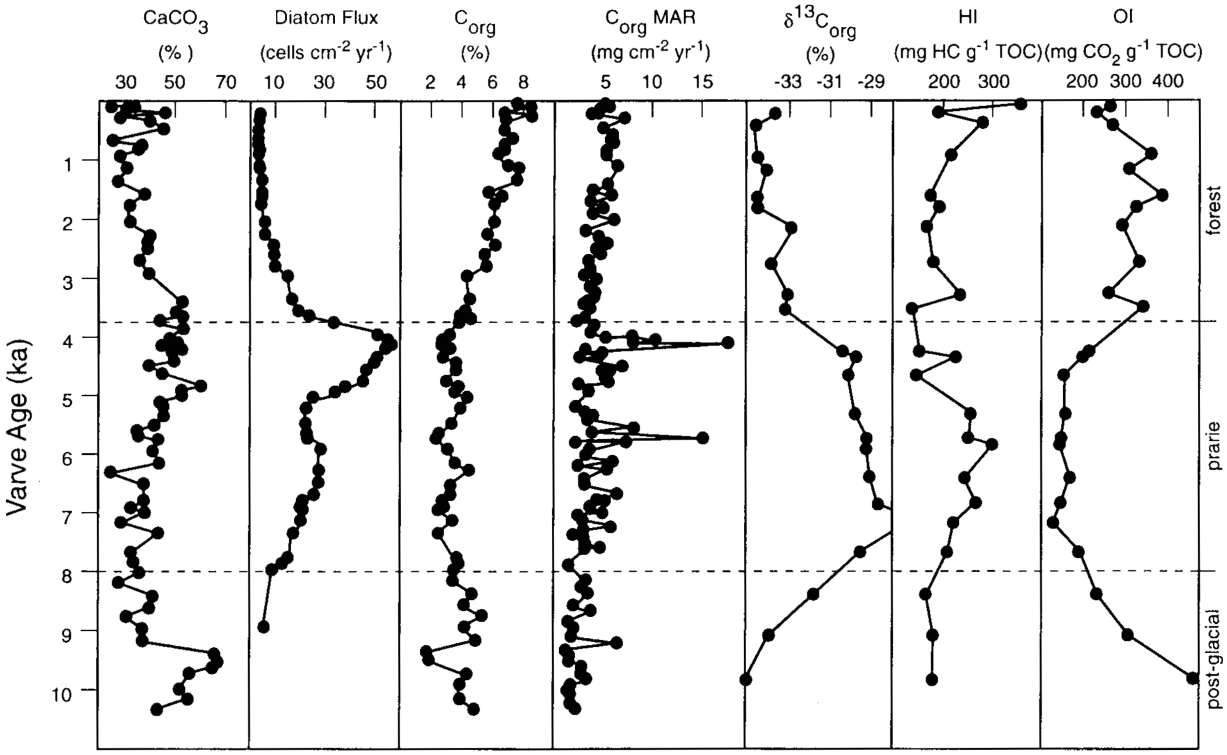

Figure 9. History of Holocene climate changes recorded in calcium carbonate concentrations, diatom fluxes, organic carbon concentrations and mass accumulation rates, $\delta^{13}C$ values, and Rock Eval HI and OI values of bulk organic matter in sediments from Elk Lake, Minnesota. The climate of the prairie period was drier and windier than earlier or later periods, and both production and preservation of organic matter were enhanced. From Bradbury & Dieterich-Rurup (1993) and Dean & Stuiver (1993).

1993). The enhanced diatom productivity probably resulted from the change in climate that induced the eastward extension of prairie conditions to surround Elk Lake. The prairie conditions signal a time of drier climate, which suppressed the pine forests that occupied the watershed during the postglacial period and in modern times and probably made the lake somewhat shallower. Partly because of the absence of tall trees and partly because of the general change in climate, winds strengthened during the prairie period. The stronger winds brought more dust to the lake, thickening the varve layers, and they increased turbulent mixing of the lake waters, enhancing diatom productivity (Bradbury & Dieterich-Rurup, 1993).

The elevated algal productivity during the prairie period is recorded in the type of organic matter preserved in the lake sediments, in addition to the doubled mass accumulation rates. Organic $\delta^{13}C$ values increase by ca. 5 ‰ to reach between –30 to –28 ‰ in this interval (Figure 9) and are paralleled by a similar shift to heavier $\delta^{13}C$ values in carbonate carbon (Dean & Stuiver, 1993). The positive carbon isotope excursion suggests that algal productivity must have been greatly inhanced in order to draw down the dissolved CO_2 available for phytoplankton. At the same time that organic matter production increased, the organic matter preservation also improved. Rock-Eval hydrogen indices are slightly elevated and oxygen indices are lower in the prairie-interval sediments (Figure 9). This pattern is the converse of that found in the sediments of Lac du Bouchet (Figure 4), in which oxidation of algal organic matter depressed HI values and elevated OI values (Patience et al., 1996). The increased sedimentation rates associated with the prairie period evidently helped to preserve the organic matter that was delivered to the sediments of Elk Lake.

Record of Holocene climate changes and human settlement, Lac du Bouchet, France

Lac du Bouchet is a crater lake situated at 1205 m altitude in the Devès volcanic massif of south-central

France. The lake is approximately 1 km in diameter and has a very restricted watershed. Water depths reach 28 meters in this maar and are controlled mainly by direct precipitation. The relatively low sedimentation rate of Lac du Bouchet provides a depositional history of more than 400 ka (Tzdakis et al., 1997). A well-established paleolimnological record, which combines magnetic susceptibility data (Lallier-Vergès et al., 1993, Thouveny et al., 1994; Williams et al., 1996) and palynological data (Reille & de Beaulieu, 1988; Tzdakis et al., 1997), provides a chronological basis to identify a succession of changes in the local environment. The types of organic matter that accumulated in Lac du Bouchet sediments during this paleoenvironmental succession were used to pioneer application of organic petrography to lacustrine sediments (Bertrand et al., 1992).

The most recent glacial-postglacial transition in paleoenvironments has caused a succession of changes in the amounts and types of organic matter that have accumulated in Lac du Bouchet. During the last glacial period (30–15 ka), a steppe environment existed under a cool regional climate. Sediments deposited during this time are marked by very low concentrations of organic matter that result from substantial dilution by mineral matter. The organic matter contains a small proportion of oxidized lignaceous debris, which indicates the absence of many land plants in the catchment, and a large proportion of highly degraded aquatic organic matter, which is made up of black amorphous organic aggregates. The oxidized and degraded character of all the organic matter reflects its very poor preservation. The lack of a large land-derived contribution, the high mineral fluxes, and an enhanced silty fraction indicate intense weathering on land. At the same time, autochthonous organic matter is poorly preserved, and Rock-Eval hydrogen index values fall below 50 (Bertrand et al., 1992). Glacial-age sediments in Lake Baikal (Figure 6) also have low concentrations of poorly preserved organic matter, as do sediments in Lake Huron (Meyers & Takeuchi, 1979) and Greifensee (Giger et al., 1980). Rapid accumulation of organic-carbon-poor sediments appears to be a general feature of glacial-age lake sediments in temperate climate zones.

Around 15 ka, accumulation of organic matter begins to increase in the sediments of Lac du Bouchet. The increase in deposition of organic matter occurs in many European lakes, and it is almost synchronous with the deglaciation that accompanied global warming in the latest Pleistocene. The organic matter in Holocene sediments of Lac du Bouchet is dominated by land-derived material, and it has very high HI values (600). These characteristics indicate increased delivery of both hydrocarbon-rich land-plant debris (pollen, cuticles, bacteria-rich forest litter) and phytoplankton-derived organic matter. From sediments in Chaillexon Lake (Jura, France), Di Giovanni et al. (1997) postulated that these characteristics indicate enhanced soil erosion and might even be considered as a proxy to gauge amounts of paleo-rain.

The Holocene is known to have had a variable climate in response to global, regional and local influences. The study of the organic content from the different climatic episodes defined by the palynology (Reille & de Beaulieu, 1988) in Lac du Bouchet shows that the organic matter record reflects this variability (Figure 10). The Boreal period (9–8 ka) is accompanied by an increase in the TOC fluxes from both aquatic and terrigenous sources (Sifeddine et al., 1996), indicating an increase in biological production. A decrease in the mineral flux reflects diminished erosion of the surrounding basin as it became progressively more covered by vegetation.

The mid-Holocene Hypsithermal (the Atlantic period: 8–4.7 ka) and associated expansion of oak-dominated forests under a warm, wet climate in western Europe is recorded in the pollen data (Reille & de Beaulieu, 1988). The delivery of organic matter to the sediments of most lakes responds to increased algal production and increased weathering of soils, both of which often accompany wetter climate. The autochthonous and allochthonous organic fluxes increase progressively during the beginning of the Atlantic period before decreasing towards the end of this period due to a cooler climate (Figure 10). A progressive decrease in the contribution of aquatic plant pollen (*Isoëtes*) is interpreted to reflect decreased delivery of soil nutrients to the lake, a conclusion that is supported by a decrease in clastic sediment components (Reille & de Beaulieu, 1988).

The period of cooling that commenced at the end of the Atlantic period and continued into the Sub-Boreal period (4.7–2.6 ka) is indicated in the pollen record of Lac du Bouchet by the maximum development of beech forests under a cool and humid climate (Reille & de Beaulieu, 1988). An increase in the flux of terrestrial organic material (Figure 10) reflects the abundance of vegetation in the surrounding basin. The low aquatic organic fluxes are probably due to diminished wash-in of soil nutrients from the now fully forested catchment.

Deliveries of land-derived organic matter to Lac du Bouchet throughout the Holocene are almost always

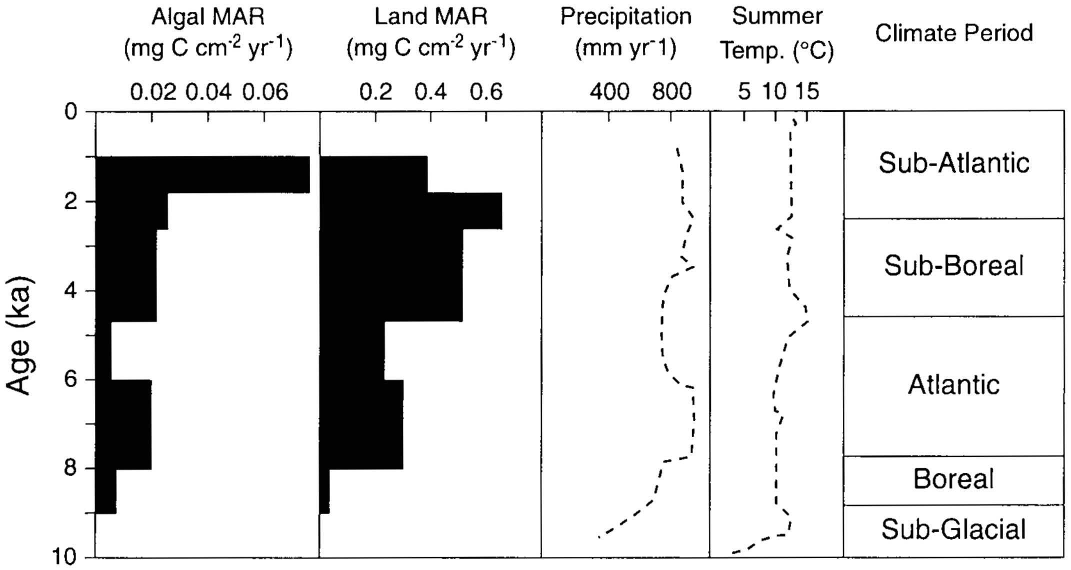

Figure 10. History of Holocene organic matter accumulation in Lac du Bouchet, France. Pollen assemblages indicate the types of climate succession that has occurred. Changes in postglacial climates affected organic matter production and delivery in this maar lake. Advent of agriculture increased algal productivity starting about 1500 yrs ago.

greater than those of algal organic matter (Figure 10) because of the abundance of terrestrial biomass around the maar. However, deforestation by humans and subsequent introduction of agriculture during the Sub-Atlantic period (2 ka to present) changed the vegetative cover of the watershed and led to an increased supply of soil-derived nutrients and a consequent increase in algal production. This anthropogenic change becomes evident in Lac du Bouchet around the middle of the Sub-Atlantic period by the appearance of pollen of cereal species and also the pollen of birch (Reille & de Beaulieu, 1988), which characteristically pioneers the ground cleared by forest fires. It is recorded also in the palynofacies by the presence of charcoal from these fires (Bertrand et al., 1992). A progressive increase in the pollen of littoral aquatic plants (*Isoëtes*) and the maximum aquatic organic flux during the Sub-Atlantic period (Figure 10) indicate enrichment of nutrients in the lake waters as a consequence of deforestation (Sifeddine et al., 1996). Similarly, deforestation of the catchment of Lac d'Annecy in eastern France, which occurred at ca. 1000 AD (Higgits et al., 1991), also led to enhanced aquatic production. The proportion of organic matter derived from algae to that from land plants becomes sufficiently large in post-deforestation sediments that variations in aquatic biomass and trophic structure can be inferred and appear to be linked to solar cycles (Buillit et al., 1997).

Late Quaternary paleoclimate record in sediments of Lake Tritrivakely, Madagascar

Lake Tritrivakely is a crater lake, one kilometer in diameter, situated at an elevation of 1778 m on a dry high plateau in Madagascar (Gasse et al., 1994). The lake has no outlet, and it receives its water mainly from direct precipitation. This hydrologic isolation makes the water level of the lake very sensitive to climate changes. Because of its latitude (20°S), the lake sediments are a monitor of changes in tropical southern hemisphere climate. The present water depth of the maar is about 1.4 m during the winter rainy season, but this diminishes to 0.7 m during the summer. The basin is approaching the terminal stage in lake succession; it contains ca. 50 m of sediment, and the lake is presently a peat-bog dominated by sedges (*Cyperus*) and rushes (*Juncus*). The sedimentary sequence consists of peat-dominated sediments from the surface to ca. 3 m sub-bottom that overlie a variety of lake muds, some with sand layers.

The sedimentary record contains abundant pollen that shows that vegetation in and around the lake has changed over the past 36 ka in response to climate variations of the latest Quaternary, which have also affected the water level of Lake Tritrivakely (Gasse et al., 1994). Pollen of shrubs of the family *Ericaceae* are dominant in sediments deposited from 36–13 ka (Figure 11). These shrubs are C_3 plants (Aucour et al., 1993)

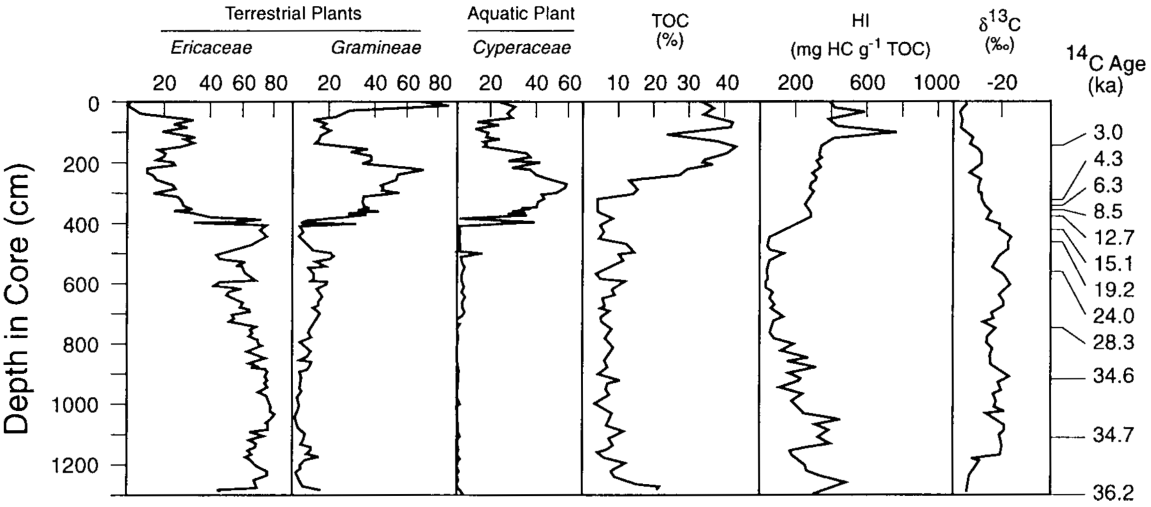

Figure 11. Evidence of end-glacial climate change in sediments from Lake Tritrivakely, Madagascar. Change in delivery of organic matter between 15 and 13 ka is recorded in organic carbon concentrations, Rock Eval HI values, $\delta^{13}C$ values of bulk organic matter, and microfossils contents of sediments. The changes in organic matter character indicate a transition from a wet climate to dry climate at this time. From Gasse et al. (1994).

that are found in Africa today at elevations above 2000 m. Their pollen dominance indicates that the climate from 36–13 ka was cooler than today. Aucour et al. (1993) similarly concluded from pollen and oxygen isotope studies of Kashiru Bog in Burundi, East Equatorial Africa (3°S), that the climate was cool and dry until 13 ka. A dramatic change appears at ca. 13 ka, when pollen of grasses (*Gramineae*) replaces that of *Ericaceae* as the dominant type (Figure 11), signaling a drier and warmer climate. Sedimentation rates drop in Lake Tritrivakely between 13 and 5 ka. A similar drop in sedimentation rates is found in Kashiru Bog between 13 and 7 ka, but this is followed by a change to warmer and wetter conditions between 7 and 4.5 ka (Aucour et al., 1993). The drop in sedimentation rate in Lake Tritrivakely is accompanied by the appearance of abundant pollen from emergent sedges (*Cyperaceae*) in the sediment record (Figure 11), which suggests that water depths decreased, either by lowered water level or basin infilling. Since ca. 5 ka, conditions like those of today have prevailed in both Lake Tritrivakely and Kashiru Bog.

The paleoclimate changes impacted the amount and type of organic matter that was delivered to the sediments of Lake Tritrivakely. Some sections of the upper, peaty sediments contain as much as 44% organic carbon, and some of the organic matter in this layer has very high Rock-Eval HI values (Figure 11). This combination suggests high production and enhanced preservation of organic matter, probably under anaerobic or dysaerobic conditions in the bog waters. The high HI values are not typical of fresh vascular plant material (Figure 3) and therefore indicate partial microbial replacement of the organic matter that was initially deposited under the modern bog conditions. A similar bog-like condition evidently existed at the base of the 13 m core (36 ka), where TOC concentration reaches 22% and HI values are elevated (Figure 11), even though the dominant vascular plant input was from land shrubs instead of emergent sedges. In both the bog-type sections, the $\delta^{13}C$ values of organic matter are between –25 and –30 ‰ (Figure 11), which are values representative of C_3 plants utilizing CO_2 (Figure 1). Because many of the *Cyperaceae* are C_4 plants (Aucour et al., 1993), the $\delta^{13}C$ values suggest that algal production has continually dominated organic matter delivery to the sediments of Lake Tritrivakely. This conclusion is supported by a ca. 50% contribution of aquatic amorphous organic matter to the total organic petrographic composition (Sifeddine et al., 1995) throughout the 13 m sediment core.

Throughout most of the sedimentary record, TOC concentrations hover near 10% and HI values are between 100 and 200 (Figure 11). The organic $\delta^{13}C$ values fluctuate between –18 and –24 ‰, which are values that are less negative than those of typical C_3 plants (Table 1). The results of organic petrographic analysis indicate that the majority of the sedimentary organic matter originates from aquatic production (Sifeddine et al., 1995). The carbon isotope values therefore suggest that algal productivity of Lake Tritrivakely was sufficiently high between 35 and 13 ka to diminish the availability of dissolved CO_2 in the lake waters, and the low HI values suggest that lake waters were sufficiently mixed to depress preservation of the algal organic matter. The combination of elevated algal production and decreased organic matter preservation is consistent with a period of cool and windy climate and consequent improved mixing of the lake waters.

Late Quaternary paleoclimate record in lake sediments of Carajas, Brazil

The Serra Sul dos Carajas is an upland plateau 750 m above sealevel that is surrounded by rainforest in southeastern Amazonia, Brazil. Lakes and bogs occupy depressions in the terrain and are filled primarily by precipitation and local runoff. Present annual rainfall is between 1.5 and 2.0 m in the uplands, which is less than in the surrounding rainforests. Vegetation on the plateau is dominated by savannah grasses, shrubs, and trees. Documented changes in vegetation indicate that climates have fluctuated during the late Quaternary in tropical South America (e.g., Servant et al., 1993).

One of the shallow, water-filled depressions, hereafter referred to as Lake Carajas, has provided a sedimentary record of climates in Amazonia for the past 60 ka. The lake, actually a small bog, is situated at 6°S and therefore documents southern hemisphere tropical zone climate changes. The sedimentary sequence consists of a surficial organic-rich clay layer underlain by alternations of gyttja and silty clastic sediments (Figure 12). The sediment record is interrupted by a hiatus associated with each clastic interval, but it otherwise appears to accumulate steadily. Pollen assemblages (Figure 12) indicate that the gyttja layers correspond to periods of wet climate and expanded rainforest, whereas the clastic layers record times of dry climate (Absy et al., 1991). Sediments deposited at the beginnings of each dry period contain notable amounts of carbonized land-derived organic particles (Siffeddine et al., 1994b), indicative of widespread forest fires that accompanied the change to a drier climate. Within the limits of the radiocarbon dating of the sediments, the wet-dry alternations appear to approximate 20 ka cycles, which is the orbital precessional cycle that affects summer-winter seasonal differences.

Short-term paleoclimatic changes are evident in the Holocene portion of the Lake Carajas sedimentary record. Occurrences of carbonized organic particles and silica sponge-spicules alternate between 7 and 4 ka and again between 2.7 and 1.5 ka. These alternations indicate successive dry (paleofires) and wet (silica spicules) periods (Sifeddine et al., 1994b). The short dry episodes are believed to be linked to temperature changes in the Equatorial Pacific Ocean similar to the present ENSO phenomena (Martin et al., 1993).

The late Quaternary paleoclimate changes evident in the pollen record from Amazonia impacted the amount and type of organic matter that was delivered to the sediments of Lake Carajas. TOC concentrations are 50–60% in the gyttja layers and 2–3% in the clastic sediments (Figure 12). Organic matter C/N ratios are high (30–60) in the gyttja and low (10–12) in the clastic layers, suggesting that vascular plants are the main source of the organic matter in the gyttja and that algae and microbes are the principal originators in the clastic sediments. This supposition is confirmed by palynofacies results. Large proportions of amorphous organic matter, indicative of a predominantly aquatic origin, are present in the clastic layers (Figure 12). Mass accumulation rates of organic matter were up to four times greater in the times of wet climate than during dry periods (Figure 12). Evidently land-derived organic matter was washed into Lake Carajas, along with soil-derived nutrients that encouraged algal production. Organic matter preservation must have been greatly enhanced to deposit sediments containing over 50% TOC. In contrast, low deliveries of land-plant organic matter and soil nutrients resulted in periods of low rates of algal-dominated production of organic matter during intervals of dry climate. The lack of impact on the isotopic composition of organic matter (Figure 12) suggests that algal production has never been high enough to draw down the supply of CO_2 dissolved in the waters of Lake Carajas. Because the amount of land runoff has been the most important factor to variations in deposition of organic matter, the sediments of this small lake serve as a recorder of paleoprecipitation on the Serra Sul dos Carajas.

Glacial-interglacial paleoproductivity cycles in Lake Biwa, Japan

Lake Biwa is located on the main Japanese island of Honshu between Kyoto and the Sea of Japan. The lake is large, having an area of 674 km^2 and a maximum water depth of 104 m, and it has been the subject of a

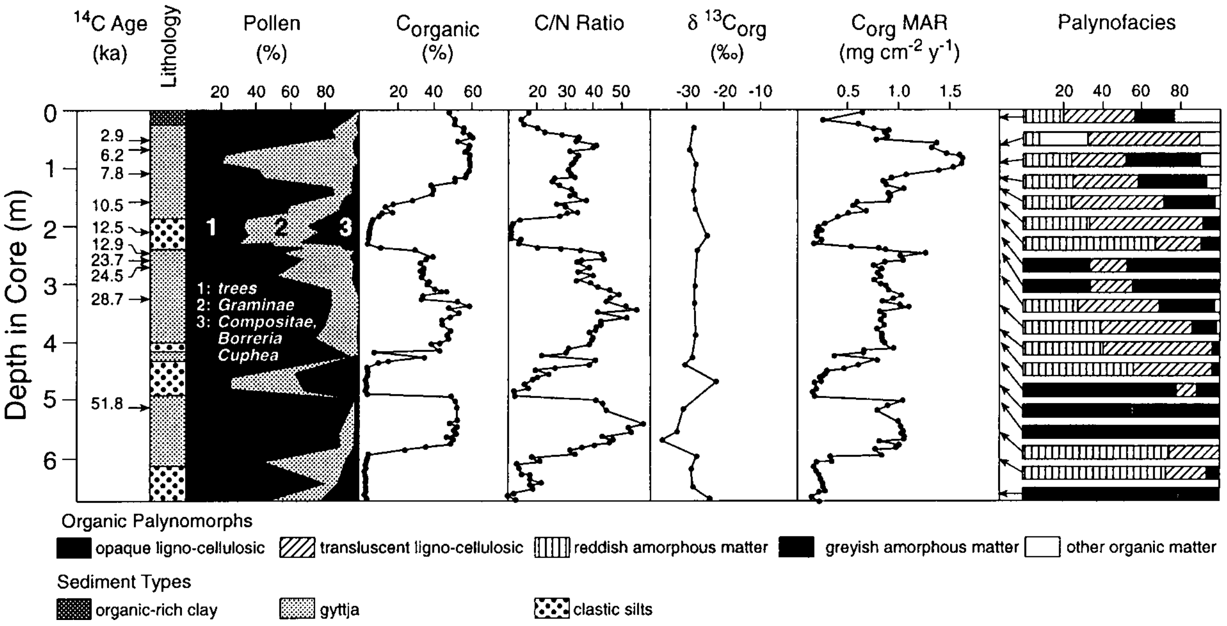

Figure 12. Record of climate-induced alternations between algal dominance to land-plant dominance of organic matter supply to sediments of Lake Carajas, Brazil. The origin of organic matter is principally from land-plants in the surrounding watershed of this small lake, except during dry periods when wash-in is attenuated. Organic $\delta^{13}C$ values are unaffected by these changes. From Sifeddine et al., 1994b.

broad variety of paleolimnological studies. In particular, glacial-interglacial changes over the past 430 ka have been documented from bulk organic matter properties in sediments that represent deepwater lake conditions similar to the present conditions (Meyers & Takemura, 1997). C/N ratios vary between 5 and 10 (Figure 13), indicating that algal sources have dominated organic matter inputs to these sediments. A gradual decline with depth is evident in the C/N ratios and in the concentrations of organic carbon. These patterns are probably the result of continuing diagenesis of organic matter during which organic carbon is converted to CO_2 or CH_4. These two gases diffuse out of the sediment, but organic nitrogen converts to NH_4^+, which binds to clay minerals and remains in the sediment. The contrasting diagenetic fates of C and N can lead to gradually smaller C/N ratios with greater time of burial (Müller, 1977; Meyers, 1997).

Nakai (1986) has observed that organic matter $\delta^{13}C$ values are generally less negative in younger sediments than deeper in the depositional sequence (Figure 13). The $\delta^{13}C$ shift may indicate a progressive change in the carbon cycle of Lake Biwa over the past 430 ka. Extensive recycling of organic matter within the water column can produce algal organic matter that is isotopically light, or having more negative $\delta^{13}C$ values (Rau, 1978). The trend to less negative $\delta^{13}C$ values in younger sediments may therefore record the converse - a progressive decrease in the amount of organic matter recycling within the waters of Lake Biwa towards modern times. A decrease in the rate of organic matter recycling might result from an increase in aquatic productivity, which might be reflected in progressively greater mass accumulation rates in younger sediments, or it could result from a gradually diminishing rate of organic matter oxidation in the lake bottom as the lake system has matured. Whether production or preservation is the principal cause, isotopically light organic carbon is removed from the epilimnion at a rate greater than the replacement of dissolved inorganic carbon, and the $\delta^{13}C$ value of the inorganic carbon gradually becomes more positive.

The C_{org} MARs of the interglacial intervals are up to nine times larger than those of the glacial intervals. The interglacial rates range between 1.19 mg cm^{-2} yr^{-1} and 4.58 mg cm^{-2} yr^{-1}, whereas the glacial MARs range between 0.52 mg cm^{-2} yr^{-1} and 1.03 mg cm^{-2} yr^{-1} (Figure 13). The C_{org} MAR depends on both the delivery and the preservation of organic matter in the lake bottom. Organic matter can originate from both algal production and from wash-in of land-derived materials. C/N ratios in the sediments show that algal organic

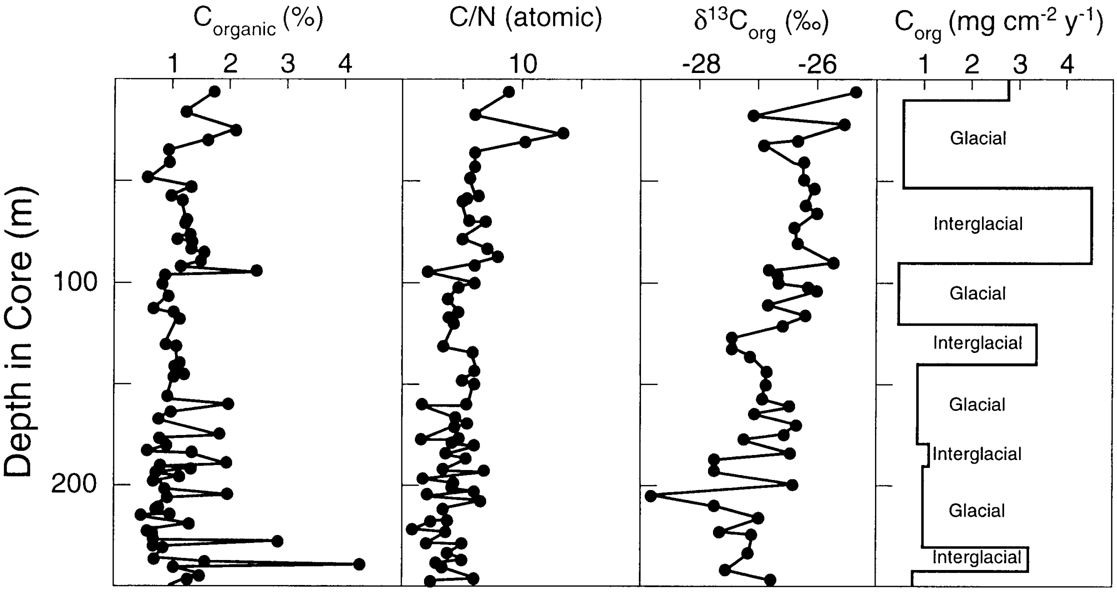

Figure 13. Evidence of glacial-interglacial cycles in lake productivity as recorded in organic carbon mass accumulation rates of sediments from Lake Biwa, Japan. Organic C/N ratios show that nearly all of the organic matter is from lake algae. Interglacial climates in Japan are wetter than glacial climates, providing greater wash-in of soil nutrients to the lake, which enhances algal productivity. The gradual upcore shift towards less negative organic $\delta^{13}C$ values suggests progressive changes in organic carbon cycling within this lake. Core data from Ishiwatari and Uzaki (1987), Nakai and Koyama (1991), and Meyers and Takemura (1997).

matter predominates throughout the entire 250-m-thick sequence, so any variations in delivery of organic matter must be mostly from changes in algal production. Organic matter preservation can be enhanced by higher sedimentation rates (Meyers & Ishiwatari, 1993), and bulk MARs are elevated in the intervals identified by pollen assemblages to correspond to interglacial climates (Meyers & Takemura, 1997). The proportions of relatively coarse silt-sized sediment particles increases in the interglacial intervals (Kashiwaya et al., 1987), indicating that it is increased delivery of land-derived sediments and not only algal production that elevated bulk sediment MARs in Lake Biwa during interglacial times. The Lake Biwa sedimentary record illustrates how glacial-interglacial climate changes can affect organic matter accumulation, which then becomes a recorder of past local climates.

Summary and conclusions

The organic matter accumulation records of lake sediments are affected by paleoclimatic change. Plants living in the lake and in its watershed are the principal sources of the organic substances initially delivered to a lake system, and the amounts and kinds of these biota reflect environmental conditions. Microbial reworking of these materials during sinking and early sedimentation markedly diminishes the total amount of organic matter while replacing many of the primary compounds with secondary ones. The magnitude and nature of the microbial activity is also influenced by environmental conditions.

Despite the generally low survival rate for most primary organic compounds, various organic matter components of lake sediments nevertheless retain source information and thereby become important parts of paleolimnological and paleoclimatological records. Progressive eutrophication of lacustrine systems, changes in watershed vegetation, and the advent of agriculture are some of the paleoenvironmental aspects that can be inferred from sediment organic matter. Bulk parameters, such as elemental and isotopic compositions, Rock-Eval pyrolysis results, and palynofacies descriptions give summaries of changes in delivery of organic matter to lake sediments. Carbon/nitrogen ratios of total organic matter reflect original proportions of aquatic and land-derived material. Carbon isotopic compositions indicate the history of productivity and carbon recycling within the lake and of changes in watershed vegetation as climate changed.

Periods of wetter climate generally result in enhanced algal productivity as a consequence of greater wash-in of soil nutrients. Under these conditions, enhanced algal production is recorded as elevated Rock-Eval hydrogen indices, lowered organic C/N ratios, and increased organic carbon mass accumulation rates. In lakes in which organic matter delivery is dominated by land-derived material, however, algal production becomes the major source during periods of arid climate, and organic C/N values and mass accumulation rates diminish in the sediment intervals corresponding to dry climates. Lowering of lake water levels, which is typically accompanied by depressed aquatic productivity because the supply of nutrients weathered from soil is terminated, can perturb organic carbon mass accumulation rates through suspension of sediments from lake margins and redeposition in deeper basins, making delivery of organic matter appear to increase. Periods of drier climate may lower water levels and create peat bogs in former lake basins. Alternations between C_3 and C_4 watershed plants accompany climate changes such as glacial/interglacial transitions and wet/dry cycles, and these changes in land-plant types are evident in the $\delta^{13}C$ values of the organic matter delivered to lake sediments from the watershed. Periods of elevated algal productivity also impact the $\delta^{13}C$ values of sedimentary organic matter by drawing down the amount of CO_2 dissolved in the epilimnion and diminishing algal preference for ^{12}C. Organic matter produced under these conditions has less negative organic $\delta^{13}C$ values. Changes in climate-driven hydrologic balances of lakes are recorded in δD values of sedimentary organic matter as the hydrogen isotopic composition of lake waters changes. Visual microscopic examination of particles of organic matter in sediment records is particularly informative in identifying changes in the origins of the organic matter delivered to lake sediments. Evidence of source and of extent of microbial reworking can be discerned by palynofacies analysis, and this information is important to reconstructing the nature of past climate changes.

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