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Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes

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Abstract—Organic matter constitutes a minor fraction of marine and freshwater sediments, yet its important contribution to the sedimentary record can be used to reconstruct marine and continental paleoenvironments. The organic matter content of sediments is the residue of past biota. The amounts and types of organic matter present in sediments consequently reflect environmental conditions that impacted ecosystems at different past times. General sources of the organic matter are inferred from bulk properties such as elemental compositions, carbon and nitrogen stable isotope ratios, Rock-Eval pyrolysis data, and organic petrography. Details of organic matter origins are refined by analyses of biomarker molecular compositions. Source changes are proxies for fluctuations in sea-level, oceanic surface currents, and continental climates. Algal paleoproductivity rates are indicated by organic-carbon mass accumulation rates and carbon and nitrogen stable isotopic compositions. These parameters record past availability of nutrients and, therefore, are proxies of surface mixing in the oceans and amount of land runoff to lakes. Sea-surface paleotemperatures are recorded by the number of carbon–carbon double bonds in lipid biomarkers produced by marine algae. Larger proportions of the double bonds are proxies for the cooler surface waters that accompanied periods of global glaciation and intervals of enhanced upwelling. The $\delta^{13}C$ and δD values of plant organic matter record past concentrations of carbon dioxide in the atmosphere and changes in delivery of atmospheric moisture, respectively. Diagenesis, which causes the concentration and composition of organic matter in sedimentary settings to differ from those of the original biologically synthesized materials, can bias organic geochemical paleoenvironmental records. The magnitude of this potential source of misinformation must always be considered and evaluated. Comparison of multiple organic geochemical proxies of past conditions helps to compensate for the effects of diagenetic alterations and thereby to improve interpretations of paleoenvironmental change. © 1997 Elsevier Science Ltd. All rights reserved

Key words—*n*-alkanes, C/N ratios, carbon isotopes, nitrogen isotopes, paleoproductivity, paleotemperatures, pigments, sterols

INTRODUCTION

Sedimentary organic matter provides a variety of indicators, or proxies, that can be used to reconstruct records of marine and continental paleoenvironments and paleoclimates. Both production and preservation of organic matter are affected by environmental change. Moreover, a substantial arsenal of biomarker compounds, together with patterns of compound classes and the isotopic compositions of bulk organic matter and of specific molecules, have enabled organic geochemists to deduce much about the past ecosystems and environments in which the sedimentary organic matter was created and deposited.

The types of information provided by the organic matter contents of sediments are diverse. Biological paleoproductivity can be inferred from mass accumulation rates of organic carbon, as can the paleoceanographic and paleolimnologic conditions that influenced preservation of organic matter. These paleoenvironmental parameters typically reflect physical circulation within water bodies, which in turn depends on climatic factors. The kinds of aquatic and continental plants that existed at a locality at different times in the past can be estimated from compositions of the organic matter in different sediment layers, and these biotic assemblages also record paleoenvironmental factors. Detailed histories of carbon cycling at both local and global scales are given by the amounts and isotopic contents of organic matter in sedimentary records. Periods of higher and lower environmental temperatures have left their imprints on the molecular residues of organisms that lived during these former times and that are now part of the sedimentary organic matter record.

In a very real sense, "geochemical fossils" exist. A truism about all fossil records, however, is that they are incomplete. Preservation of the fossil contents of sediments is typically not uniform, thereby introducing bias into the information retained by fossil records. This is certainly true for the organic geochemical fossil record, and one of the goals of

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this overview is to evaluate the potential skewing of paleoenvironmental information provided by organic geochemical data.

The organization of this overview of organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes is: (1) to consider first the production of organic matter, because the amount of organic matter produced is an indicator of the aquatic and continental paleoenvironmental conditions under which plants grew, (2) to consider organic matter preservation, because the paleo-conditions that influence preservation integrate biological and physical factors, (3) to discuss elemental, isotopic, and molecular indicators of organic matter sources, and (4) finally to present examples of paleoenvironmental reconstructions that have employed organic geochemical data.

CONTROLS ON PRODUCTION OF ORGANIC MATTER

Primary production of organic matter

Photosynthetic production by phytoplankton in surface waters is the dominant source of primary organic matter in most aquatic systems. This biosynthetic process uses energy captured from sunlight by photosensitive pigments to convert dissolved inorganic carbon and nutrients into organic matter. Redfield (1942) summarized the process for diatoms as:

$$106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2$$

This biogeochemical relationship between non-living mineral materials and living algal organic matter is useful in understanding the general primary production of organic matter. Of foremost importance is the requirement for light to energize photosynthesis. Light is abundant nearly everywhere on the continents, but it is limited in aquatic environments. Light intensities diminish rapidly with water depth in lakes and oceans, with the result that light energy becomes insufficient to permit photosynthesis at depths of 100–200 m in the clearest waters. As a consequence, aquatic photosynthesis is limited to a shallow surface zone — the photic zone — that typically is less than 100 m deep and more commonly is only a few tens of meters in depth. Chemosynthesis, in which chemical energy is released by the oxidation of reduced substrates, can proceed in the deep waters of lakes and oceans, but this biosynthetic process is not a major producer of organic matter.

Nearly as important as the availability of light, the proper proportions of C, H, N, O, and P are needed to produce organic matter. Carbon, as dissolved HCO_3^- or CO_2, and water are abundant in aquatic environments, but the availability of liquid water can limit photosynthesis in dry or frigid continental areas. Combined forms of nitrogen and phosphorus, represented in the Redfield relationship as nitrate and orthophosphate, are required, and these essential nutrients are often in limited supply in natural waters. Nitrogen fixation, the conversion of atmospheric N_2 to NO_3^-, is done principally on continents by soil microbes, whereas phosphate is derived from the weathering of continental rocks. The waters of lakes and oceans are, therefore, highly dependent on runoff from land areas for maintenance of their nitrate and phosphate supplies.

Large variations that exist in the availability of nutrients in surface waters of different parts of the world result in large contrasts in phytoplanktonic productivities (Table 1). Two factors are involved. The first is that the transport of nitrate and phosphate from land areas to lakes and oceans varies from place to place. Lakes, being surrounded by land, typically have more abundant inventories of nutrients than most oceanic areas, and smaller lakes are generally more productive than larger ones. Within the marine realm, coastal areas generally are richer in nutrients than open-ocean areas far from land. This is particularly true of marine waters near river mouths where nutrient delivery is most active.

The second factor involves the efficiency of nutrient recycling within aquatic systems. Vertical mixing is important in returning dissolved nutrients to the photic zone. Removal of nutrients occurs during their incorporation into biomass, which depletes the supply of dissolved nutrients remaining in the photic zone and limits continued phytoplankton growth. Dead and dying algal cells commonly sink into the depths of lakes and oceans, where they decompose after having taken the essential nutrients away from the photic zone. Nutrient recycling from deep parts of lakes and oceans is generally not efficient because of density stratification of waters, but it does occur at certain times and places. The waters of most temperate lakes, for example, undergo annual or semiannual overturn as surface waters

Table 1. Summary of annual rates of algal production in marine and freshwater ecosystems

Aquatic ecosystem	Annual productivity range ($g\,C\,m^{-2}\,yr^{-1}$)
Marine areas	
Open ocean	25–50
Coastal ocean	70–120
Upwellings	250–350
Freshwater areas	
Oligotrophic lakes	4–180
Mesotrophic lakes	100–310
Eutrophic lakes	370–640

Data complied from Ryther (1963) and Wetzel (1977).

seasonally pass through 4°C and become more dense than deeper waters. The lakes thereby become well-mixed.

The interplay of nutrient delivery from land and upward mixing of nutrient-enriched deep waters combines to give different types of aquatic ecosystems their different rates of productivity (Table 1). The modern open-ocean, which constitutes about 90% of the ocean surface area, has a low rate of annual productivity because of thermal and salinity stratification that separates surface waters from the deep ocean. Nutrient availabilities are very limited. Coastal areas of the ocean have moderate productivities because of nutrient supply from land runoff and because shallow water depths (<200 m) allow water turbulence to return dissolved nutrients to the photic zone. Upwelling areas, constituting only 0.1% of ocean area, have markedly elevated productivities because of upward circulation of subsurface waters and their entrained nutrients. Because the efficiency of nutrient recycling depends on winds, waves, and surface currents, paleoclimatic changes have affected oceanic paleoproductivity. More vigorous circulation of the surface ocean during glacial intervals has been postulated to have stimulated paleoproductivity (e.g. Lyle, 1988). For example, paleoproductivities in glacial intervals are up to twice as high as during preceding interglacial intervals at DSDP Site 594 on the Chatham Rise southeast of New Zealand (Kowalski and Meyers, 1997), partly from more efficient nutrient recycling and partly from greater deliveries of land-derived nutrients.

Lacustrine productivities are also affected by environmental changes. Delivery of nutrients from the surrounding watershed is increased or decreased as local precipitation varies, sometimes making the accumulation of organic matter in sediments a useful paleoprecipitation proxy. Moreover, increased erosion of soil nutrients typically follows such natural and human environmental perturbations as fires, deforestation, and agricultural tilling. Increased lake productivity follows the enhanced delivery of nutrients that these disturbances produce. In addition, lake productivity is very sensitive to the magnitude of surface-water wind-mixing. Both nutrient recycling and residence times of phytoplankton in the photic zone are enhanced during periods of stronger winds, and changes in wind strengths typically have accompanied changes in paleoclimates. The organic matter that is buried in the lake sediments is part of the record of these environmental changes.

Secondary production of organic matter

Primary organic matter created by autotrophic photosynthetic or chemosynthetic production is used by animals and microbes as an energy source and as a source of carbon and nutrients for the secondary production of organic matter. Bacteria, archaebacteria, and other microbes in the water and sediment continually rework and degrade aquatic and land-derived organic matter. Although some microbes are capable of primary production, most environments contain enough organic matter so that the dominant role of microbes is the heterotrophic decomposition of organic detritus. Microbes generally diminish the total mass of organic matter in the paleoenvironmental sedimentary record while contributing their own characteristic forms of organic matter. An important exception exists in specialized situations in which strongly stratified bodies of water allow photosynthetic and chemosynthetic microbes to become major producers of primary organic matter.

Summary of sources of organic matter to sediments

The major source of primary organic matter to the sediments of both lakes and oceans is from the detritus of single-celled phytoplankton that have lived in their photic zones. Detritus from land plants can be an important additional contribution to the organic matter in sediments of many lakes and in marine sediments close to river mouths. The relative contributions from these two general sources of organic matter to sediments is influenced strongly by algal productivity, land-plant productivity, and transport processes. As a consequence, determinations of these and similar factors are important components of paleoenvironmental reconstructions. Organic matter from animals is rarely a significant fraction of the sedimentary total, although geochemical evidence of the abundance and forms of animal life provides important details of paleoenvironmental conditions. For example, the isoprenoid hydrocarbon pristane is a byproduct of zooplanktonic digestive processing of chlorophyll *a* (Blumer *et al.*, 1971). Its absence in some modern lacustrine sediments reflects the absence of calanoid copepods in the foodchains of these lakes (Ho and Meyers, 1993). Microbe-derived organic matter, in contrast to animal-derived organic matter, can become a major portion of the organic matter that remains in sediment records, even though it is secondary, rather than primary, organic matter. The various sources and processes affecting organic matter incorporation into sediments are summarized in Fig. 1.

In addition to the types of organic matter that reflect local production, winds commonly transport materials such as land-plant pollen, soot from fires, and fine soil from distant sources (e.g. Simoneit, 1977; Poynter *et al.*, 1989; Gogou *et al.*, 1996). The eolian component is typically a small fraction of the total organic mixture, but, because it can contain distinctive components that record atmospheric transport routes, it is potentially useful to paleoclimatologic studies.

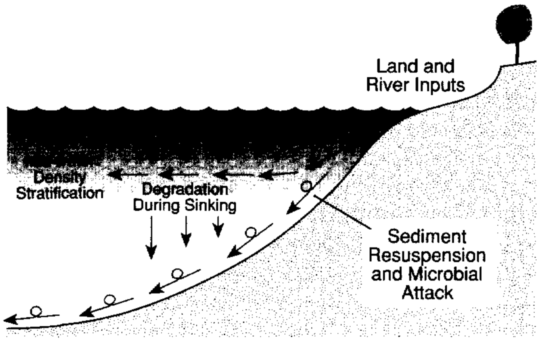

Fig. 1. Summary of the principal sources and alteration processes that affect the sedimentation of organic matter. Organic matter from algal production in the photic zone and from plants on nearby land areas are the major initial sources. Suspended particles congregate at midwater density discontinuities and can be advected laterally. Resuspension and downslope transport moves sediments from coastal locations to basinal depths. Microbial reprocessing of organic matter is intense in the upper water column and in the surface sediments, diminishing the total amount and substituting microbial contributions for original components.

CONTROLS ON PRESERVATION OF ORGANIC MATTER

Organic matter, being a reduced form of carbon and hence at an elevated free energy state, is intrinsically unstable in oxidizing environments. Degradation of organic matter is rapid in the photic zone, continues during the sinking of organic particles, and is intense in the bioturbated surface layer of sediments. Typically no more than a maximum of a few percent of the original amount of primarily produced organic matter survives remineralization to CO_2 to become buried in the sediments of lakes and oceans (e.g. Suess, 1980; Wakeham *et al.*, 1980; Knauer and Martin, 1981; Eadie *et al.*, 1984; Emerson and Hedges, 1988). A small proportion of primary and secondary organic matter, however, becomes preserved in sediments, and this material constitutes the organic geochemical record of past conditions in the water, on surrounding land, and in the bottoms of lakes and oceans. Environmental conditions influence how much of the original organic matter survives to enter the sedimentary record.

Organic matter degradation and alteration in oxic and anoxic water columns

Under normal oxygenated sea-water conditions, the amount of particulate organic matter that sinks to a given depth in the ocean per unit of time, expressed as the organic carbon flux, is determined by both the rate of primary production and the water depth, the latter controlling how long the organic matter is exposed to microbial oxidation in the water column (Fig. 2). The log–log relationship between productivity and depth in Fig. 2 recognizes that the rate of remineralization is greatest in and near the photic zone and actually decreases with depth. This pattern reflects to a large degree the relatively greater susceptibility of fresh organic matter to oxidation and the progressively greater resistance to oxidation of the ever smaller fraction of residual detritus. The productivity–depth relationship is the basis for an empirical expression derived by Betzer *et al.* (1984) that predicts the flux of the surviving organic carbon to the seafloor:

$$\text{carbon flux, g C m}^{-2}\text{ y}^{-1} = \frac{0.409\ (\text{primary production})^{1.41}}{\div\ (\text{water depth})^{0.63}}$$

This expression describes the expected delivery of organic matter to the seafloor from a known rate of primary production under typical marine conditions, that is in an oxygen-containing water column. Under these conditions, the amount of organic carbon reaching progressively greater depths would logarithmically decrease.

The productivity–depth relationship can be used to estimate former rates of primary production from the amount of organic matter that is present in surficial sediments on the seafloor. Because both the downward carbon flux and the productivity are time-dependent functions, organic carbon mass accumulation rates in the seafloor must be considered to calculate paleoproductivity rates. Several empirical expressions have been derived to arrive at paleoproductivity estimates; the one by Stein (1986) is representative:

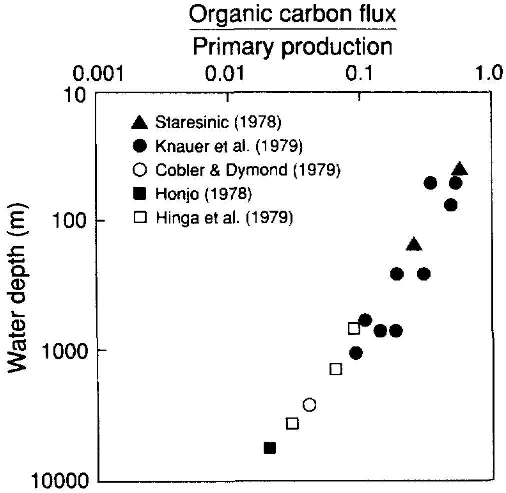

Fig. 2. Concentrations of organic carbon on sinking particles collected by sediment traps at various depths in the ocean. Decreased fluxes with greater depth reflect microbial utilization and degradation of organic matter as particles sink. The linear fit to the logarithmic scales means that organic matter degradation is most rapid in the uppermost part of the water column. Data compiled from sources indicated.

$$\text{paleoproductivity, g G m}^{-2}\,\text{y}^{-1} =$$

$$5.31\,[C_{org}(DBD)]^{0.71} \times LSR^{0.07} \times WD^{0.45}$$

where C_{org} is the weight percent of marine organic carbon, DBD is the dry sediment bulk density in g cm^{-3}, LSR is the linear sedimentation rate in cm kyr^{-1}, and WD is water depth in m.

Important information is required to arrive at these estimates. The magnitude of the marine-derived fraction to the total sedimentary organic matter must be determined. The sediment mass accumulation rate must be estimated, demanding good dating of the sedimentary sequence and determinations of the dry bulk densities of its lithologic units. Some idea of the water depth at the time of sediment deposition needs to be known — sea-level could have been higher or lower in the past, affecting the size of the surviving fraction of sinking organic matter. These kinds of information are often available, particularly in multi-investigator studies such as the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP), and allow good estimates of paleoproductivity.

Most natural waters mix quickly enough to re-equilibrate with the atmosphere and replenish the dissolved oxygen that is removed by organic matter oxidation and animal respiration. In situations such as strongly stratified water columns or times of particularly elevated primary production, dissolved oxygen is expended before it can be replenished, and anoxic conditions develop. Organic matter preservation appears to be improved under these conditions. Unlike within oxic water columns, organic carbon fluxes in anoxic waters do not appear to decrease with depth (e.g. Karl and Knauer, 1991), implying that continued degradation of organic matter is minor.

Because organic matter fluxes appear not to decrease with depth, the expressions derived to estimate paleoproductivity from the usual productivity -depth relationship are not applicable to anoxic environments. Bralower and Thierstein (1984) combined paleoproductivity estimates from microfossil data with organic carbon concentrations in sediments deposited under anoxic waters to derive an empirical expression to calculate paleoproductivities in these special environments:

$$\text{paleoproductivity} = 5 \times C_{org} \times DBD \times LSR$$

where paleoproductivity is measured in g C per m^2 y^{-1}, C_{org} is the weight percent of marine organic carbon, DBD is the dry sediment bulk density in g cm^{-3}, and LSR is the linear sedimentation rate in cm kyr^{-1}.

This expression is useful for postulated anoxic paleoenvironments.

Degradative processes typically modify some of the character of organic matter, in addition to its concentration, in the relatively short time between production and permanent burial in sediments (cf. Wakeham and Ertel, 1988; Hedges *et al.*, 1988; Wakeham and Lee, 1989; Wakeham, 1990). The more labile fractions of organic matter are selectively degraded, creating compositional changes as particles sink. The fluxes of algal biomarkers collected by sediment traps at water depths of 5000 m, for instance, are diminished to less than 1% of their photic zone values. Similar studies in Lake Michigan show proportionately greater losses of algal biomarkers than of land-plant indicators (Meyers *et al.*, 1980, 1984; Meyers and Eadie, 1993). The lacustrine studies mimic the upper part of the marine water column and emphasize how much change can occur in relatively short sinking times.

Despite evidence for substantial alteration during its sedimentation, organic matter retains considerable information about its source and its depositional environment. The sediment trap studies in Lake Michigan, for example, revealed that organic matter concentrations decreased approximately 90% between the lake surface and the bottom sediments, yet C/N ratios and δ^{13}C values did not substantially change from their initial, algal-dominated values (Meyers and Eadie, 1993). If the source information of bulk organic matter is preserved, then at least some of the source and paleoenvironmental information provided by the biomarker molecules is also retained.

Organic matter degradation and alteration in bottom sediments

The small fraction of initially produced organic matter that remains after sinking to the bottoms of lakes and oceans is the foundation of the benthic foodchain, and the metabolism of bottom-dwelling organisms compounds the organic matter alteration and degradation that occurs during sinking. Organic matter consumption is extensive in the bioturbated surface layer of sediments, and the fraction that is not preserved is related to the rate of delivery. For example, Cobler and Dymond (1980) compared organic matter fluxes in a near-bottom sediment trap and in bottom sediments to conclude that about 75% of the organic carbon reaching the seafloor under the relatively productive surface waters of the eastern Equatorial Pacific Ocean is destroyed in the bioturbated layer. In comparison, Prahl *et al.* (1989) estimated that the destruction rate is 98% under the less-productive waters of the central Equatorial Pacific.

Benthic oxidation of organic matter in the transition from oxic → suboxic → anoxic sediment conditions follows a general sequence of oxidants: interstitial oxygen, nitrate, Mn(IV) oxides, Fe(III) oxides, and finally sulfate (Froelich *et al.*, 1979; Schulz *et al.*, 1994). The succession of different oxidants means that organic matter consumption can continue later below the bioturbated surface. Indeed, evidence exists that methanogenic bacteria appear capable of continuing organic matter degradation after interstitial sulfate is depleted to sub-bottom depths of several hundred meters (e.g. Meyers *et al.*, 1996). Most models of organic matter degradation and related geochemical processes, however, assume that steady-state reaction and diffusion are dominant, yet non-steady-state conditions prevail in many depositional areas — for example, in regions where deep-sea turbidites accumulate (Buckley and Cranston, 1988). Under such conditions, episodes of rapid burial of organic matter can improve its preservation by shortening or even eliminating its residence time in the bioturbated zone where extensive benthic metabolism occurs.

One of the classical tenets of organic geochemistry is that the absence of bottom water oxygen favors organic matter preservation in sediments (e.g. Demaison and Moore, 1980; Emerson and Hedges, 1988; Stein, 1991). This concept stems from the common observation that sediments and sedimentary rocks that are rich in organic carbon accumulated under anoxic conditions, whereas organic-carbon-poor sediments accumulated under oxygenated waters. The absence of bottom-water oxygen precludes benthic fauna, thereby eliminating their metabolic stress on sedimented organic matter and preventing sediment bioturbation. Furthermore, sulfate-reducing and methanogenic bacteria are considered to be less efficient at degrading organic matter than aerobic microbes. Several lines of evidence, however, challenge this tenet. For example, Canfield (1989) has concluded that rates of organic matter degradation in anoxic and well-oxygenated environments are actually similar. Calvert and Pederson (1992) point out that other oxidants exist in natural sediments, so that organic matter oxidation continues in the absence of dissolved oxygen. They postulate that the increased fluxes of organic matter that accompany elevated productivities can produce organic-carbon-rich sediments in oxygenated water columns by overloading the oxidative capacity of the benthic environment. In other words, initially deposited organic matter is sacrificed to improve preservation of subsequently delivered organic matter. It is difficult to reconstruct how the very high concentrations of organic carbon (10–30%) present in some sediments came to be without invoking a combination of elevated primary production, enhanced rate of organic matter delivery, improved organic matter preservation, and limited clastic dilution.

In addition to the diagenetic effects from degradation of primary material and substitution of secondary components that modify organic matter character, compositional changes can occur as a consequence of physical sorting during transport and sinking. Different organic matter components are commonly associated with particles of different size (e.g. Thompson and Eglinton, 1978). Particles are typically sorted by hydrodynamic properties during dispersion by water movement (e.g. Prahl, 1985), with the result that sediments having different textures generally contain organic matter that differs not only in concentration but also in source characteristics (e.g. Meyers and Takeuchi, 1979; Keil *et al.*, 1994; Prahl *et al.*, 1994; Tenzer *et al.*, 1997). Differential particle dispersion can complicate interpretations of organic matter sources in sedimentary records, but it can also yield important additional information about paleoenvironmental conditions.

COMPARISON OF SEDIMENTARY ORGANIC MATTER OF LAKES AND OCEANS

Sedimentary environments of lakes and oceans have many similarities, yet several important differences exist that impact the deposition of organic matter. These differences arise largely because of the contrasts in size and age between the basins of lakes and oceans. Lake basins, being smaller by far than the deep ocean basins, receive proportionally more land-derived clastic sediment particles. The result of this is that sedimentation rates in lakes exceed significantly those of the oceans, and organic matter is buried more rapidly. Land-derived nutrients accompany the sediments washed into lakes, enhancing lake fertility and aquatic production of organic matter (Table 1). Lacustrine benthos are not as diverse as those of marine areas, and their depth of bioturbation is less than that of marine fauna. This lesser amount of bioturbation diminishes the exposure of organic matter to oxidation in lake sediments. Working against the generally greater preservation of organic matter in lake sediments is the large amount of turbulent mixing of bottom sediments found in the waters of shallower lakes. Turbulent resuspension can be very significant, even in lakes as deep as 100 m (e.g. Eadie *et al.*, 1984), and it re-exposes organic matter to oxidative processes.

Chemical differences between lakes and oceans ultimately affect organic matter in their sediments. Sea-water is rarely devoid of dissolved oxygen, whereas the hypolimnion of many lakes becomes anoxic during summer thermal stratification. The absence of dissolved oxygen impacts the rates and the types of organic matter degradation that can occur. Another difference is that dissolved sulfate is a major ion in sea-water but not in the water of most lakes. Sulfate reduction is consequently an important aspect of the microbial reworking of marine organic matter but usually not lacustrine organic matter.

Differences in ages and sedimentation rates of ocean basins and lake basins make their depositional records different. Modern ocean basins date from the Late Jurassic, whereas most lakes are Holocene in age. Slow-acting diagenetic processes that become important in marine settings may not appear in younger lacustrine sediments. Sedimentation rates in deep-sea basins are on the order of a few centimeters per 1000 years. In contrast, sedimentation rates in lakes are about a meter per 1000 years. Marine sedimentary records are therefore good indicators of long-term paleoenvironmental changes of regional and global nature, such as the effects of glacial–interglacial cycles and paleoceanographic changes that occurred millions of years ago. Except in special situations, such as the varved sediments of Santa Barbara Basin, oceanic sediments seldom have the temporal resolution to reveal decadal to century-scale paleoclimate changes. Lacustrine sediments, however, are better suited to high-temporal-resolution studies of short-term paleoenvironmental changes than for longer-term processes. Furthermore, sedimentary records of lakes are usually more responsive to local and regional environmental conditions than to global factors.

Because of differences in productivity and sedimentation rates, lake sediments generally contain more organic matter than do deep-sea sediments. The organic carbon concentration of lacustrine sediments is commonly between several and several tens of percent, whereas the organic carbon content of ocean sediments is typically a few tenths of a percent. Furthermore, the organic matter of lacustrine sediments often has a larger land-derived contribution than most marine sediments.

Coastal marine sediments, unlike deep-sea deposits, have strong similarities to lake sediments. They accumulate in relatively shallow water, often receive large proportions of land-derived organic matter, are deposited relatively rapidly (tens of centimeters per 1000 years), and are geologically young because of the latest glacial–interval sea-level lowstand. A number of coastal marine basins were in fact freshwater lakes prior to being flooded by sea-water as a consequence of the Holocene postglacial sea-level rise.

BULK ORGANIC MATTER SOURCE INDICATORS

Despite the extensive early diagenetic losses of organic matter in general and of some of its important biomarker compounds in particular, several bulk parameters are relatively reliable indicators of organic matter sources. Elemental, isotopic, and petrologic compositions provide a record of the biological origins of the organic matter that has been deposited in the sediments of oceans and lakes over time.

Organic matter source identification from C/N ratios

C/N ratios determined from elemental analyses of organic matter have been widely used to distinguish between algal and land-plant origins of sedimentary organic matter (e.g. Prahl *et al.*, 1980; Premuzic *et al.*, 1982; Ishiwatari and Uzaki, 1987; Jasper and Gagosian, 1990; Prahl *et al.*, 1994; Silliman *et al.*, 1996). Algae typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of 20 and greater (Meyers, 1994). This distinction arises from (1) the absence of cellulose in algae and its abundance in vascular plants, and (2) the protein richness of algal organic matter. Selective degradation of organic matter components during early diagenesis has the potential to modify C/N ratios of organic matter in sediments. Partial degradation of algal organic matter during sinking can selectively diminish proteinaceous components and thereby raise C/N ratios. The converse — the lowering of C/N ratios — has been observed in soils (e.g. Sollins *et al.*, 1984) and in ocean sediments (e.g. Müller, 1977), where it involves the absorption of ammonia derived from decomposition of organic matter accompanied by the remineralization and release of carbon. The C/N ratio is usually preserved well enough in subaqueous sediments, however, so that reliable source information is retained. For example, the C/N values of vascular plant debris ranged between 30 and 40 in a coastal marine sediment in which the bulk C/N was 15, preserving elemental evidence of contributions from cellulosic land plants to the total organic matter (Ertel and Hedges, 1985).

Different-sized sediment fractions typically have C/N ratios that are different (Thompson and Eglinton, 1978; Keil *et al.*, 1994; Prahl *et al.*, 1994). Hydrodynamic sorting of sediment by grain size can therefore impact the C/N ratios and thereby bias source assignments based on these ratios. In general, the C/N ratios of organic matter in fine-sized sediments are lower than those of coarse sediments (Table 2). The effect of sediment grain-size reflects two factors — the types of organic detritus and the mineral compositions — that vary with particle size. Coarse sediment fractions contain a larger proportion of intact land-plant debris than fine fractions and thereby have elevated C/N ratios. Fine sediment fractions contain larger proportions of clay minerals, which have both large surface areas and negative surface charges and therefore adsorb ammonia well. Their C/N ratios can be depressed by uptake of inorganic nitrogen.

Situations can consequently occur when C/N ratios give misleading indications of bulk organic matter origin. Problems can arise because analysts typically measure the carbon and nitrogen contents

Table 2. Effects of grain size on the organic carbon concentrations, C/N ratios, and $\delta^{13}C_{org}$ values in surficial sediments from the Columbia River and Washington margin

Source and size fraction (μm)	C_{org} (%)	C/N (atomic)	$\delta^{13}C_{org}$ (‰)
Columbia River, Wells Dam			
Bulk	0.5	10.9	−24.9
< 64	0.7	10.6	−25.6
64–125	0.3	8.0	−25.4
125–250	0.2	6.4	−25.3
250–500	0.5	11.3	−25.3
> 500	29.5	33.5	−26.6
Columbia River mouth			
Bulk	1.34	13.0	−22.3
1–3	3.48	9.4	−22.9
9–17	3.25	11.9	−23.5
36–63	1.24	16.1	—
64–250	0.23	15.8	−23.3
> 250	3.05	25.4	−23.2
Mid-shelf silt deposit			
Bulk	1.02	13.2	−22.5
1–3	3.99	9.9	−23.1
9–17	2.34	13.7	−22.8
36–63	0.64	14.9	—
64–250	0.60	17.5	−23.6
> 250	17.7	33.4	−24.4
Continental slope			
Bulk	2.70	12.1	−22.0
1–3	3.21	9.9	−22.1
9–17	3.13	14.0	−23.4
36–63	2.02	12.4	—
64–250	3.39	11.0	−21.9
> 250	2.76	10.7	−22.4

Data compiled from Keil *et al.* (1994) and Prahl *et al.* (1994).

of sediment samples that remain after removal of carbonate carbon and obtain a residual nitrogen value that combines organic nitrogen and inorganic nitrogen. In most sediments, inorganic nitrogen concentrations are small compared to those of organic nitrogen, and this analytical approach yields C/N ratios that faithfully represent organic matter origins. In sediments having low organic matter concentrations ($C_{org} < 0.3\%$), however, the proportion of inorganic nitrogen can sometimes be a large fraction of the residual nitrogen, and C/N ratios based on residual nitrogen could be artifactually depressed.

Sediments from Nakaumi Lagoon, on the Japan Sea coast of Honshu, Japan, illustrate the consequence of employing total nitrogen concentrations to calculate C/N ratios in organic-carbon-poor samples (Sampei, pers. comm., 1997). The sediments record a progressive change in depositional environment from a river bed to a coastal lagoon as sea-level rose during the Holocene. Organic carbon concentrations increase from < 0.5% in fluvial sands to reach 1–2% in lagoonal muds (Fig. 3). Atomic C/N ratios derived from organic carbon and residual nitrogen are approximately 12 over most of the sediment record, but they are below five in the fluvial sands (Fig. 3), implying that lagoonal organic matter has a smaller algal component than the riverine organic matter. Although this interpretation is plausible, it is unlikely, because river sediments typically contain a large contribution of organic matter from land plants (e.g. Peters *et al.*, 1978; Huang and Meinschein, 1979; Tenzer *et al.*, 1997). Sampei and Matsumoto (unpublished data) also determined the concentrations of organic nitrogen so that they could arrive at C/N ratios of organic matter that were free from inorganic nitrogen artifacts. These C/N ratios are elevated in the fluvial sediments and show that they actually are dominated by land-plant organic matter (Fig. 3). The C_{org}/N_{org} ratios are consistently higher than the C_{org}/N_{total} ratios, indicating that inorganic nitrogen remains after removal of carbonate carbon in all of these sediment samples. The proportion of inorganic nitrogen evidently becomes dominant in the organic-carbon-poor fluvial sediments and results in their misleading C/N source signature.

Source and paleoproductivity evidence from carbon stable isotopic compositions

Carbon isotopic ratios are useful to distinguish between marine and continental plant sources of sedimentary organic matter and to identify organic matter from different types of land plants. The carbon isotopic compositions of organic matter reflect principally the dynamics of carbon assimilation during photosynthesis and the isotopic compositions of the carbon source (e.g. Hayes, 1993). Most photosynthetic plants incorporate carbon into organic matter using the C_3, Calvin pathway, which biochemically discriminates against ^{13}C to produce a $\delta^{13}C$ shift of about −20‰ from the isotope ratio of the inorganic carbon source. Some plants use the C_4 Hatch-Slack pathway, which creates a diffusional isotope shift of approximately −7‰. Other plants, mostly succulents, utilize the CAM (crassulacean acid metabolism) pathway, which discriminates variably against ^{13}C depending on growth dynamics.

Organic matter produced from atmospheric CO_2 ($\delta^{13}C \approx -7‰$) by land plants using the C_3 pathway has an average $\delta^{13}C$ (PDB) value of approximately −27‰ and by those using the C_4 pathway approximately −14‰ (cf. O'Leary, 1988). Freshwater algae utilize dissolved CO_2, which is usually in isotopic equilibrium with atmospheric CO_2. As a consequence, the carbon isotopic composition of lake-derived organic matter is typically indistinguishable from that of organic matter from the surrounding watershed (e.g. Nakai, 1972; Benson *et al.*, 1991; Tenzer *et al.*, 1997). The source of inorganic carbon for marine algae is dissolved bicarbonate, which has a $\delta^{13}C$ value of approximately 0‰. Marine organic matter consequently typically has $\delta^{13}C$ values between −20 and −22‰ (Meyers, 1994). The ≈7‰ difference between organic matter produced by C_3 land plants and marine algae has successfully been used to trace the sources and distribution of organic

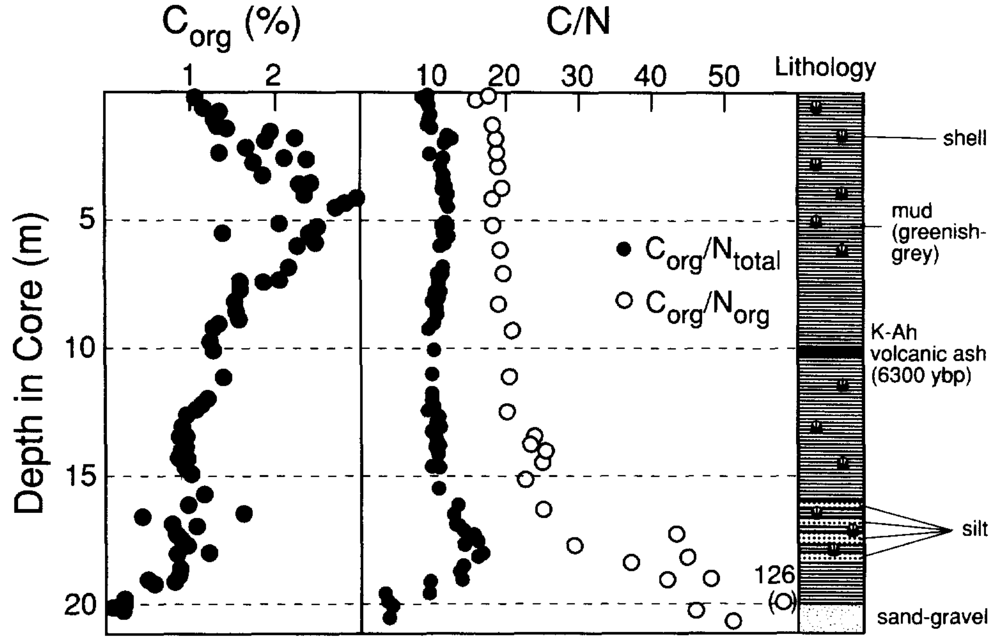

Fig. 3. Concentrations of organic carbon in sediments deposited since the beginning of the Holocene in Nakaumi Lagoon, Honshu, Japan, with comparison of atomic C/N ratios determined from total nitrogen and organic nitrogen concentrations. Major disagreement between low C_{org}/N_{total} ratios and high C_{org}/N_{org} ratios at base of core results from the presence of a large proportion of inorganic nitrogen in organic-carbon-poor sediments. From Sampei and Matsumoto (unpublished data).

matter in coastal ocean sediments (e.g. Hunt, 1970; Newman *et al.*, 1973; Gearing *et al.*, 1977; Prahl *et al.*, 1994). Unlike C/N ratios, $\delta^{13}C$ values are not significantly influenced by sediment grain size (Table 2), making them useful in reconstructing past sources of organic matter in places with histories of changing depositional conditions. The isotopic source signal can become complicated in coastal areas that receive contributions of organic matter from algae and both C_3 and C_4 vascular plants, however (e.g. Fry *et al.*, 1977). In these areas, and also in lakes, addition of C/N ratios to $\delta^{13}C$ determinations improves identification of organic matter sources.

Four distinctive suites of C/N and $\delta^{13}C$ values in plants are evident in Fig. 4. These combinations of elemental and carbon isotopic values distinguish sources of organic matter in sediments and in settling particles. A particular benefit to using these bulk identifiers of organic matter origins is that they represent the whole mixture of organic matter components. In contrast, biomarker molecules typically are a very small fraction of the total mixture and may not be representative of the whole, even though they convey important information about details of individual sources and diagenetic pathways.

The availability of dissolved CO_2 impacts the carbon isotopic composition of algal organic matter because isotopic discrimination towards ^{12}C increases when pCO_2 is high and decreases when it is low (e.g. Fogel and Cifuentes, 1993). Organic $\delta^{13}C$ values, therefore, become indicators not only of origins of organic matter but also of paleoenvironmental conditions. Concentrations of CO_2 available to algae are affected by surface water temperatures in oceans and lakes, increasing during cooler times and decreasing during warmer periods. In addition, concentrations in the photic zones can be drawn down during times of elevated productivity. Lake waters are more sensitive to productivity-driven CO_2 depletion than marine waters because of their much smaller dissolved carbonate pools.

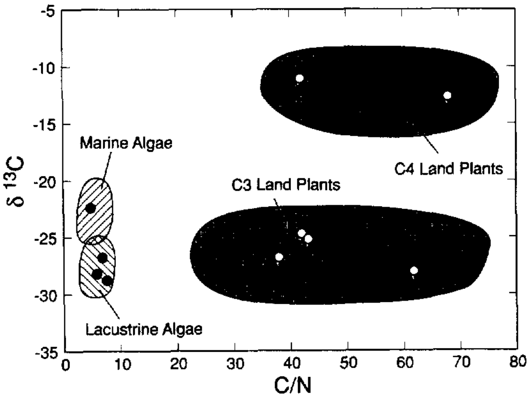

Fig. 4. Elemental (atomic C/N ratio) and isotopic ($\delta^{13}C$ value) identifiers of bulk organic matter produced by marine algae, lacustrine algae, C_3 land plants, and C_4 land plants. Data points are from Meyers (1994).

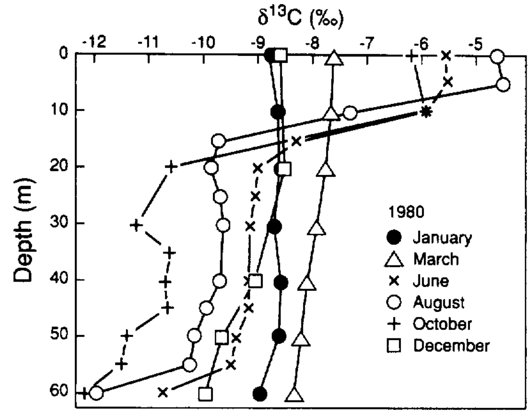

Fig. 5. Seasonal changes of dissolved inorganic carbon $\delta^{13}C$ values with depth in Lake Washington. More positive surface $\delta^{13}C$ values and more negative deeper values in summer months result from photosynthetic removal of ^{12}C from surface waters and transfer to deeper waters where isotopically light organic matter is oxidized. From Quay *et al.* (1986).

Rau *et al.* (1989) have shown that organic matter produced by marine algae living in cold polar waters has $\delta^{13}C$ values as low as –28‰, which is in the range of lacustrine algae (Fig. 4). The explanation for these exceptionally negative values is that the cold waters are capable of holding substantially more dissolved CO_2 than temperate or tropical waters, thereby allowing greater isotopic discrimination by the algae. This effect has been invoked by Kowalski and Meyers (1997) to explain similarly negative organic $\delta^{13}C$ values from sediments deposited during the last glacial maximum at DSDP Site 594 on the Chatham Rise southwest of New Zealand. They hypothesize that the subpolar front occasionally migrated northward and allowed incursions of cold Antarctic surface waters to reach this location.

Seasonal changes impact the $\delta^{13}C$ values of dissolved inorganic carbon in temperate lakes. During summer thermal stratification, preferential incorporation of ^{12}C into algae, followed by sinking of algal detritus, transfers ^{12}C from the epilimnion to the hypolimnion (Fig. 5). Oxidation of the detritus returns the ^{12}C to the dissolved inorganic carbon pool of waters beneath the seasonal thermocline, where it accumulates until fall/winter overturn. The seasonal variation in inorganic $\delta^{13}C$ values is about 4‰ in the upper 50 m of Lake Washington (Fig. 5), and some of this difference between summer and winter can appear in the $\delta^{13}C$ values of algal organic matter produced at different times of the growing season (cf. Hollander and McKenzie, 1991). Even the much larger inorganic carbon pool of sea-water is affected by the surface-to-deep transfer of isotopically light organic carbon; Deusser and Hunt (1969) have shown that dissolved inorganic carbon in surface waters of the Atlantic is depleted in ^{12}C by *ca.* 2‰ relative to deep waters by this process. This depletion is possible because the oceans mix on a time span of about 1000 years, rather than annually.

If the surface-deep transfer of organic carbon is sustained over multiple years in a lake, a long-term depletion in inorganic ^{12}C can develop in the photic zone. In this fashion, past changes in aquatic productivity can leave an imprint on the $\delta^{13}C$ values of the algal organic matter in sediments. Changes in

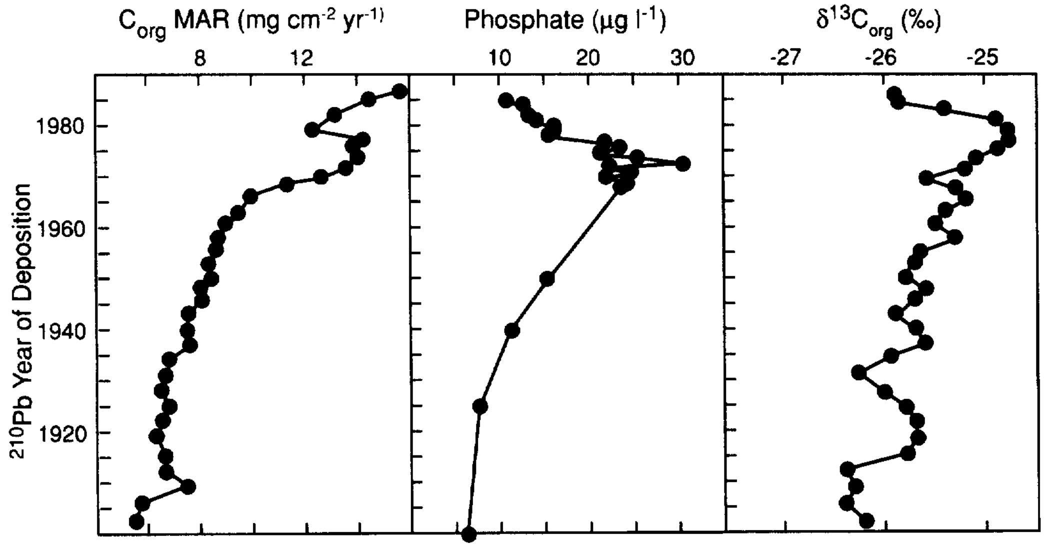

Fig. 6. Effect of cultural eutrophication of waters of Lake Ontario on the $\delta^{13}C$ values of algal organic matter. Greater phosphorus loadings increased algal production of organic matter, which accelerated drawdown of dissolved CO_2 and diminished algal isotopic discrimination. This process has been reversed since *ca.* 1975 by improved wastewater treatment, and $\delta^{13}C$ values in sediments deposited since that time have returned to pre-eutrophication levels. Adapted from Schelske and Hodell (1991).

the $\delta^{13}C$ record of sediments deposited over the past century in Lake Ontario illustrate the effects of enhanced algal productivity. Algal growth began to be stimulated in this lake by watershed deforestation, which occurred between 1820 and 1850 (Schelske *et al.*, 1983) and resulted in increased delivery of soil-derived phosphorus to the lake. Schelske *et al.* (1988) note that organic carbon concentrations in Lake Ontario cores follow the increases in phytoplankton abundance expected from the phosphorus enrichments. Organic carbon concentrations in sediments gradually increased in response to the higher productivity until about 1950. After this, postwar growth of urban and suburban areas greatly enhanced phosphate concentrations in the Great Lakes (Fig. 6), causing a marked increase in both aquatic productivity and the rate of organic carbon accumulation in sediments. The $\delta^{13}C$ values of buried organic carbon reflect the productivity increase by becoming over 1‰ less negative, maximizing at –24.8‰ in sediments deposited in 1975–1980 (Fig. 6). The subsequent shift to more negative values in more recent sediments mirrors the decrease in dissolved phosphate concentrations in showing that improved wastewater treatment has successfully reversed the eutrophication of Lake Ontario.

Carbon isotope compositions of sinking and sedimented organic matter can potentially be modified by diagenesis. Algal organic matter consists of a spectrum of constituents that vary in resistance to degradation and that have a range of $\delta^{13}C$ values (Fig. 7). Selective loss of a large fraction of the isotopically heavy proteins and carbohydrates, for example, would leave residual organic matter that is isotopically lighter than the original algal material. However, the effects of selective diagenesis of organic matter fractions that are isotopically heavy or light appear to be small, usually less than 2‰ (Dean *et al.*, 1986; Hayes *et al.*, 1989; Fontugne and Calvert, 1992; McArthur *et al.*, 1992; Meyers, 1994). The absence of a large diagenetic isotopic shift suggests that microbes utilize a large enough fraction of the initial organic matter and incorporate this carbon into their biomass that the potentially significant effect is minimized.

Source and paleoproductivity evidence from nitrogen stable isotopic compositions

$\delta^{15}N$ values of sediment organic matter can be used to distinguish between algal and land-plant sources of organic matter. The basis of the organic matter source distinctions is that the isotopic compositions of the sources of inorganic nitrogen to aquatic and land plants differ. The $\delta^{15}N$ value of dissolved nitrate ranges between +7‰ to +10‰, whereas the of $\delta^{15}N$ of atmospheric N_2 is about 0‰ (cf. Peters *et al.*, 1978). Peterson and Howarth (1987) have shown that the nitrogen reservoir difference is preserved in the isotopic contents of organic matter produced by plankton ($\delta^{15}N$ of +8.6‰) and C_3 land plants ($\delta^{15}N$ of +0.4‰) in an estuarine ecosystem. The difference between $\delta^{15}N$ values of marine and continental organic matter was employed by Peters *et al.* (1978) to estimate the sources of organic matter to sediments of the California margin (Fig. 8). This approach generally is valid, but aspects of nitrogen biogeochemical cycling introduce complications (cf. Fogel and Cifuentes, 1993).

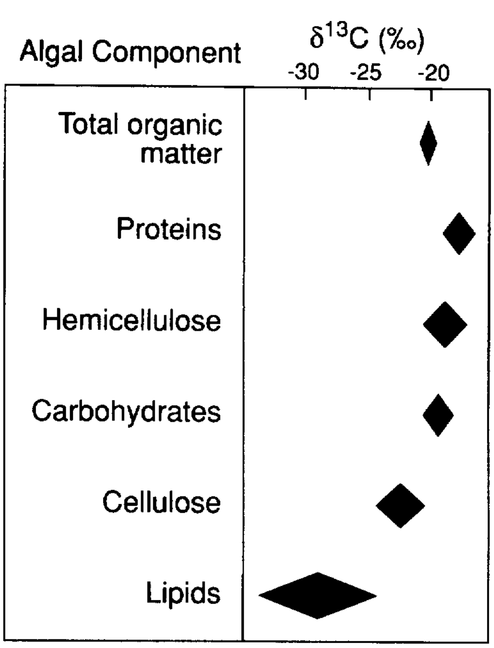

Fig. 7. $\delta^{13}C$ values of organic matter constituents isolated from marine algae. The range in values illustrates the potential for isotopic shifts of sedimented organic matter as a consequence of its selective, partial degradation. Data adapted from Degens *et al.* (1968).

Environmental changes, for example, can affect the $\delta^{15}N$ values of sediments. Meyers *et al.* (1997) note a 2‰ shift towards higher $\delta^{15}N$ values that accompanied the lowering of the water level in Pyramid Lake, Nevada, 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 $\delta^{15}N$ 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 depletion of dissolved nitrate available to the lake algae as environmental conditions changed.

Another factor that can complicate source identifications is denitrification of dissolved NO_3^- in oxygen-depleted waters. This process selectively releases

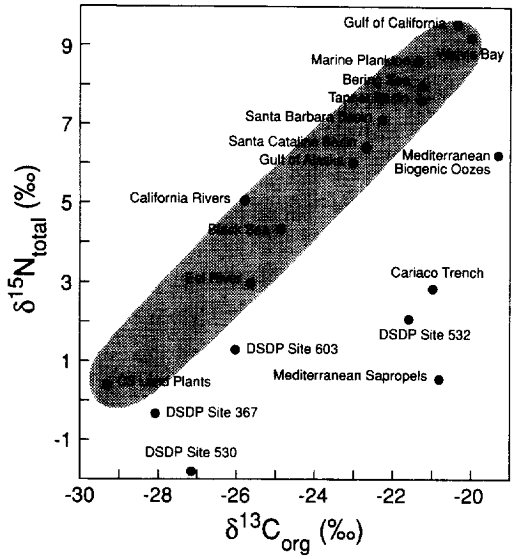

Fig. 8. Organic matter source information provided by sedimentary $\delta^{15}N$ and $\delta^{13}C$ values (stippled area) originally noted by Peters *et al.* (1978). Additional data: C_3 land-plant and marine plankton end-members (Peterson and Howarth, 1987); Gulf of California sediment traps (Pride *et al.*, unpublished data); Mediterranean Upper Pleistocene sapropels and biogenic oozes (Calvert *et al.*, 1992; Fontugne and Calvert, 1992); Pleistocene–Pliocene sediments from DSDP Site 532 (Meyers *et al.*, 1986a); Cenomanian–Turonian black shales from DSDP sites 367, 530, and 603 (Rau *et al.*, 1987).

$^{14}N_2$, leaving the remaining nitrate enriched in ^{15}N (Cline and Kaplan, 1975). The $\delta^{15}N$ values of sediment trap samples from the Gulf of California, Mexico, and surface sediments from Walvis Bay, Namibia, are elevated relative to other marine areas (Fig. 8). Both of these areas have strongly developed oxygen-minimum zones beneath productive surface waters. Denitrification apparently modifies the isotopic composition of the dissolved nitrate pool that is available for algal utilization in the Gulf of California, and paleoceanographic examples of this process may appear in sedimentary records (C. Pride, pers. comm., 1997).

Other factors modify the marine-continental nitrogen isotope pattern and result in marine sediments that have exceptionally low $\delta^{15}N$ values. This effect is particularly evident in modern organic-carbon-rich sediments from the Cariaco Trench and in some sediments that were deposited in the past (Fig. 8). Organic matter in Pliocene–Pleistocene sediments from the Walvis Ridge (DSDP Site 532) and the Mediterranean Sea have $\delta^{13}C$ values (Fig. 8) that indicate a marine origin. Similarly, the organic matter in the Cenomanian–Turonian black shales from DSDP sites 367, 530, and 603 is marine in origin (Dean *et al.*, 1986; Meyers, 1989), although the $\delta^{13}C$ values mimic those of land plants (Figs 4 and 8) because atmospheric pCO_2 was much higher than at present (Dean *et al.*, 1986). The low $\delta^{15}N$ values consequently do not result from incorporation of large proportions of land-derived organic matter in any of these sediments. Instead, utilization of dissolved N_2 by nitrogen-fixing algae is possibly responsible for these anomalous isotopic values, as well as for the elevated organic matter production recorded by these sediments (Peters *et al.*, 1978; Meyers *et al.*, 1986a; Rau *et al.*, 1987). Alternatively, the low $\delta^{15}N$ values in the organic-carbon-rich sediments may record episodes of enhanced nitrate availability that allowed greater algal discrimination in favor of ^{14}N (Calvert *et al.*, 1992).

Source evidence from Rock-Eval pyrolysis

Rock-Eval pyrolysis was initially developed to evaluate the hydrocarbon-generating potential of petroleum source rocks (Espitalié *et al.*, 1977). It has also been shown to be of value to paleoceanography and 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°C to 600°C, three main signals, which correspond to gaseous hydrocarbons (S_0), volatile hydrocarbons (S_1), and hydrocarbon components produced due to thermal cracking of the kerogen (S_2), are generated. Some systems may 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 C_{org}, and (2) the Oxygen Index (OI), which roughly represents the amount of oxygen in mg CO_2/g 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.*, 1977). These parameters relate to the origin of the total organic matter (Tissot and Welte, 1984) and are commonly plotted against each other in a van Krevelen-type plot (Fig. 9). 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 diagenetic alteration routes 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

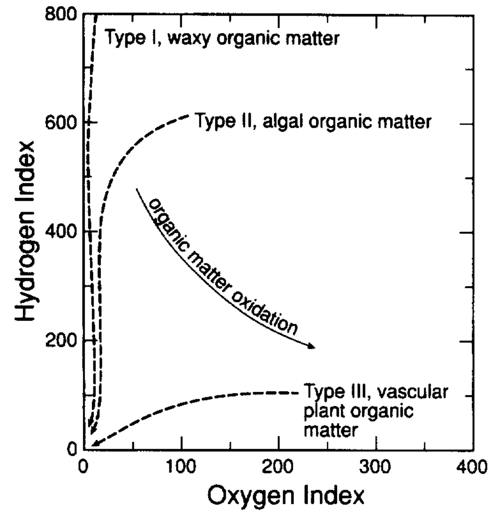

Fig. 9. Rock-Eval van Krevelen-type diagrams for sedimentary organic matter. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO_2 per gram TOC. Thermal alteration pathways of organic matter Types I, II, and III from source material to graphite 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.

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 petrographic organic composition. Talbot and Livingstone (1989) summarize the bulk characteristics of the major types of organic matter delivered to lake sediments, and their typical H/C ratios, HI values, and petrographic descriptions are equally applicable to marine sediments.

Post-depositional oxidation of organic matter, particularly algal organic matter, can bias source determinations based on Rock-Eval data. For example, partial oxidation of the organic matter in the sediments of Lac du Bouchet is evident (Fig. 10) in decreases in TOC concentrations, C/N ratios, HI values, and increases in OI values (Patience *et al.*, 1996). Hydrogen-rich Type I or II organic matter can come to resemble Type III organic matter by such partial oxidation, thereby providing misleading source characterization. For this reason, determination of additional bulk source identifiers, such as C/N ratios and $\delta^{13}C$ values, is wise.

Source and paleoenvironmental information from organic petrography

Organic petrography entails the microscopic analysis of organic matter particles in sediments and rocks (Teichmüller, 1986). In practice, it describes the different constituents of organic matter that remain after HCl and HF treatment to remove mineral particles. Visual observations are made by light microscopy, and different types of particles are quantified from estimations with charts, counting points, or image analysis.

Organic petrography becomes important to establishing organic matter origins because of the oxic and anoxic microbial processing that occurs before and after deposition. As a consequence, the metabolizable fraction of organic matter has been strongly degraded, and the main part of the surviving sedimentary organic matter is the resistant residue of the initial organic matter. The resistant character is either inherited from the original, refractory biological tissues, or it is acquired as a result of bacterial degradation. Visual examination can identify the origin of this resistant material.

Petrographic studies on different sedimentary records have identified three main groups of organic constituents that reflect the origin of the organic matter, its preservation, and its mode of transport to the depositional basin (Lallier-Vergès *et al.*, 1993; Patience *et al.*, 1995; Sifeddine *et al.*, 1995):

1. "*Autochthonous*" or "*aquatic*" organic particles are produced by the aquatic community. They are mainly composed of grayish unstructured, amorphous organic flakes and the recognizable debris of algae and zooclasts. Transmission electron microscopy of ultra-thin sections of unstructured organic matter from Lac du Bouchet, France, has revealed nanoscopic laminae, cell-walls and microbial structures (Patience *et al.*, 1995). Both pyrolytic and ultrastructural studies show that the amorphous organic matter is residual material partly derived from microbial degradation of micro-algal detritus (Derenne *et al.*, 1992, 1993).
2. "*Allochthonous*" or "*terrestrial*" organic particles include a variety of variably preserved ligno-cellulosic debris and soil-derived organic material. This type of organic matter is most common in environments dominated by vascular plants, such as mangrove swamps and soils. In some specific environments like peat-bogs, however, ligno-cellulosic particles are paludal and therefore should be considered autochthonous. This is particularly true of lakes that have abundant emergent vegetation, such as Lake Tritrivakely in Madagascar (Sifeddine *et al.*, 1995).
3. The third organic fraction is composed of spores, pollen, and forest-fire debris brought to lakes and oceans by winds. It usually represents relatively local origins, particularly in the case of hydrologically isolated settings such as maars and other closed lake systems. For lakes and coastal marine areas with riverine inputs, oxidized lignaceous debris can also be regionally characteristic (Di Giovanni *et al.*, 1994; Buillit *et al.*, 1997).

The analysis of palynofacies, which has classically been used in the study of ancient organic-rich sedi-

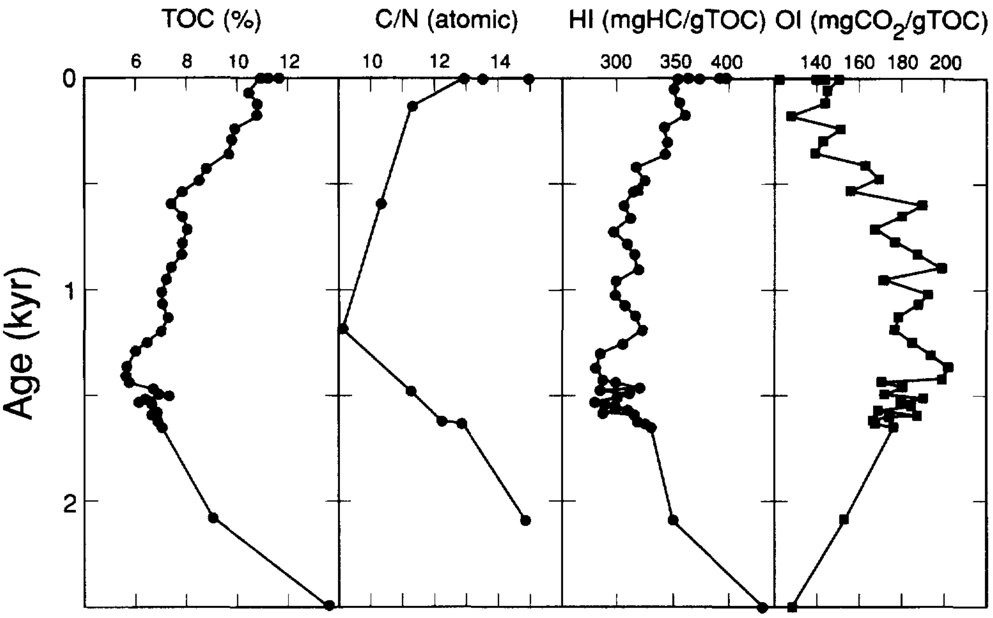

Fig. 10. Comparison of TOC concentrations, organic matter atomic C/N ratios, and Rock-Eval hydrogen index (HI) and oxygen index (OI) values in sediments from Lac du Bouchet, France. High TOC concentrations positively correlate with higher C/N ratios and higher HI values and reflect improved preservation 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.

ments, can be applied to recent sediments. 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), and organic matter is likely to have undergone substantial oxidation at the sediment/water interface. In contrast, algal debris in the sediments of Annecy Lake, France, is associated with grayish 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 altered bulk geochemical indicators of organic matter sources, such as C/N ratios or Rock-Eval HI values (Patience *et al.*, 1996).

MOLECULAR SOURCE INDICATORS

Whereas bulk characteristics are important in identifying general origins of organic matter, it is the molecular constituents of sedimentary organic matter that provide the details of production, delivery, and preservation. As a consequence, molecular organic geochemistry is an important aspect of paleoceanographic, paleolimnologic, and paleoclimatologic studies.

n-Alkane, n-alkanoic acid, and n-alkanol biomarkers

Lipid extraction of sediments yields hydrocarbons and the hydrocarbon-like carboxylic acids, alcohols, ketones, aldehydes, and related compounds. Many of these compounds have fairly specific biological origins, and all of them reflect enzymatic control on their molecular structures. Retention of their biological heritage earns the name "biological marker", which is commonly abbreviated to "biomarker", for many of these compounds. Biomarkers are particularly valuable to paleoenvironmental reconstructions. This is partly because of the source information that they provide. It is also because they are less sensitive to alteration and destruction than most forms of organic matter, although they are not immune to diagenesis. The term "geolipid" is sometimes used to describe the materials obtained from sediments because of the differences that exist between the molecular compositions of unaltered biological matter and the contents of geological samples.

The concentrations and compositions of geolipid biomarker compounds in sediments reflect both paleoenvironmental changes and diagenetic alterations. The alterations evident in the biomarker fraction can be used as proxies for the general processes affecting all forms of sedimentary organic matter, but it is important to remember that geolipids total only a few percent of this material.

Contributions of lipid matter from vascular land-plants and algae are distinguished principally by differences in the chainlengths of their molecular suites. For example, the presence of C_{27}, C_{29}, and C_{31} *n*-alkanes indicates that land-plant epicuticular waxes have been important sources of geolipids to the sediments (cf. Eglinton and Hamilton, 1967; Cranwell, 1973; Rieley *et al.*, 1991a). Algal contributions, in contrast, are indicated by the presence of *n*-C_{17} (cf. Blumer *et al.*, 1971; Giger *et al.*, 1980; Cranwell *et al.*, 1987). Long-chain *n*-alkanoic acids, such as C_{24}, C_{26}, and C_{28}, are major components of the waxy coatings on land-plant leaves, flowers, and pollen (e.g. Rieley *et al.*, 1991a). Shorter-chain C_{12}, C_{14}, and C_{16} *n*-acids are produced by all plants, but are the dominant lipid components of algae (e.g. Cranwell *et al.*, 1987).

Studies of settling particles intercepted by sediment traps in lakes show that the geolipid fraction experiences substantial degradative alteration during sinking. The relative contributions of alkanoic acids and of alkanols become smaller in particles collected at progressively deeper depths in Lake Michigan (Meyers *et al.*, 1980, 1984). Moreover, the *n*-C_{16} and *n*-C_{18} acids and alcohols from algal material become less dominant, whereas the even-chain C_{24}–C_{30} components from the waxy coatings of land plants become proportionally more important. Fatty acid decomposition rates show that *n*-C_{16} degrades *ca.* 10 times faster than *n*-C_{30} during sinking (Meyers and Eadie, 1993). Similar selective loss of short-chain biomarkers was found by Kawamura *et al.* (1987), who found that the proportion of the C_{17} *n*-alkane algal biomarker was lower in surficial sediments from Lake Haruna, Japan, than in sediment trap material. Aquatic lipid matter is evidently preferentially degraded during the sinking of particulate material, partially because of the relative freshness of this material. In contrast, land-derived organic matter has been microbially reworked before arrival in the lake, and only its most durable lipid components survive to become part of the sedimentary record.

Continued alteration of initial biomarker components is particularly active in surficial sediments. Canuel and Martens (1993) found that microbial degradation of organic matter can significantly alter the source signature of many lipid biomarkers in as little as a year in the coastal marine sediments of Cape Lookout Bight, North Carolina. The distributions of fatty acids, *n*-alkanes, and sterols were dominated by algal components in sediments that accumulated in the spring, but the distributions changed to microbial dominance during summer months. Vascular plant contributions from coastal marshes were evident in this coastal system, but they were not major. Lipids from algae, and probably seagrasses, were evidently converted into microbial biomass and lipid components. The newly synthesized microbial biomarkers were combined with intact and partially altered primary biomarkers to form a complicated geolipid source record of sedimentary organic matter deposition.

Comparison of the geolipid contents of surficial sediments of four lakes of differing productivities further illustrates the interplay of production and preservation in affecting the resulting sedimentary record. The *n*-alkane distributions in sediments from oligotrophic lakes Motosu and Biwa, Japan, are dominated by the C_{29}, C_{31}, and C_{33} components diagnostic of land-plant waxes (Fig. 11). The *n*-alkanol distributions from these two low-productivity lakes similarly contain dominant-to-large proportions of long-chain, plant-wax components (Kawamura and Ishiwatari, 1985. The chain-length distributions of the *n*-alkanoic acid fractions, however, are markedly different. The dominant C_{16} *n*-alkanoic acid in these distributions is ubiquitous in the biosphere; it can be found in land plants, in aquatic algae, and in bacteria and other microbes. Its dominance in these sediments, where both the *n*-alkanes and the *n*-alkanols record major contributions of land-plant lipids, indicates that microbial utilization and resynthesis of the more-reactive fatty acids have occurred. The sediment from eutrophic Lake Suwa contains a notable amount of the C_{17} *n*-alkane diagnostic of algal production, and the *n*-alkanol and *n*-alkanoic acid fractions are dominated by C_{16} components. The relatively small contributions of the more readily preserved long-chain acids and alcohols indicate that initial contributions of land-plant lipids to Lake Suwa are small compared to the algal contributions.

The factors that produce the differences in geolipid contents of surface sediments of the four Japanese lakes can be applied to exploring past variations in delivery of organic matter in sedimentary records. The historical changes in the Lake Ontario environment that produced the change in productivity evident in the $\delta^{13}C$ record (Fig. 6) provide an example of how *n*-alkane and *n*-alkanoic acid distributions can be affected. Organic carbon concentrations in sediments increased as phytoplankton productivity responded to nutrient enrichments in Lake Ontario (Schelske *et al.*, 1988). Organic carbon levels in sediments increased gradually until about 1950, when a marked increase in both aquatic productivity and the rate of carbon accumulation occurred because of postwar growth of urban and suburban areas, which greatly enhanced nutrient delivery to the Great Lakes (Schelske *et al.*, 1983).

Bourbonniere and Meyers (1996) show that sedimentary geolipid contents were impacted by the changes in the Lake Ontario environment. They

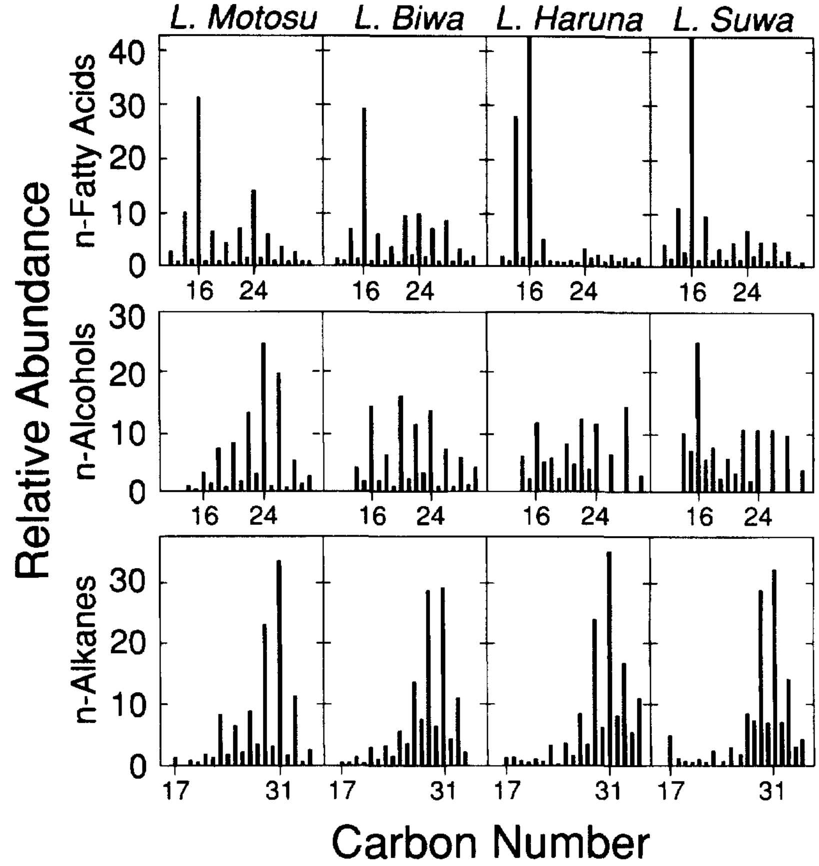

Fig. 11. Chain-length distributions of *n*-alkanes, *n*-alkanols, and *n*-alkanoic acids in surficial sediments from four Japanese lakes. Proportions of the components in each lipid fraction are given as percentage of the total fraction. Long chain-length components originate from land plants, whereas short components are produced by aquatic organisms. The productivities of the lakes increase progressively from oligotrophic Lake Motosu to eutrophic Lake Suwa, and the relative proportions of long-to-short components decrease as lake productivities increase. Data are from Kawamura and Ishiwatari (1985).

employed a ratio of *n*-alkane source indicators to identify changes in the terrigenous/aquatic mixture of hydrocarbons. The ratios of terrigenous-to-aquatic *n*-alkanes were estimated as:

$$\text{terrigenous/aquatic ratio } (\mathrm{TAR_{HC}}) = (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19}).$$

Higher values for this parameter indicate increased watershed sources of lipid matter relative to aquatic sources.

The $\mathrm{TAR_{HC}}$ is generally larger than one and quite variable in Lake Ontario sediments deposited since the beginning of the 1900s, but it is smaller and less variable deeper in the sedimentary record (Fig. 12). Contributions of land-derived organic matter typically contain higher proportions of *n*-alkanes than do those from aquatic algae, and consequently parameters like the $\mathrm{TAR_{HC}}$ may over-represent the absolute amounts from terrigenous sources (cf. Cranwell *et al.*, 1987; Goossens *et al.*, 1989; Meyers and Ishiwatari, 1993). This ratio nonetheless is valuable for determining changes in relative contributions of organic matter from land and lake flora. The twentieth century sediments record progressively larger pulses of land-derived hydrocarbon delivery to Lake Ontario. This pattern reflects the increasingly urbanized character of the watershed, which has accelerated land runoff from paved roadways and from domestic wastewaters.

Bourbonniere and Meyers (1996) also used a ratio of *n*-alkanoic acid source indicators to identify changes in the terrigenous/aquatic mixture of fatty acids:

$$\text{terrigenous/aquatic acid ratio}(\mathrm{TAR_{FA}}) = (C_{24} + C_{26} + C_{28})/(C_{12} + C_{14} + C_{16}).$$

Higher values for this parameter may indicate increased watershed sources of lipid matter relative to aquatic sources, but they may also indicate preferential degradation of aquatic fatty acids relative to land-derived components. An increase in $\mathrm{TAR_{FA}}$ values starting at approximately 1940 (Fig. 12) agrees with the pattern of progressive growth in the suburban population of the Lake Ontario watershed, which has accelerated land runoff. However, the $\mathrm{TAR_{FA}}$ profile records greater proportions of

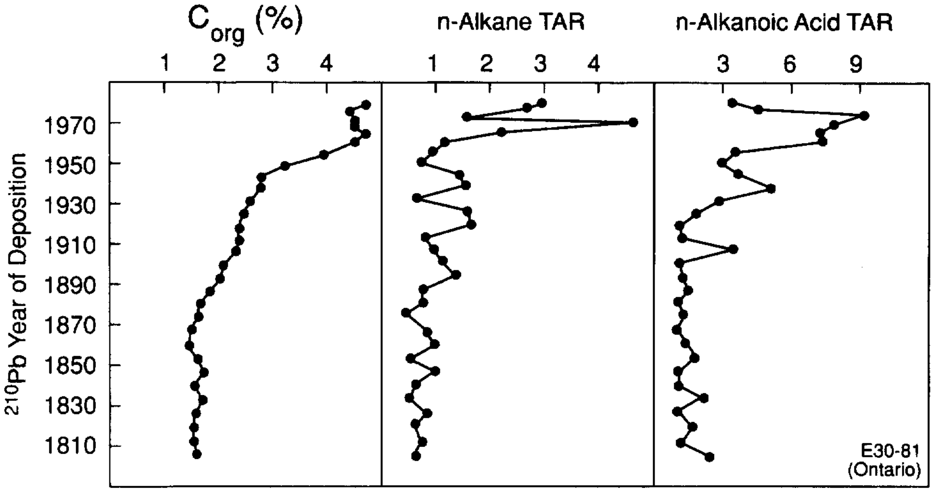

Fig. 12. Record of increasing organic carbon concentrations in sediments from eastern Lake Ontario as nutrient loadings increased. Terrigenous/aquatic geolipid ratios (TAR) are calculated as $(C_{27}+C_{29}+C_{31}) \div (C_{15}+C_{17}+C_{19})$ for *n*-alkanes and $(C_{24}+C_{26}+C_{28}) \div (C_{14}+C_{16}+C_{18})$ for *n*-alkanoic acids. Year of deposition determined by ^{210}Pb dating. From Bourbonniere and Meyers (1996).

land-derived material than is indicated by the TAR_{HC} profile. This difference suggests that the fatty acid source records have been altered by diagenesis, with the result that the Lake Ontario TAR_{FA} values exaggerate the land-plant *n*-alkanoic acid contributions. Diagenesis has evidently modified the *n*-alkanoic acid distributions, which therefore do not record source changes as well as do the *n*-alkanes.

It is important to note that both the *n*-alkane and *n*-alkanoic acid patterns show that terrigenous geolipid contributions have increased more than algal contributions, even though the principal cause for greater organic matter accumulation in the sediments of Lake Ontario has been increased algal production. This apparent paradox illustrates two points. First, geolipids constitute a small fraction of total organic matter, and their origins may not be representative of the dominant material. Second, even biomarker compounds, which are relatively resistant to microbial attack, are subject to diagenetic overprinting that can bias their source information. In the case of Lake Ontario, increased runoff of watershed nutrients, both from soil and from sewage, fueled the increase in algal productivity. The *n*-alkane record appears to reflect this environmental change. The *n*-alkanoic acid record shows the effect of selective loss of its short-chain, algal components in its exaggerated TAR values (Fig. 12).

Sterol biomarkers in sediment records

Sterols and their derivatives are important geochemical biomarker compounds. Molecular structures of some paleoenvironmentally important representatives of this family of tetracyclic alcohols are shown in Fig. 13. The presence or absence of double bonds, of methyl groups at various positions on the carbon framework, the length of the branched sidechain at the C_{17} position, and the stereochemistry of the substituent bonds create a variety of distinctive compounds (e.g. Mackenzie *et al.*, 1982; Brassell *et al.*, 1983; de Leeuw and Baas, 1986; Volkman, 1986).

Sterol compositions have been used to distinguish aquatic contributions of organic matter in sediments from land-derived material. Comparisons of algae and vascular plants from Lake Suwa (Japan) and the area around the lake showed that cholesterol is the dominant algal sterol, whereas 24-ethylcholesterol (β-sitosterol) is the major sterol in emergent water plants and in watershed plants (Nishimura and Koyama, 1977; Nishimura, 1977a). Similarly, Rieley *et al.* (1991a) report that leaf waxes contain C_{28} and C_{29} sterols but lack C_{27} sterols. A ternary plot of the percentages of total C_{27}, C_{28}, and C_{29} sterols in various algae and vascular plants shows that inputs from aquatic and land sources appear to be quite different (Fig. 14). These biomarker relationships were used by Huang and Meinschein (1976) to show that the source of organic matter progressively changed from predominantly land plants to algae in a river-bay-ocean transect of sediments in Baffin Bay, Texas. The sterol patterns were also applied by Nishimura (1977b) to infer that the sediments of alpine, oligotrophic Lake Shirakome-ike contain mostly land-derived organic matter. Sterol compositions, however, must be used as source indicators cautiously. Volkman (1986) has noted that the large number of uncharacterized potential sources of sterols in most oceanic and lacustrine environments could make it difficult to assign origins to even some of the major sterols present in sedimentary records.

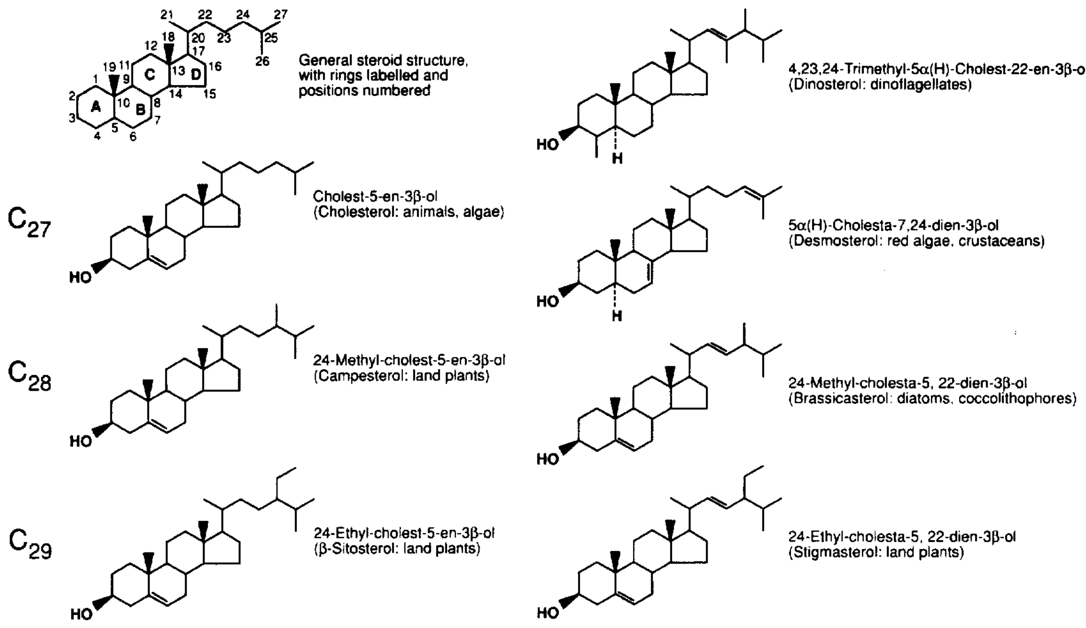

Fig. 13. Representative sterol compounds that have been used as source indicators in sedimentary records of lakes and oceans. C_{27} compounds (e.g. cholesterol) are major contributors to the sterol compositions of aquatic plants, whereas C_{29} compounds (e.g. sitosterols) constitute most of the sterols of land plants. C_{28} compounds derive from both aquatic and land plants. Some sterols have more specific sources. Dinosterol and other 4-methylsterols, for example, indicate dinoflagellate production.

Sterol compositions can nonetheless be employed to infer paleoenvironmental changes that have impacted the sources of these biomarker compounds in sediments deposited at different times. In a study of sediments of Lake Leman, Switzerland, Mermoud *et al.* (1985) noted that epicholestanol [5α(H)-cholestan-3α-ol] is present in surficial sections of a core from the anoxic, deep part of this lake but absent from oxygenated sediments in other parts of the lake and in older parts of the core. They concluded that modern eutrophication of the lake has created seasonal anoxia in the hypolimnion and has enabled anaerobic microbes to produce this uncommon C_{27} sterol. A paleoenvironmentally related change in sterol source has also been reported for Motte Lake, France. Sediments throughout a 6-m core contain gorgostanol, believed to be derived from microbial reduction of gorgosterol (22,23-methylene-23,24-dimethyl-cholest-5-en-3β-ol), which is probably produced by the dinoflagellate phytoplankton abundant in this lake (Wünsche *et al.*, 1987). The deepest core sections contain aplystanol [24,26-dimethyl-5α(H)-cholestan-3β-ol], for which a freshwater source organism is not known. The absence of aplystanol in the younger sediments suggests that the unknown freshwater organism that synthesized the precursor compound no longer populates Motte Lake.

Organic geochemical paleothermometry

Determination of paleotemperatures is an important element of paleoceanographic and paleoclimatic studies. Records of sea-surface temperatures, in particular, provide information about changes in ocean currents, intensity of upwelling, and stratification of the surface ocean, all of which are influenced by past climates. Sea-surface temperatures have been traditionally estimated from the microfossil contents of sediments and their $CaCO_3$ oxygen isotope compositions. Carbonate $\delta^{18}O$ values vary with the temperature of the environment, the types of carbonate-secreting plankton, and the $^{18}O/^{16}O$ ratio of sea-water. Because the volume and isotopic composition of seawater respond strongly to changes in the volume of isotopically light continental ice, almost two-thirds of the glacial–interglacial $\delta^{18}O$ change is attributed to changes in volume of polar ice caps. Furthermore, changes in planktonic assemblages almost always accompany environmental changes and consequently add uncertainty to $\delta^{18}O$-based temperature estimates. Because of these complications, and the fact that $CaCO_3$ microfossils tend to dissolve in deep-sea sediments and create gaps in paleotemperature records, paleoceanographers have sought an indicator of past sea-surface temperatures that is independent of the ice-volume effect and of carbonate preservation.

The biochemical requirement for organisms that can inhabit a range of thermal conditions to maintain a constant fluidity of their cell membranes has provided several organic geochemical answers to the search for novel ways to determine paleotemperatures (e.g. Brassell, 1993). Most of the organic geochemical paleotemperature proxies are based on

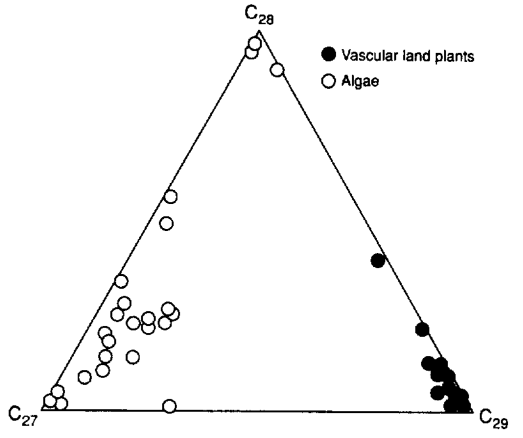

Fig. 14. C_{27}, C_{28}, and C_{29} sterol source characteristics. Data compiled from Orcutt and Patterson (1975), Gaskell and Eglinton (1976), Huang and Meinschein (1979), Nishimura (1977b), Nishimura and Koyama (1977), Lee *et al.* (1980), Marlowe *et al.* (1984), Volkman *et al.* (1981) and Volkman (1986).

the general chemical property that the melting points of related organic molecules are inversely related to the number of their carbon–carbon double bonds. For example, the melting points of fatty acids become lower as the number of double bonds increases, with the result that fish that live in cooler waters have a larger proportion of polyunsaturated fatty acids in their total lipid contents than fish that live in warm waters (e.g. Farkas and Csengeri, 1976). The lipid compositions of fish, however, often represent the sum of environments between which the fish migrate, and they are partially affected by diet. For a biochemically based paleotemperature proxy to be useful for paleoceanographic reconstructions, it should be derived from an organism that represents a known environment and that is relatively unaffected by foodchain dynamics.

Long-chain alkenones (n-C_{37}–C_{39}) and alkyl alkenoates (n-C_{37}–C_{38}) derived from Haptophycean algae are found in marine sediments and seem to satisfy many of the requirements to be useful paleotemperature proxies. These biomarker compounds occur widely in marine locations, and they evidently resist diagenetic destruction in sediments as old as Eocene (Marlowe *et al.*, 1984, 1990). The principal producers of these suites of molecules are coccolithophoroid algae of the family Gephrocapsaceae (formerly Prymnesiophyceae). Alkenones and alkyl alkenoates are particularly abundant in *Emiliania huxleyi*, a coccolith that becomes even more paleoceanographically important because it has ubiquitously populated near-surface oceanic waters since the mid-Pleistocene. The number of double bonds in the distributions of methyl and ethyl alkenones of *E. huxleyi* varies between one and four, and the proportion of double bonds increases as water temperatures decrease. An expression was developed and then improved by simplification (Brassell *et al.*, 1986; Prahl and Wakeham, 1987) to express the degree of alkenone unsaturation

$$U^{k'}_{37} = [C_{37:2}] \div \{[C_{37:2}] + [C_{37:3}]\}$$

in which the concentrations of only the $C_{37:2}$ and $C_{37:3}$ methyl alkenones are used, because they are the most abundant, temperature-sensitive molecules. The $U^{k'}_{37}$ value that is obtained from sediment samples is used to estimate paleotemperatures by the empirical expression

$$\text{sea} - \text{surface temperature} = (U^{k'}_{37} - 0.039) \div 0.034$$

that is based on laboratory cultures of *E. huxleyi* that have been grown over a range of temperatures. This paleotemperature proxy has proven useful in a variety of studies because it can reconstruct past temperatures that are independent of changes in seawater salinity, algal assemblages, ice volumes, and preservation of carbonate microfossils.

A variety of complications nonetheless impose limitations on estimates of former sea-surface temperatures based on the $U^{k'}_{37}$ index. Foremost among these is quantifying the relationship between water temperatures and the degree of alkenone unsaturation. Comparison of $U^{k'}_{37}$ values obtained from different strains of *E. huxleyi* grown in laboratory studies gives the same general temperature-unsaturation relationship, but different calibration curves (Fig. 15). Moreover, comparisons of $U^{k'}_{37}$ values obtained from particulate matter and sediment trap material from different parts of the ocean show differences that are similar to those of the laboratory comparisons (Brassell, 1993). Nutrient availability appears to influence the depth in the photic zone at which the coccoliths live (Ohkouchi *et al.*, 1997), and part of the variability in the $U^{k'}_{37}$ values themselves may arise from nutrient availability (Epstein *et al.*, 1997). Because geographic differences that are not related to temperature exist in the modern ocean, then it is possible that some of the changes in the $U^{k'}_{37}$ values in sedimentary records may similarly be related to environmental factors other than temperature. Moreover, the calibrations used to estimate paleotemperatures are by necessity based on laboratory cultures of modern algae. Because the first appearance of *E. huxleyi* was *ca.* 265 kyr during Oxygen Isotope Stage 8 (Thierstein *et al.*, 1977), a limit is imposed on how far back in time the temperature-unsaturation relationship can be validly quantified. Finally, algal blooms typically occur over a few weeks of the annual cycle. Paleotemperatures inferred from $U^{k'}_{37}$ values are not likely to represent the average winter or summer sea-surface temperatures that are important to paleoclimate modeling.

Carbon–carbon double bonds are generally considered to be relatively sensitive to diagenetic

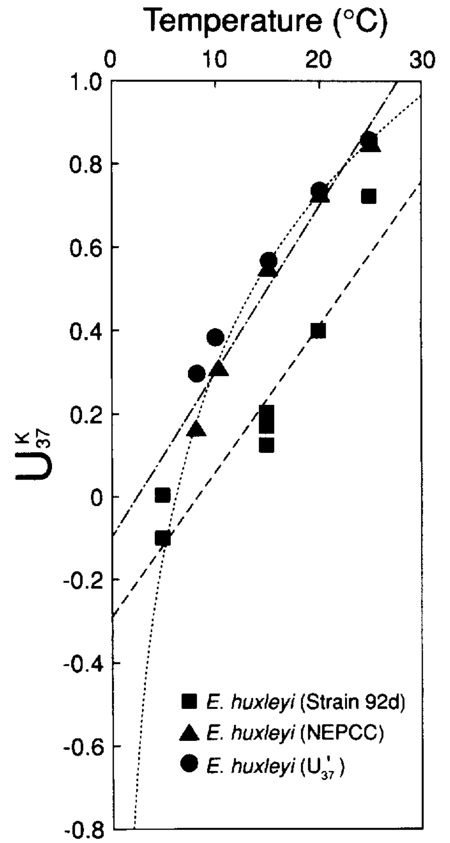

Fig. 15. Calibration curves that show the similar but different relationships between sea-surface temperature and alkenone $U^{k'}_{37}$ indices obtained from laboratory cultures of three strains of *Emiliania huxleyi*. From Brassell (1993).

attack, raising the question of how well the alkenones resist diagenetic alteration. It is easy to imagine that the more unsaturated molecules could be preferentially degraded, thereby biasing $U^{k'}_{37}$ values and leading to sea-surface temperature estimates that are systematically too high. The length of the alkenone carbon chain imparts some diagenetic resistance to these molecules, however, and the existence of alkenones in Eocene sediments (Marlowe *et al.*, 1984) indicates that they can indeed be long-lived. Evidence of the potential biasing of paleotemperature records has not been found so far (Brassell, 1993). Conte *et al.* (1992) have compared sea-surface temperatures with the distributions of two types of temperature-sensitive biomarkers, the alkenones and the alkyl alkenoates, in sediment traps and ocean surface sediments in the North Atlantic Ocean. The alkyl alkenoates appear to resist diagenesis better than the alkenones and therefore give improved temperature information, but the alkenones also appear to retain reliable evidence of water temperatures. The prospect of using multiple proxies to infer the paleotemperature record of a single environment is an attractive outgrowth of this kind of comparative study.

Because alkenones are distinctive biomarkers of coccolithophores, their abundance in sedimentary records can be used as an indicator of the paleoproduction of these algae. Prahl *et al.* (1989) found that alkenone concentrations at MANOP Site C in the Equatorial Pacific Ocean are five-fold higher in sediments deposited at the last glacial maximum than in post-glacial sediments (Fig. 16). The evidence of elevated coccolith production is accompanied by similar increases in dinosterol and total $C_{27}+C_{28}$ 4-methylstanols, all of which are dinoflagellate biomarkers. Glacial-age sea-surface temperatures, calculated from $U^{k'}_{37}$ values, are about 1°C lower (Fig. 16) and indicate that upwelling was probably responsible for the period of increased productivity. The evidence of upwelling, in turn, is an indicator of formerly stronger winds during the last glacial maximum at this open-ocean location.

Alkenones also exist in some lacustrine sediments. Algal assemblages in brackish and salt-water lakes evidently include Haptophycean species similar to the marine species that produce long-chain unsaturated ketones, and these temperature-sensitive biomarkers have been found in the sediments of salty lakes. Alkenones have also been detected in the sediments of some freshwater lakes. For example, Cranwell (1985) reported the presence of C_{37} to C_{39} unsaturated methyl and ethyl ketones in the sediments of three English lakes but their absence in those of three others, and Volkman *et al.* (1988) found alkenones in the sediments of a freshwater lake in Antarctica. Although the specific source of these freshwater ketones has not been identified, it may also be algae that are similar to the marine source. The presence or absence of the ketones in the English lake sediments suggests that algal populations differed in the lakes, possibly in response to

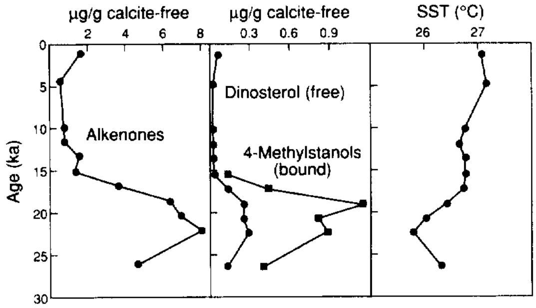

Fig. 16. Sedimentary record of glacial–postglacial changes in algal productivity and sea-surface temperatures at MANOP Site C (1°N, 139°W) in the Equatorial Pacific Ocean. Concentrations of total $(C_{37}+C_{38}+C_{39})$ alkenones are a proxy for coccolithophore production. Concentrations of dinosterol and total $C_{28}+C_{29}$ 4-methylstanols are proxies for dinoflagellate production. Biomarker concentrations are expressed on a calcite-free basis to adjust for variable amounts of carbonate preservation. Sea-surface temperatures are estimated from U^{k}_{37} indices. From Prahl *et al.* (1989).

different environmental conditions. The existence of alkenones in the various lake settings offers the tantalizing possibility of estimating local paleotemperatures and thereby improving paleoclimate reconstructions in continental settings. However, the brackish and freshwater algae that produce these important biomarker compounds remain to be identified so that calibrated lacustrine paleotemperature records can be created from the sedimentary alkenone records.

Paleoenvironmental information from pigment contents of sediments

Higher plants and algae synthesize a variety of pigmented organic compounds, principally for use in photosynthesis. Some of these molecules are biomarkers specific to various types of plants (Table 3), and their preservation in sedimentary records therefore provides evidence of the biota of former times, which in turn are evidence of paleoenvironmental conditions. Pigments contain chromophore groups, typically conjugated C=C bonds, which absorb portions of the visible solar spectrum and give the molecules their characteristic colors. In addition, many of the pigments have oxygen-containing functional groups (Fig. 17). The double bonds and functional groups provide sites for microbial attack, making these compounds especially sensitive to diagenetic alterations. Despite this liability, a portion of the pigment input to oceans and lakes can become stabilized by diagenetic alterations. The major types of stabilizing alterations are complete aromatization of the chlorophyll tetrapyrrole ring to lead to porphyrins and hydrogenation of carotenoid carbon–carbon double bonds to form isoprenoid alkanes. These stabilized products of diagenesis are found in ancient sediments, not in young sediments, because the transformations proceed slowly.

The principal photosynthetic pigments used by plants are the chlorophylls, of which chlorophyll *a* (Fig. 17) is the most common. The various chlorophylls differ principally in the alkyl sidechains attached to the central tetrapyrrole ring. The most significant sidechain of chlorophyll *a* is the ester-linked diterpenoid alcohol, phytol. Chlorophylls absorb solar energy most efficiently in the red portion of the visible spectrum, which are wavelengths that do not penetrate deeply into water. For this reason, aquatic plants have evolved different carotenoid compounds that they utilize as accessory pigments to broaden the range of wavelengths useful for photosynthesis (Table 3). Many of the accessory pigments are characteristic of different algae and can be used to help identify past sources of organic matter in lake sedimentary records.

Table 3. Selected pigments indicative of different types of plants (compiled from Schwendinger, 1969; Züllig, 1981, and Leavitt *et al.*, 1989). The chlorophylls are the primary pigments involved in photosynthesis and capture mostly red wavelengths of light. The other, accessory pigments expand energy capture to additional wavelengths

Pigment	Taxa
chlorophyll *a*	Plantae
chlorophyll *b*	Tracheophyta, Chlorophyta, Euglenophyta
chlorophyll *c*	Chrysophyta, Pyrrophyta
alloxanthin	Cryptophyta
fucoxanthin	Chrysophyta
lutein	Chlorophyta, Charophyta, Euglenophyta
peridinin	Pyrrophyta
β-carotene	Plantae
myxoxanthophyll	Cyanophyta
canthaxanthin	Cyanophyta
oscillaxanthin	Cyanophyta

Both source changes and the effects of diagenesis affect the amounts and types of pigments present in sediments. Sanger (1988) and Leavitt (1993) have reviewed the factors important to the accumulation of pigments in lacustrine sediments and note that these organic compounds are seldom preserved intact. In general, preservation is improved in lakes having higher aquatic productivities, with the result that the sedimented organic matter contains greater proportions of pigments (e.g. Gorham *et al.*, 1974; Gorham and Sanger, 1976). Land-derived pigments do not typically survive transport to lakes. Even algal-derived pigments are rapidly degraded if they do not quickly become incorporated into sediments. Carpenter *et al.* (1986) found that photodegradation

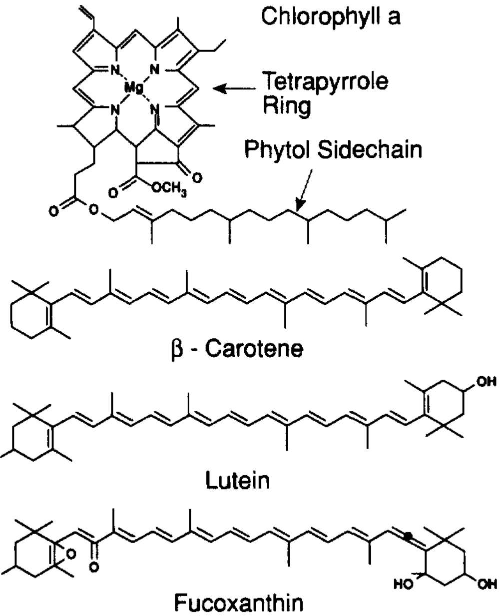

Fig. 17. Molecular structures of representative types of pigments found in lake sediments. Chlorophyll *a* is the dominant chlorophyll, which are the primary photosynthetic pigments and are present in all photosynthetic plants. The carotenes and xanthophylls are secondary pigments and are present in different amounts in different plants, thereby becoming indicators of plant types (Table 3).

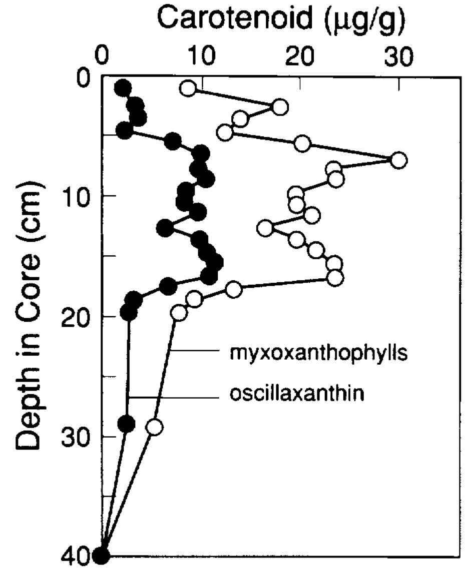

Fig. 18. Concentrations of two carotenoid pigments characteristic of blue-green algae found in sediments of Esthwaite Water, England, by Griffiths (1978). Bottom of core corresponds to *ca.* 1885. Progressive eutrophication and then remediation of this lake is indicated by the increases of these pigments in younger sediments and following decreases in modern sediments.

of chlorophyll derivatives was virtually complete after only 3 days in the photic zones of lakes. Increased grazing by zooplankton, which leads to more rapid sedimentation, appears to be the major factor in enhancing preservation of pigments and their derivatives in sediments (e.g. Leavitt *et al.*, 1989). After incorporation in sediments, pigments continue to undergo diagenesis. Keely and Brereton (1986) documented the progressive conversion of chlorophylls *a* and *b* into pheophytins *a* and *b* in a core representing a 100-yr accumulation of sediment in Priest Pot, England. The dominance of pheophytins, the de-metallized versions of chlorophylls, rather than pheophorbides, in which both magnesium and ester sidechains are lost, probably results from the absence of abundant grazing zooplankton in this eutrophic lake, inasmuch as cleavage of this ester linkage typically occurs in marine foodchains (Blumer *et al.*, 1971), in which these animals are prominent.

The reactivity of pigments makes them sensitive indicators of changes in aquatic environments. For example, the diagenetic conversion of chlorophyll to pheophytin is enhanced by acid conditions. This property has been employed by Guilizzoni *et al.* (1992) to reconstruct the progressive acidification of lakes in the Central Alps. The ratio of chlorophyll to pheophytin is depressed in modern sediments, but increases in older sediments. This pattern is opposite to what would be produced by diagenesis alone and instead records the onset and increase in acid precipitation in Europe over the past half century.

Changes in past algal populations evidently can be recorded in the pigment compositions of sediments. Progressive eutrophication of Esthwaite Water in the English Lake District is documented by increases in sediment concentrations of the carotenoid pigments characteristic of cyanophytes (Fig. 18). Diminished concentrations in the uppermost, most eutrophic sediments appear to result from replacement of cyanophytes by other algae (Griffiths, 1978). This decrease may possibly be due to a preservational effect, but the younger sediments, rather than the older, would be expected to display enhanced preservation. A related history of the development of eutrophication in Zürichsee, Switzerland, is evident in the pigment contents of a century-long core of sediment (Züllig, 1981). In this case, ten different pigment groups were used to identify changes in algal populations as lake conditions changed. Although their multiple double bonds make them reactive compounds, pigments can be sufficiently preserved in sediments to record paleoenvironmental conditions extending back thousands and even millions of years. For example, pigments in the sediments of Kirchner Bog, Minnesota, contain a history of postglacial plant succession spanning nearly 14 kyr (Sanger and Gorham, 1972). As another example, Kimble *et al.* (1974) found that the major extractable tetraterpane in the Eocene Green River shale is perhydro-β-carotene. This hydrocarbon is derived from the important algal accessory pigment β-carotene (Table 3); its dominance indicates that algal photosynthesis was evidently the primary source of organic matter to the Green River paleolimnologic system.

Source information from lignin derivatives

Lignins are phenolic polymers synthesized by higher plants as part of their vascular systems. Nearly all vascular plants grow on land, and therefore this organic matter fraction of sediments largely records the contributions and diagenetic alterations of land-derived organic matter. The proportion of continental organic matter in coastal marine sediments can be estimated from the fraction of lignin that is present. Because gymnosperms (nonflowering plants) and angiosperms (flowering plants) synthesize distinctive types of lignin, past changes in watershed vegetation can be inferred from the lignin contents of lake sediments. Moreover, lignin is relatively resistant to diagenesis, making its sedimentary record longer-lived than many other forms of primary organic matter.

Characterization of lignin in sediments typically involves oxidative depolymerization to release various phenolic aldehyde, ketone, and acid monomers like those illustrated in Fig. 19. Monomers have been grouped by Hedges and Mann (1979) to ident-

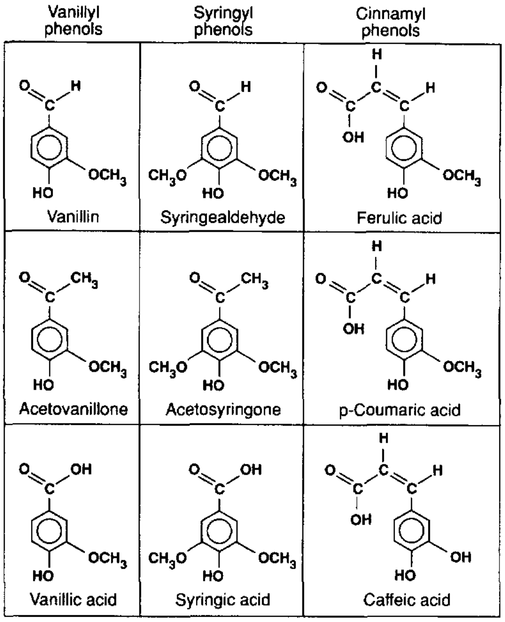

Fig. 19. Molecular structures of phenolic compounds obtained from the oxidative depolymerization of lignins. Caffeic acid is a minor product compared to the other eight compounds.

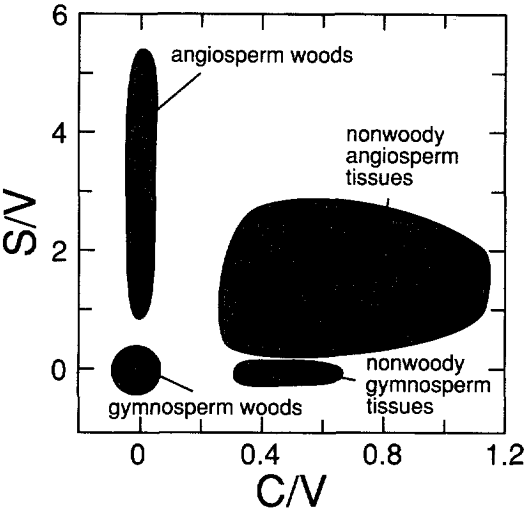

Fig. 20. Lignin parameters S/V *vs* C/V with their general source assignments indicated. Data adapted from Hedges and Mann (1979).

ify the general vascular plant sources of sedimentary lignins (Fig. 20). A measure of the relative contributions of woody and non-woody land-plant tissues is given by the C/V ratio, which is the sum of *p*-coumaric acid plus ferulic acid concentrations divided by the sum of the three vanillyl phenols. Gymnosperm sources of land-plant residues are distinguished from angiosperm sources by the S/V ratio, which is the sum of the amounts of the three syringyl phenols divided by the sum of the vanillyl phenols. Oxidative diagenesis of lignin components can be inferred from an increase in the total acid phenols relative to the total aldehyde phenols, expressed as the Ad/Al ratio (Hedges *et al.*, 1982; Ertel and Hedges, 1985).

Pollen and lignin compositions that provide independent paleoclimate records from the 14-kyr postglacial succession in watershed plants have been compared in an 11-m-long core from northern Lake Washington (Leopold *et al.*, 1982; Hedges *et al.*, 1982). Pollen compositions indicate that an early pine-dominated forest was replaced approximately 10 ka by an alder and fern-bracken mixture. Since approximately 7 ka, the dominance of western red cedar pollen records a cooler, more moist climate. A potential problem with pollen paleoclimate reconstructions is that pollen can be easily transported by winds from distant areas. Lignin residues are contained in water-carried plant debris, and they consequently give a better record of local, rather than distant, types of vegetation.

The watershed succession interpreted from the lignin components of Lake Washington sediments generally agrees with the pollen reconstruction, except for the early interval dominated by pine. A sequence of four watershed types is indicated by compositional changes within the lignin-derived phenols. In the basal meter of the core, low S/V and C/V ratios result from an approximately equal mixture of woody and nonwoody gymnosperm (conifers and ferns) plant tissues (Hedges *et al.*, 1982). Low concentrations of total lignin-derived phenols relative to organic carbon indicate that small inputs of land-plant organic matter occurred at this time. In contrast, C/N values are between 11 and 15 here and throughout the core and suggest an approximately equal mixture of land and algal material, but these elemental ratios are less specific than the lignin parameters. Between 10 m and 8 m in the core, high S/V and C/V ratios record a predominance of nonwoody angiosperm tissues, probably originating from marsh or grassland sources typical of a tundra ecosystem. The lignin plant reconstruction in this interval contradicts the pollen data, leading Leopold *et al.* (1982) to conclude that the pine pollen dominance is an artifact resulting from eolian transport from regions outside the watershed. High S/V and low C/V ratios from 7 m to 4 m suggest large contributions of angiosperm wood, a conclusion that is consistent with the abundance of alder pollen, indicative of a boreal biome. The decrease in the S/V ratio while the C/V ratio holds constant between 4 m to the core top indicates a gradual replacement of deciduous trees by conifers. This interpretation of attainment of present-day climate conditions agrees with the pollen reconstruction.

Paleoenvironmental information from compound-specific carbon isotope analyses

Carbon isotope analyses of individual biomarker compounds provide a powerful source of paleoenvironmental information. This analytical combination offers ways to explore the origins of organic matter, the effects of diagenesis, and the types of depositional settings that neither bulk organic matter characterizations nor traditional biomarker analyses can individually provide. The advantages arise partly because different organisms that synthesize the same biomarker will often fractionate carbon isotopes differently, thereby adding source specificity, and partly because the $\delta^{13}C$ values of individual molecules are not affected by diagenesis as long as the carbon skeleton remains intact, thereby preserving source specificity.

Nearly all vascular land plants synthesize long-chain *n*-alkanes for use as waxy coatings. Application of *n*-alkane distributions to deciphering the changes in continental climates that would modify the types of land plants has therefore been blunted by this kind of non-specificity of hydrocarbon biomarker synthesis. Plants that use different carbon-fixing pathways, however, produce *n*-alkanes that have different carbon isotopic signatures (Table 4). The lipid products, as well as the bulk organic matter, of the leaves of C_3, C_4, and CAM plants clearly have different $\delta^{13}C$ values. The distinction between the isotopic compositions of *n*-alkanes from land-plants using different metabolic pathways has been used by Bird *et al.* (1995) to trace the history of changes in the amounts of C_3 and C_4 plants in the watershed of the Johnstone River, North Queensland, Australia. Clearing of forests for sugarcane production and pastures is recorded in a +3‰ shift in the $\delta^{13}C$ values of river sediments deposited since the late 1800s. A smaller shift of +1‰ that occurs in sediments deposited *ca.* 6000 years ago may record either a transition to dryer climate or the onset of aboriginal slash-and-burn agriculture.

The differences in lipid isotopic compositions evident in the comparison of land plants have been useful in identifying the origins of organic matter to sediments, even where C_3 plants have remained dominant. Rieley *et al.* (1991b) compared the $\delta^{13}C$ values of individual *n*-C_{25} to *n*-C_{29} hydrocarbons extracted from sediments of Ellesmere Lake, England, to those from the leaves of trees near the lake. Their analyses have shown that willow leaves appear to be the major source of the sedimentary *n*-alkanes.

Compound-specific carbon isotopic analyses can also be useful in ancient paleoenvironmental reconstructions. For example, Schoell *et al.* (1994) interpret an increase in the difference between the carbon isotopic compositions of algal and microbial biomarker molecules to reflect Miocene strengthening of upwelling offshore of California. The $\delta^{13}C$ values of C_{27} steranes derived from phytoplankton in the upper photic zone hold nearly constant at −25.4‰ in sediments deposited from the Early Miocene to the Late Miocene, a value very close to the −26.4‰ of modern C_{27} sterols from this region. In contrast, the $\delta^{13}C$ values of C_{35} hopanes derived from bacterial plankton living at the base of the photic zone decrease from −25‰ in the Early Miocene to −30.5‰ in the Middle Miocene, recording the onset of upwelling of cold, CO_2-rich water. The difference in the patterns of the two types of biomarker isotopic signatures indicates a change from a well-mixed to a highly stratified photic zone along the California Margin and development of the productive paleoenvironmental conditions that led to deposition of the organic-carbon-rich Monterey Formation.

PALEOENVIRONMENTAL RECONSTRUCTIONS

The amounts and types of organic matter in sedimentary records provide integrated histories of past life, paleoenvironmental conditions, and paleoclimatic changes. Organic geochemical investigations have been done in which combinations of the ana-

Table 4. Carbon isotopic compositions of representative C_{31} *n*-alkane biomarkers produced by land plants using C_3, C_4, and CAM carbon-fixing pathways. The magnitude of isotopic fractionation between bulk $\delta^{13}C$ values and the $\delta^{13}C$ values of various lipid components differ among plants using the different pathways

Plant	CO_2-fixing metabolism	Total $\delta^{13}C$ (‰)	Wax $\delta^{13}C$ (‰)	Alkane $\delta^{13}C$ (‰)	*n*-C_{31} $\delta^{13}C$ (‰)
Quercus turneri	C_3	−28.8	—	−33.2	−35.7
Quercus rober	C_3	−30.5	—	−35.8	−36.9
Acer campestre	C_3	−30.4	—	−34.7	−35.0
Magnolia delabayi	C_3	−28.7	—	−33.8	−34.3
Cyprus alternifolius	C_3	−27.6	−32.2	−35.1	−35.3
Saccharum officinarum	C_4	−10.7	−18.4	−24.5	−23.4
Miscanthuys sacchariflorum	C_4	−11.9	−19.2	−18.5	−18.4
Zea mays	C_4	−11.2	−18.9	−20.5	−20.5
Selenecereus grandiflorus	CAM	−13.0	−22.1	−26.8	−26.4
Tillandsia usneoides	CAM	−14.9	−22.5	−25.2	−29.2
Aechmeade albata	CAM	−16.2	−24.2	−25.2	−25.2

From Collister *et al.* (1994).

lytical approaches described in this paper have been applied to a single record. A sampling of lacustrine and marine studies is provided here. The examples illustrate the organic geochemical records of first Holocene climate changes, then Pleistocene–Holocene glacial–interglacial changes, and finally Cenozoic and Mesozoic paleoceanographic changes.

Paleoprecipitation record from Austin Lake, Michigan

The hydrogen 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 about 12 ka 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 composition of the lake waters is virtually the same as 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.

The sediments are rich in organic matter, containing up to 20% TOC, and are virtually carbonate-free (Krishnamurthy *et al.*, 1995). Total organic matter C/N ratios remain between 8 and 15 throughout the Holocene (Fig. 21) and indicate 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 higher than those of the total organic matter and are between 14 and 18 for most of the core. The difference between total organic matter and humin C/N ratios is greatest in sediments deposited during the last 2 kyr (Fig. 21). This pattern may reflect climate-induced change in lake biota since that time. Humin H/C ratios are between 0.8 and 0.9 through most of the core, but they reach values greater than 1.0 in the upper section (Fig. 21). This pattern again suggests an alteration in organic matter source but agrees with total C/N ratios that the change was a minor one.

A very large shift in $\delta^{13}C$ values, from −23‰ to −14‰, occurs in both total organic matter and in its humin fraction in the postglacial sedimentary record of Austin Lake (Fig. 21). This pattern is curious, particularly because it implies that land-plant contributions dominate organic matter delivery to this lake and that a shift has occurred from C_3 land-plants at 12 ka to C_4 plants in modern times. Neither implication is valid — C/N ratios of total organic matter show that algal production dominates organic matter delivery, and land-plants since at least 2 ka, and probably before, have been predominantly C_3 plants. The absence of important inflows and outflows in the Austin Lake hydrologic balance may create a situation in which in-lake processes strongly influence the isotopic balances of the lake waters. Over time, preferential removal of ^{12}C by aquatic plants and burial in sediments may shift the dissolved inorganic carbon isotopic balance to one that is not in equilibrium with atmospheric CO_2 and that is enriched in ^{13}C. Organic matter produced by lake plants would therefore have progressively less negative $\delta^{13}C$ values as the lake becomes more isotopically "mature". A similar shift to less negative $\delta^{13}C$ values, from −7‰ to 0‰ in ostracod valves (carbonates), 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). These two examples illustrate potential interpretative pitfalls in using sedimentary $\delta^{13}C$

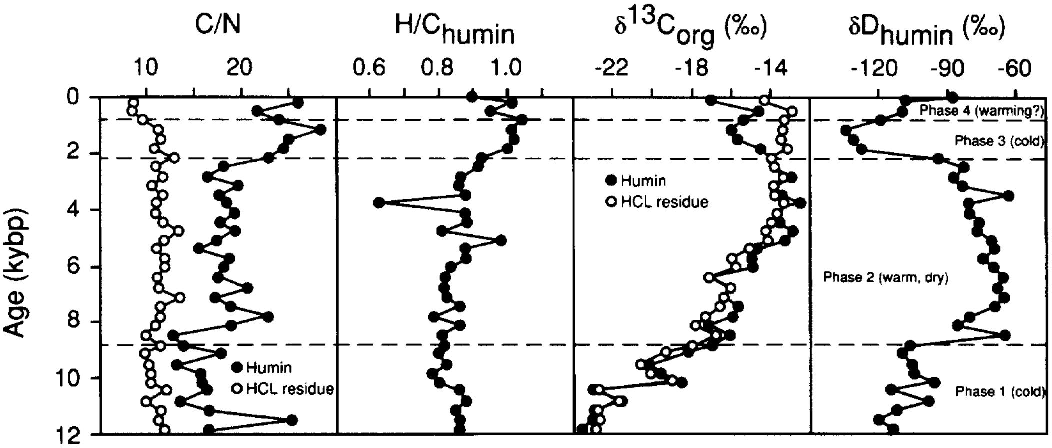

Fig. 21. Record of postglacial climate change in hydrogen isotope contents of organic matter in sediments of Austin Lake, Michigan. Bulk C/N ratios indicate that most of the organic matter is from algal production and therefore humin δD values reflect lake water isotopic composition. Variations in δD 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).

records without having additional evidence of changes in paleoenvironmental histories.

Because the hydrogen contents of aquatic organic matter originate from lake waters, the δD values of lake-derived organic matter can be used as recorders of the hydrologic balance of a lake and also of the sources of meteoric water to a lake. Krishnamurthy *et al.* (1995) employ the δD values of the humin fraction of sediment organic matter to minimize complications from possible downcore diagenetic changes in the composition of the total organic matter. The δD values separate into four time intervals (Fig. 21), which Krishnamurthy *et al.* (1995) interpret to reflect changes in Midwestern climate. Especially prominent among these intervals is the period between 9 ka and 2 ka, during which δD values increase to approximately −75‰ from values that average −110‰ (Fig. 21). This period generally corresponds to a time of aridity that was widespread 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 a warm, dry climate. Another factor that may contribute to the four isotopic intervals is a change 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 $\delta D = -35‰$) 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 other types of sediment records in Lake Ontario (Silliman *et al.*, 1996) and Owasco Lake (Dwyer *et al.*, 1996), both farther to the east in New York State, indicate wetter climates from 9 kyr to 3 kyr. 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.

Record of glacial–postglacial change in organic matter source at DSDP site 619, Gulf of Mexico

Newman *et al.* (1973) inferred from $\delta^{13}C$ differences as great as 6‰ that the origin of organic matter in sediments of the northern Gulf of Mexico changed from terrigenous dominance to marine dominance as a consequence of the sea-level rise that accompanied the Pleistocene–Holocene boundary. DSDP Site 619 was hydraulic-piston-cored in 1983 to obtain an expanded record of this postulated change in delivery of organic matter. This site is located at 2259 m water depth in the Pygmy Basin on the continental shelf of the northern Gulf of Mexico. This oxic basin is a trap for continental and coastal marine sediments. The 209-m core of sediment from this site represents approximately the last 100 000 years of deposition and includes the most recent glacial–interglacial transition.

Concentrations of total organic carbon generally remain between 0.5 and 1.0%, but a significant enhancement is present in sediments deposited between 25 ka and 8 ka, which roughly corresponds to maximum C/N ratios and minimum $\delta^{13}C$ values (Fig. 22). These patterns have been interpreted by Jasper and Gagosian (1990) to represent changes in the proportional contributions of land-derived and algal organic matter that correspond to the isotopic evidence of source change found by Newman *et al.* (1973). During the last glacial sea-level lowstand (25–10 ka), continental organic matter from the Mississippi River evidently dominated accumulation at this location. In contrast, sediments deposited before 90 ka and subsequent to 10 ka contain larger proportions of marine organic matter.

The C/N and carbon isotopic ratios appear to record the organic matter source changes reliably, yet *in situ* degradation of sedimentary organic matter is evident from biomarker analyses (Jasper and Gagosian, 1993). Both sulfate reducing and methanogenic bacteria are active in these sediments. Pore water sulfate diminishes with depth, and this trend is presumably accompanied by organic carbon oxidation. Methane with $\delta^{13}C$ values between −95‰ and −72‰ is present in sediments at depths of 76–178 m and signifies active microbial populations. Jasper and Gagosian (1990) noted that concentrations of organic carbon seem to diminish following a first-order decay. Deeper concentrations are indeed less than those in the upper sediments (Fig. 22), but much of this pattern reflects addition of continental organic matter during the last glacial lowstand to a low background of marine organic matter and probably not postdepositional degradation. The indirect evidence of microbial activity strongly indicates that organic matter is being destroyed deep in the sediments, but probably not at high rates. Fluctuations in organic carbon concentrations appear to record mostly variations in initial deposition rather than variations in diagenetic destruction of organic matter.

Alkenone contents of Site 619 sediments yield several types of paleoceanographic information (Jasper and Gagosian, 1989; Jasper and Hayes, 1990). First, $U^{k'}_{37}$ values indicate that sea-surface temperatures were approximately 6°C lower in glacial Oxygen Isotope Stage 2 than in postglacial Stage 1 or interglacial Stage 5e (Fig. 22). This temperature change is substantially greater than the approximately 2°C derived from $\delta^{18}O$ values of samples of the planktic foram *Globigerinoides sacculifer* from nearby locations in the Gulf of Mexico (Jasper and Gagosian, 1989). The disagreement in the two paleotemperature proxies may result from

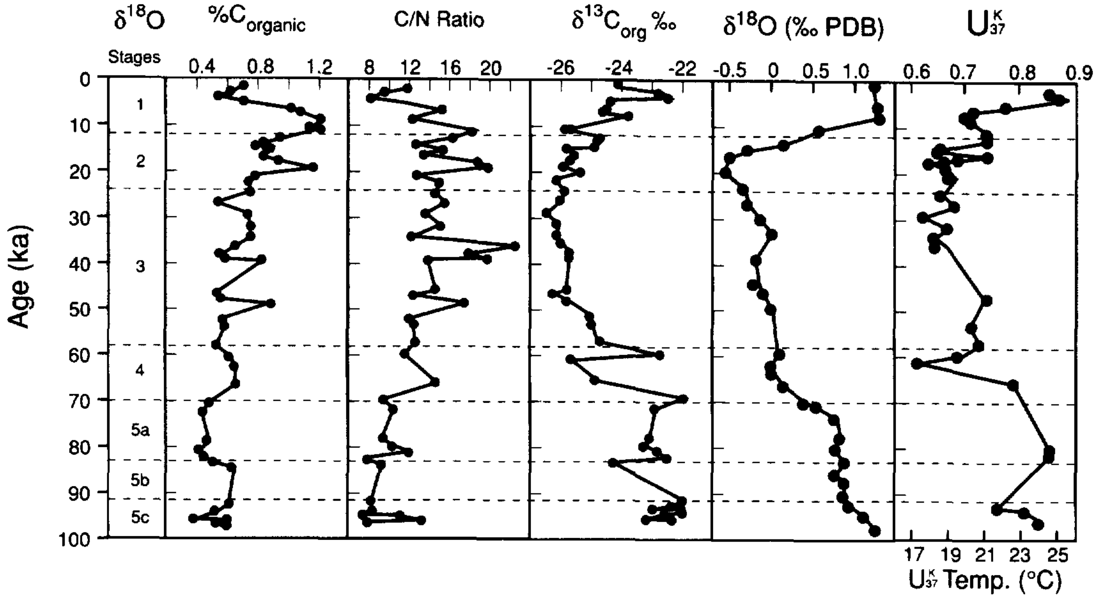

Fig. 22. Glacial–interglacial changes in delivery of organic matter to sediments from DSDP Site 619 in the Pygmy Basin, northern Gulf of Mexico. Lowered sea-level increased delivery of land-derived material to this site during Oxygen Isotope Stages 2 and 3, as evidenced by atomic C/N ratios and $\delta^{13}C$ values. Sea-surface temperatures simultaneously cooled by approximately 6°C according to $U^{k'}_{37}$ values and approximately 2°C according to $\delta^{18}O$ values of the planktic foram *Globigerinoides sacculifer*. Data adapted from Jasper and Gagosian (1989, 1990).

changes in coccolith populations and their alkenone compositions that accompanied the glacial–interglacial environmental changes at Site 619, or it may indicate an actual difference in temperatures at the two locations. A second feature of the alkenone paleotemperature record is that it contains short-term fluctuations that do not appear in the oxygen isotope record (Fig. 22). These are probably real, inasmuch as similar fluctuations are common to other alkenone paleotemperature records. They represent rapid, local changes in sea-surface temperature that the global oxygen isotope record cannot reproduce. At the same time, the excursion to more negative $\delta^{18}O$ values in Oxygen Isotope Stage 2 are not mirrored in periods of lower temperatures in the temperatures derived from the $U^{k'}_{37}$ values (Fig. 22). This disagreement probably results from the sensitivity of the oxygen isotope record to runoff of isotopically light freshwater near the end of the last glacial interval and the minor impact that this kind of environmental change would have on the alkenone compositions.

Another important paleoceanographic function of the alkenone data is to serve as a proxy of past concentrations of atmospheric CO_2. The alkenones are well-suited for this function because they are produced by primary producers that inhabit the surface waters of the sea. Jasper and Hayes (1990) combine $\delta^{13}C$ values from compound-specific isotope analyses of the alkenones with isotopic fractionation values that depend on dissolved CO_2 concentrations to reconstruct atmospheric CO_2 levels for the past 100 kyr. Their use of compound-specific carbon isotope analyses of a marine biomarker is particularly apt in view of the record of changing mixtures of marine and continental organic matter at this location. Their calculations yield a record of changing atmospheric pCO_2 that is very similar to the record obtained by Barnola *et al.* (1987) from measurements of air trapped in Antarctic ice cores. The effectiveness of paleo-pCO_2 determinations from alkenone $\delta^{13}C$ values depends on many factors, foremost of which is equilibrium between atmospheric CO_2 and the dissolved CO_2 surrounding the coccoliths that synthesize the alkenone molecules. In locations where this criterion is not met, disagreements between alkenone and ice-core paleo-pCO_2 reconstructions can help to identify the nature of other paleoenvironmental changes that affect carbon isotope concentration or fractionation.

Glacial–interglacial changes in organic matter accumulation in Lake Biwa, Japan

Lake Biwa, the largest lake in Japan, has been the subject of paleolimnological studies since the 1960s. The maximum water depth is 102 m, and the surface area of the lake is 674 km^2. The lake has existed for approximately 6 My, although major tectonic reorganizations of its basin evidently occurred (e.g. Takemura, 1990), which have interrupted the sedimentary record. Organic geochemical studies have concentrated on the T-Bed, which is the upper 250 m of sediments that represents an apparently continuous sedimentary record of approximately the past 430 kyr (Meyers *et al.*, 1993). The results of a number of these investigations are reviewed by Ishiwatari and Ogura (1984) and Ishiwatari (1991).

C/N ratios in the T-Bed fluctuate between 5 and 10 (Fig. 23), a pattern that indicates that algal sources dominated organic matter inputs to these sediments. Gradual declines with depth occur in the C/N ratios and in the concentrations of organic carbon. These trends 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.

Nakai (1991) has observed that organic matter $\delta^{13}C$ values are generally less negative in younger sediments of the T-Bed than deeper in the depositional sequence (Fig. 23). The $\delta^{13}C$ shift may indicate a progressive change in the carbon cycle of Lake Biwa over the past 430 kyr. Extensive recycling of organic matter within the water column can produce algal organic matter that is isotopically light, that is 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. A decrease in the rate of organic matter recycling might result from an increase in aquatic productivity, which would 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.

Meyers and Takemura (1997) determined that organic carbon mass accumulation rates (C_{org} MARs) in the sediments of Lake Biwa varied between interglacial and glacial periods. The C_{org} MARs of the interglacial intervals are up to nine times larger than those of the glacial intervals (Fig. 23). 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. Because C/N ratios in the T-Bed show that algal organic matter predominates throughout the entire 250-m-thick sequence, the changes in delivery of organic matter must be mostly from changes in algal production. This conclusion is supported by changes to diatom assemblages that reflect enhanced algal productivity during the periods of greater C_{org} MARs (Mori and Horie, 1975).

The explanation for enhanced algal productivity is related to glacial–interglacial climate changes. The modern climate of Japan is moist and mild, but the climate was drier and cooler during the last glaciation (Tsukada, 1983). Aquatic productivity in the Holocene evidently has been increased by the greater delivery of soil nutrients to the lake waters that accompanied the greater precipitation during

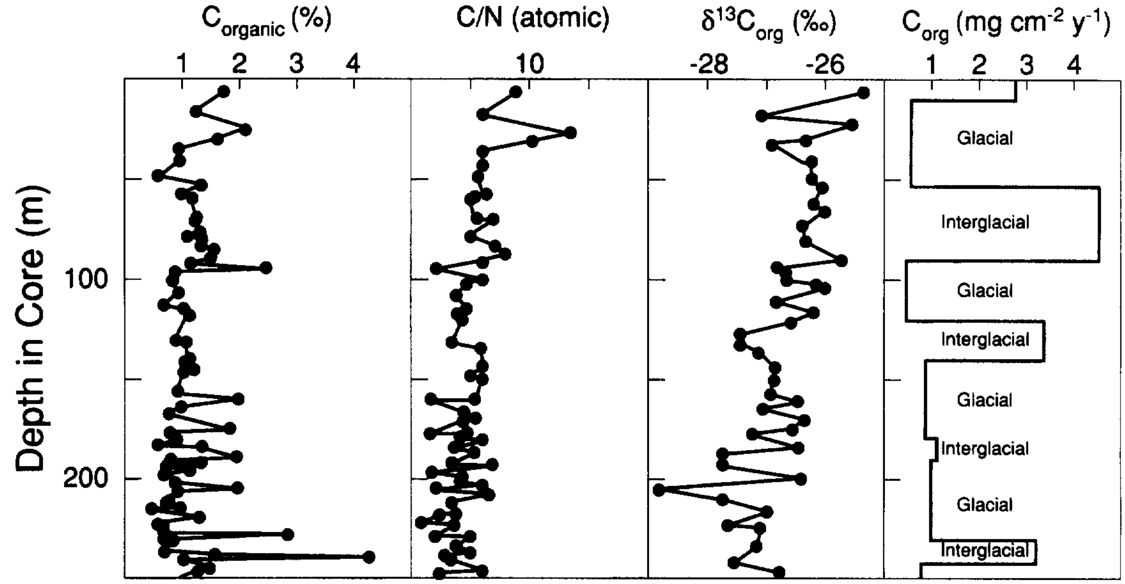

Fig. 23. Evidence of glacial–interglacial cycles in lake productivity as recorded in organic carbon mass accumulation rates in the 250-m thick T-Bed of sediments from Lake Biwa, Japan. Organic C/N ratios show that nearly all of the organic matter is from lake algae. Interglacial climates in Japan are 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).

the postglacial period. Similar glacial–interglacial climate changes evidently extend back through the earlier three glacial–interglacial cycles and are recorded in the C_{org} MAR of Lake Biwa sediments.

Paleoclimate change in organic contents of Mediterranean sapropels

Multiple, dark-colored sapropels have been recognized as common features of the post-Messinian deepwater sedimentary record of the eastern Mediterranean Sea (e.g. Cita and Grignani, 1982; Thunell *et al.*, 1984; Rossignol-Strick, 1985; Fontugne and Calvert, 1992). Drilling in 1995 by the Ocean Drilling Program has shown that sapropel occurrences extend westward into the Alboran Sea. Upper Pliocene–lower Pleistocene layers are especially rich in organic carbon, some approaching 30% (Rullkötter *et al.*, 1995). Castradori (1993) postulated from nannofossil assemblages that the triggering mechanism for the enhanced preservation in the deepwater sapropels was increased productivity. Molecular and isotopic organic geochemical compositions confirm that the sapropels originated from enhanced marine productivity (Ten Haven *et al.*, 1987; Calvert *et al.*, 1992; Rullkötter *et al.*, 1995).

Fontugne and Calvert (1992) noted that the $\delta^{13}C$ values of bulk organic matter in upper Pleistocene deepwater sapropels in the eastern Mediterranean are consistently more negative than in intercalated oozes (Fig. 8). They interpret the more negative values to reflect periodic freshwater flooding of the photic zone of the eastern Mediterranean. The notably low $\delta^{15}N$ values of the organic matter in the sapropels (Fig. 8) is evidence that nitrogen-fixing microbes were probably important primary producers during these intervals (Calvert *et al.*, 1992). Precessional (19–23 kyr) regional changes in climate appear to be central to formation of the Mediterranean laminated sediments. The basic premise is that summer–winter differences greater than at the present (the Earth is now farthest from the Sun at northern summer solstice, and modern laminites/sapropels are not being deposited) increased precipitation in the Mediterranean region (Rossignol-Strick, 1985). Increased runoff delivers nutrients to sea-water, thereby enhancing algal production and the delivery of marine organic matter to the seafloor.

Rock-Eval analyses of sapropels from ODP Site 969 on the Mediterranean Ridge south of Crete indicate that variable oxidation of marine organic matter has occurred (Fig. 24). The range in degree of organic matter preservation, from good to moderate, suggests that elevated productivity contributed to improving organic matter preservation by exceeding the benthic oxidizing ability. When the delivery of organic matter was great enough, sediments rich in organic carbon accumulated. Such sediments were deposited during some precessional minima, when seasonality was at a maximum, but not at all minima, because other Milankovitch cyclicities also affected regional paleoclimates.

Atomic C/N and C/S ratios of organic matter in an upper Pleistocene sapropel from Site 969 add support to the scenario of improved preservation from elevated productivity (Fig. 25). C/N ratios of 18 are higher than in typical algal organic matter, yet similar elevated values are found regularly in sediments under areas of high productivity and probably indicate formation of lipid-rich algal organic matter. C/S ratios are low immediately above and below the sapropel layer, partly because organic carbon concentrations are low but also because sulfide concentrations are elevated. Microbial oxidation evidently destroyed most of the organic carbon and depleted the interstitial sulfate in the sediment deposited prior to sapropel emplacement, thus improving the preservation of the organic matter that subsequently reached the seafloor. After the pulse of increased flux of organic matter diminished, organic matter already at the seafloor was "burned down" by microbial oxidation. The sapropel layers therefore appear to be recorders of times when marine production of organic matter increased in response to periods of wetter climate in the Mediterranean region.

Eocene depositional environment of the Messel Shale

The Messel shale of Germany was deposited in a relatively short period *ca.* 47 Ma at the bottom of an anoxic lake. Compound-specific carbon isotope

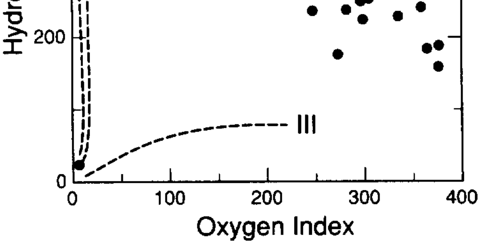

Fig. 24. Rock-Eval van Krevelen-type diagrams for Pliocene–Pleistocene sapropels from ODP Site 969, western Mediterranean Sea. Varying amounts of oxidation of algal Type II organic matter have partially altered the contents of some sapropels into Type III organic matter. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO_2 per gram TOC.

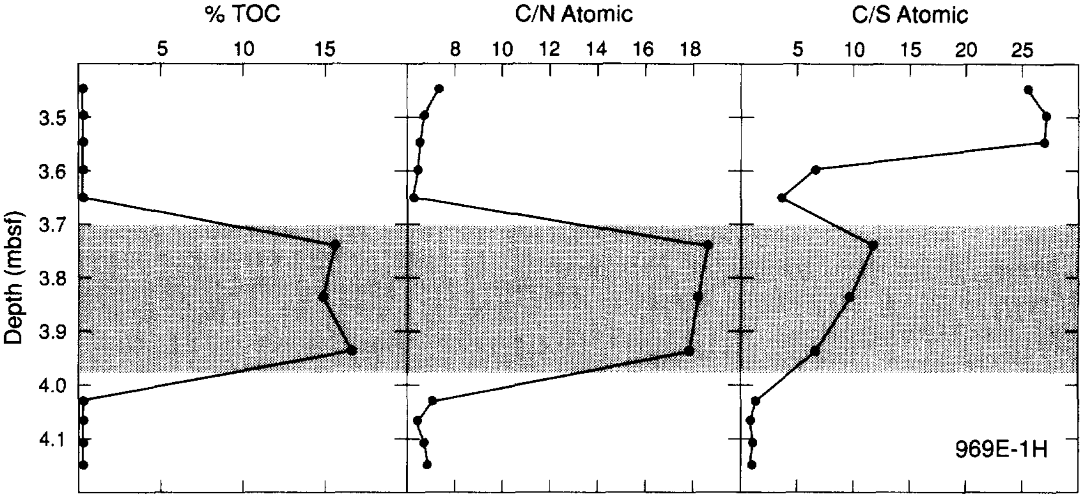

Fig. 25. Concentration of total organic carbon (TOC) and atomic C/N and C/S ratios of organic matter in an upper Pleistocene sapropel (stippled) and surrounding sediments from ODP Site 969, eastern Mediterranean Sea.

measurements made on porphyrins isolated from the Messel shale give $\delta^{13}C$ values averaging −23.4‰ (Hayes *et al.*, 1987; Freeman *et al.*, 1990). Porphyrins are diagenetic products derived principally from the chlorophylls of plants. The Messel porphyrins were derived from chlorophylls *a*, *c*, and *d*, based on the positions and structures of their tetrapyrrole ring sidechains. Their carbon contents consist almost entirely of the intact tetrapyrrole ring (Fig. 17) inherited from their biological precursor compounds. As such, the carbon isotope compositions of the porphyrins are protected from possible diagenetic effects, and they are believed to record accurately the carbon isotope signatures of their source organisms. The combination of the $\delta^{13}C$ value of −23.4‰ and the types of chlorophyll-derived biomarkers suggest that the organic matter in this lacustrine deposit was synthesized primarily by a consortium of algae and photosynthetic archaebacteria, even though abundant land-plant fossils and biomarkers are present in the shale. Among other algae, dinoflagellate production in particular was evidenced by the presence of 4-methyl stanols. The significance of the photosynthetic archaebacteria is that they indicate that part of the photic zone of the lake was anoxic. Further evidence of important microbial contributions of photosynthesized organic matter to the Messel paleoenvironment is given by a series of tetraterpenoid hopanes and the presence of lycopane but not β-carotane (Kimble *et al.*, 1974). Acyclic carotenoids such as lycopene are found in photosynthetic archaebacteria, but they are not major pigments in algae. The organic geochemical evidence for microbial photosynthesis indicates that this lake was strongly stratified and that the epilimnion was very shallow, allowing the photic zone to extend downward into the anoxic hypolimnion.

The Cenomanian–Turonian boundary event

The latest Cenomanian–earliest Turonian (*ca.* 91 Ma) was a time during which unusually high accumulations of organic carbon occurred in marine sediments. The occurrence of organic-carbon-rich sediments from this period has been documented over much of the world (e.g. Schlanger *et al.*, 1987; Arthur *et al.*, 1987; Kuhnt *et al.*, 1990). An example from the Indian Ocean, obtained by ODP Leg 122 from the Exmouth Plateau off northwestern Australia, typifies these anomalous deposits. Two thin layers (4 cm and 12 cm) of organic-carbon-rich black claystone were encountered at the Cenomanian–Turonian boundary at Site 763. Organic carbon contents were measured as high as 26% in the thinner of these layers and as high as 9% in the thicker one (Rullkötter *et al.*, 1992). Rock-Eval hydrogen index values in the range of 350–500 mg hydrocarbon/g TOC (Haq *et al.*, 1990; Rullkötter *et al.*, 1992) are similar to those reported for other examples of Cenomanian–Turonian black shales (e.g. Fig. 26). The high hydrogen index values indicate that these layers contain Type II marine organic matter. Organic petrography confirms the marine origin (Rullkötter *et al.*, 1992). The existence of two organic-carbon-rich layers present in the Site 763 sequence reveals that multiple events of enhanced production and preservation of marine organic matter occurred at the time of the Cenomanian–Turonian boundary.

An organic geochemical characteristic common to organic-carbon-rich marine sediments in general and Cenomanian–Turonian black shales in particular is C/N ratios that are atypically high for marine organic matter (Meyers *et al.*, 1986b). Values from DSDP Site 603 on the Hatteras continental rise of the western North Atlantic Ocean are between 20

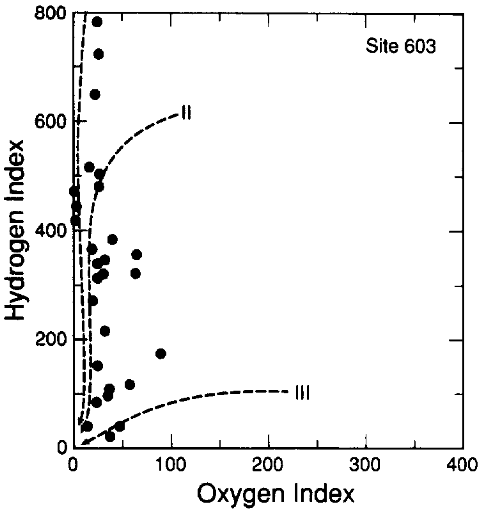

Fig. 26. Rock-Eval van Krevelen-type diagrams for Cenomanian–Turonian black shales from DSDP Site 603, Hatteras Rise, North Atlantic Ocean. Hydrocarbon-rich Type I and Type II organic matter dominates the organic matter in these black shales and presumably originates from microbes and algae. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO_2 per gram TOC. Data compiled from various sources by Meyers (1989).

and 45 in Cenomanian–Turonian shales that contain 4–13% organic carbon (Fig. 27). Two factors are probably involved. First, algae are able to synthesize lipid-rich organic matter during times of abundant nutrient supply, hence creating C/N ratios that may be as high as 18. Second, partial preservation of algal organic matter during sinking and sedimentation selectively favors carbon-rich components while degrading nitrogen-rich components, thereby diagenetically elevating C/N ratios. Both enhanced production of organic matter and enhanced preservation work towards the high C/N ratios that are atypical of algal organic matter.

Rullkötter *et al.* (1992) postulate that the Cenomanian–Turonian Boundary Event represents a time of worldwide oxygen depletion in bottom waters that improved preservation of the organic matter produced in overlying waters. Differences in surface paleoproductivity were responsible for site-to-site contrasts. Alternatively, Thurow *et al.* (1992) conclude that the oxygen depletion occurred at mid-water depths and that deeper waters were oxygenated, resulting in organic-carbon-rich sediments accumulating only in the oxygen minimum zone. The intensity of the oxygen minimum zone, coupled with water depths, controlled organic matter accumulation. Both scenarios imply that local paleoenvironmental conditions, particularly those influencing marine productivity and near-bottom oxygen availability, apparently overprinted global factors important to the Cenomanian–Turonian Boundary Event in the world ocean.

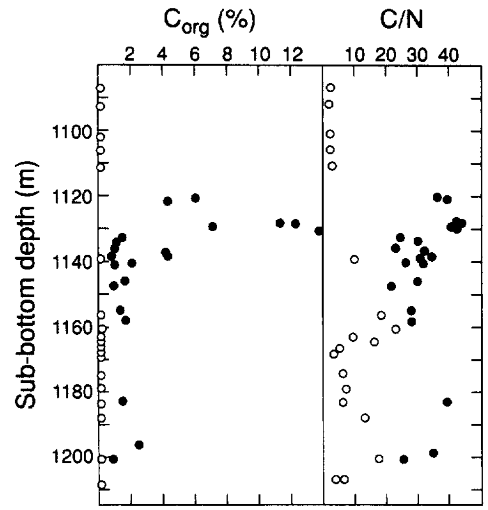

Fig. 27. Organic carbon concentrations and atomic C/N ratios of Cenomanian–Turonian black shales and surrounding sediments from DSDP Site 603, Hatteras Rise, North Atlantic Ocean. Solid circles represent data from black shales; open circles are data from surrounding organic-carbon-poor claystones. From Meyers (1989).

Several features are globally common to Cenomanian–Turonian black shales and therefore reflect the special ocean-wide conditions under which they were deposited. First, Rock-Eval results show that the organic matter is hydrocarbon-rich Type I (e.g. Figure 26). Second, $\delta^{15}N$ values from DSDP Sites 367, 530 and 603, which are widely separated in the Atlantic Ocean, are exceptionally light for marine organic matter (Fig. 8). These two characteristics of the organic matter in the black shales are typical of microbial biomass and suggest that photosynthetic, nitrogen-fixing bacteria dominated marine productivity at this time in ocean history. A third feature is also noteworthy — the notably low $\delta^{13}C$ values of Cenomanian–Turonian black shales (Fig. 8). This isotopic excursion is good evidence that atmospheric pCO_2 was very high during the middle Cretaceous, a time of warm, ice-free global climate (Dean *et al.*, 1986; Arthur *et al.*, 1988). The organic matter in the black shales may therefore provide strong confirmation of the Greenhouse World that is believed to have existed before onset of the Icehouse World of today.

CONTINUING NEEDS AND FUTURE DIRECTIONS

This overview of the organic geochemical aspects of paleoceanography, paleolimnology, and paleoclimatology would not be complete if it did not include some comments on the directions that should be taken by future research. Continued improvements in analytical capabilities present new, more sophisticated opportunities for studies of sediment organic matter. Organic geochemical studies have progressed beyond the necessary step of describing what is present in sediments to now being more quantitative and more inquisitive. The important question has always been "Why are these organic substances here?", but the questions can now be answered in better ways.

Several areas merit special attention as continuing needs and future directions for improving organic geochemical contributions to paleoceanography and paleolimnology:

1. Analyses need to become more quantitative and to be linked with modern environmental parameters so that interpretations of paleoenvironmental records can be improved. Measurements of primary production rates, transport fluxes, and remineralization rates of organic matter in the biosphere are important to evaluating accumulation and preservation records in the geosphere.
2. Interpretation of many organic geochemical parameters has proven more difficult than initially thought. These challenges should be viewed as opportunities to learn more about paleoenvironmental conditions, rather than obstacles. The complexities that have sometimes constrained interpretations of, for example, pigment data, sterol biomarker compositions, nitrogen isotope records, compound-specific carbon isotope results, and alkenone paleotemperature determinations, indicate that these parameters are sensitive to a greater range of environmental and depositional factors than originally believed. As understanding of these factors and how they affect the geochemical parameters grows, these measurements will become even more informative and useful as paleoenvironmental proxies.
3. The collection of useful biomarker compounds needs to be expanded. Paleoceanographers and paleolimnologists can define questions that organic geochemists can help answer. Indicator organisms, characteristic of different types of environments, can be identified and their molecular and isotopic compositions can be scanned for new biomarker information.
4. Quantitative relationships between organic geochemical indicators of autochthonous and allochthonous forms of organic matter need better definition. As an example, land-derived organic matter is generally over-represented by biomarker evidence. Identification of representative indicators of organic matter sources — different types of pollen, algal microfossils, land plant debris, bacteria, etc. — and measurements of their respective contributions to sediment organic matter are needed to provide balanced source assessments. Better understandings of diagenetic intermediates and end products in product-precursor pathways can expand interpretations of paleoenvironmental conditions.
5. Diagenetic interactions between different individual compounds and different classes of compounds in sedimentary records should be investigated. Most studies have concentrated on the changes that occur to single compounds or to single types of compounds. Dynamic diagenetic interrelationships may exist that could be useful to interpreting organic geochemical contributions to paleodepositional records.
6. The different roles played by high-molecular-weight forms of sediment organic matter are not well understood and need clarification. Progress in understanding the general details of how humic substances form, for example, has been slow. This information is critical to defining the paleoceanographic and paleolimnologic significance of humic materials. Does humin/kerogen predictably incorporate and enhance preservation of elemental ratios, isotopic compositions, and biomarker molecules of primary organic matter? What characteristics of these major forms of organic matter reflect paleoenvironmental conditions?

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