Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments

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Abstract—The factors affecting the amounts and types of organic matter in lacustrine sediments are summarized in this review, and synthesis, of published studies. Biota having in the lake and in its watershed are the sources of the organic compounds initially contributed to the lake system. Microbial reworking of these materials during sinking and early sedimentation markedly diminishes the total amount of organic matter while replacing many of the primary compounds with secondary ones. Much of the organic matter content of sediments is the product of this microbial reprocessing. Various organic matter components of lake sediments nonetheless retain source information and thereby contribute to the paleolimnological record. Carbon/nitrogen ratios of total organic matter reflect original proportions of algal and land-derived material. Carbon isotopic compositions indicate the history of lake productivity and carbon recycling. Biomarker compounds provide important information about contributions from different biota. Sterol compositions and chainlength distributions of n-alkanes, n-alkanoic acids, and n-alkanols help distinguish different algal and watershed sources and also record diagenetic alterations.

Stabilization of functional-group-containing biomarkers by conversion into saturated or aromatic hydrocarbons or by incorporation into bound forms improves their preservation and hence record of source information. Lignin components provide important evidence of watershed plant cover, and pigments reflect algal assemblages. The interplay of the factors influencing the organic matter content of lake sediments is illustrated by overviews of sedimentary records of four lake systems—Lake Biwa (Japan), Lake Greifen (Switzerland), Lake Washington (Pacific Northwest), and the Great Lakes (American Midwest).

Key words — lake sediments, carbon isotopes, C/N ratios, biomarkers, pigments, humic substances, lignin, diagenesis, paleolimnology

INTRODUCTION

Organic matter constitutes a minor but important fraction of lake sediments. It is made up of a complex mixture of lipids, carbohydrates, proteins, and other biochemicals contained in the tissues of living benthic micro-organisms and contributed from the detritus of organisms formerly living in the lake and its watershed. Humic substances are diagenetically formed from these biochemical starting materials and constitute the major part of the complex mixture of organic materials.

Significance of sediment organic matter

The organic matter content of lake sediments participates in a variety of biochemical and geochemical processes. Benthic animals and microbes depend on organic matter for their nutrition. Because many components of organic matter are relatively easily oxidized forms of reduced carbon, the dissolved oxygen concentration of sediment pore water is controlled largely by the availability of oxidizable organic matter below the sediment/water interface. Furthermore, redox reactions, in which oxidized inorganic species become reduced by interaction with organic matter, are common in sediments. Organic matter is consequently a dynamic biogeochemical component of sediments.

Organic matter also forms part of the paleolimnologic record preserved in lake sediments. The different types of biota populating a lake and its watershed produce organic matter having distinctive biochemical compositions. Changes in the community structure of these biota create variations in the amounts and types of organic matter deposited at different times in the history of a lake. During the process of deposition in the lake bottom, organic matter is subject to microbial reworking, with the result that its original composition becomes altered. The degree of alteration provides yet more information about past lake environments, particularly the amount of water column mixing that occurred during sediment deposition.

Sources of organic matter in lake sediments

The particulate detritus of plants that have lived in the waters and on the land surrounding a lake comprises the primary source of organic matter to the bottom deposits. Plants can be divided into two
geochemically significant groups on the basis of their biochemical compositions: (1) nonvascular plants that lack woody and cellulosic tissues, such as simple algae, and (2) vascular plants that have these tissues, such as grasses, shrubs, and trees. These latter types of plants exist on land in the shallow parts of lakes as bottom-rooted, emergent vegetation. The relative contributions from these two plant groups is influenced strongly by lake morphology, watershed topography, and the relative abundances of lake and watershed plants. Organic matter in lake sediments covers the spectrum of being predominantly algal in some lakes to being land-derived in others.

Bacteria and other microbes in the water and sediment of lakes and the soil of the lake watershed rework and degrade aquatic and land-derived organic matter. Although some bacteria are capable of photosynthesis or chemosynthesis, lake environments generally provide enough organic substrate that the dominant role of bacteria is the heterotrophic decomposition of organic detritus. An important exception exists in strongly stratified lakes where bacteria can become major producers of primary organic matter. Bacteria biosynthesize characteristic forms of organic matter while breaking down the preformed material remaining from the plants and animals of the lake and watershed.

In addition to these local sources of organic matter, winds commonly transport material, such as pollen, from sources outside the local watershed. The eolian component is typically a small fraction of the total organic mixture, yet it can contain distinctive components potentially useful to paleolimnological studies.

A budget of organic matter sources to Lake Michigan, a large oligotrophic freshwater lake, gives an illustration of their relative magnitudes. About 90% of the organic carbon in the waters of the lake originates from algal production, 5% is carried to the lake by rivers, and 5% is brought in with airborne particles and precipitation (Andren and Strand, 1981). These contributions of organic matter are subject to selective degradation as they sink to the lake bottom, and therefore the initial source proportions may not be preserved in the sediment record.

Depositional processes affecting organic matter

A variety of processes act to alter the character of organic matter in the relatively short time between its origin and its burial in a lake bottom. Foremost among these processes is its degradation during sinking. Sediment trap studies in Lake Michigan show that only 6% of the organic carbon photosynthetically formed in the surface water of the southern part of this lake reaches the sediment surface 100 m below (Table 1). Nearly 85% of the carbon is oxidized before leaving the epilimnion, that part of the water column above the thermocline (Eadie et al., 1984). In more shallow depths, organic matter would have shorter sinking times and consequently shorter exposures to oxidation in the water column. Shallow-water lakes consequently usually have sediments richer in organic matter than found in deep lakes like the Laurentian Great Lakes.

Once reaching the bottom, organic matter continues to be subject to oxidative alteration and destruction. Resuspension of sedimented organic matter can be substantial (e.g. 75 g C$_{org}$/m$^2$yr at a depth of 100 m in Lake Michigan (Table 1), or nearly 10 times the annual flux of organic carbon to the bottom; Eadie et al., 1984; Meyers et al., 1984a; Meyers and Eadie, 1993). Organic matter so resuspended is re-exposed to oxidation in the water column. Resuspension is usually greater in large, well-mixed lakes than in small lakes.

Bioturbation, or biological mixing, of surface sediments also prolongs the exposure of organic matter to oxidation and adds to this the degradation due to the nutritional needs of benthic fauna. The depth of bioturbation in the Great Lakes, as an example, averages about 10 cm (Robbins and Edgington, 1975). By analogy to marine studies (Cobler and Dymond, 1980), about 75% of the organic carbon reaching the surface of bottom sediments is destroyed in the bioturbated layer. Where seasonal or permanent anoxic bottom-water conditions exist, bioturbation is diminished or absent, because benthic animals required dissolved oxygen for respiration. Many temperate-zone lakes experience periods of anoxia during summer thermal stratification, and the sediments of these lakes typically have higher concentrations of organic matter than do permanently oxygenated lakes. Varved sediments, in particular, indicate little or no resuspension and the absence of bioturbation.

Once buried below the zone of bioturbation, organic matter is subject to alterations by anaerobic bacteria. The waters of most lakes contain insufficient dissolved sulfate to make sulfate reduction an important process. Instead, methanogenic bacteria continue degradational processes if the sedimented organic matter contains a sufficient fraction of labile materials to sustain microbial activity. In general, components from aquatic sources are more sensitive to the bacterial degradative processes than are materials from land sources. Organic matter in lacustrine sediments consequently often has a large and relatively unreactive fraction of land-derived organic residues.

Less reactive forms of organic matter become more dominant as the more reactive forms are utilized.
by microbes and by deposit-feeding animals. For example, humic substances and lipids are less reactive than amino compounds and carbohydrates, and therefore become larger proportions of the organic matter with depth in sediments of Lakes Ontario, Erie, and Huron (Kemp and Johnston, 1979). In heavily reworked sediment, only the most resistant forms of the original organic mixture remain. Throughout this reprocessing, residues of microbially synthesized organic matter are added to the mixture, some to be modified in turn or destroyed, but others to be preserved.

The final result of these multiple processes is that the organic matter in sediments is often markedly different from that which is produced by the biota in and around the lake. Furthermore, the amount of organic matter buried in subsurface sediments is a small fraction of that originally introduced into the surface waters.

**INDICATORS OF SOURCES AND ALTERATIONS OF TOTAL ORGANIC MATTER IN LAKE SEDIMENTS**

**Organic carbon stable isotopes**

Most photosynthetic plants incorporate carbon into organic matter using the C3 Calvin-Benson pathway which preferentially incorporates $^{13}$C into organic matter, producing a shift of about $-20\%$ from the carbon isotope ratio of the inorganic carbon pool. Some plants use the C4 Hatch-Slack pathway, and others, mostly succulents, utilize the CAM (crassulacean acid metabolism) pathway. The isotope shift for the C4 pathway is $-8$ to $-12\%$; that of the CAM pathway can vary from $-10$ to $-20\%$. Organic matter produced from atmospheric CO$_2$ by land plants using the C3 pathway consequently has an average $\delta^{13}$C (PDB) value of $-28\%$ and by those using the C4 pathway $ca-14\%$ (cf. O'Leary, 1988).

Lake-derived organic matter is normally isotopically indistinguishable from organic matter from the surrounding watershed (Table 2), except under special conditions as seen later.

The existence of the several isotopic signatures of photosynthetically fixed organic carbon would seem to offer opportunities to trace sources of organic matter in lacustrine food webs and to lake sediments. In the sedimentary organic matter of most lakes, however, the differences originally present in the total carbon isotopic contents of specific floras are lost because of food web integration of the different carbon sources. For example, photosynthesizers living in Fayetteville Green Lake, New York, have $\delta^{13}$C (PDB) values ranging from $-15$ to $-41\%$. Despite this range among available food sources, most animals in the lake have isotope signatures between $-25$ and $-30\%$, and bottom sediments have a $\delta^{13}$C value of $-28\%$ (Fry, 1986), which is close to the isotopic compositions of organic matter from other lakes (Table 2).

Microbial reworking of organic matter during early diagenesis can potentially modify its bulk carbon isotopic content. Organic matter is a mixture of different types of compounds which deviate differently in isotopic content from the inorganic carbon pool. Amino acids of marine plankton, for example, are depleted in $^{13}$C by $-17\%$ on average, whereas the lipid fraction has a $\delta^{13}$C value of $-28\%$ (Degens, 1969). Selective loss of more reactive fractions of the total organic matter may create a diagenetic shift in the isotope ratio which will mask the original source signature. Laboratory decomposition of the C4 marsh grass, *Spartina alterniflora*, produced progressive losses of isotopically heavy organic material which created an extrapolated isotope shift in bulk organic carbon from $-13$ to $-17\%$ (Benner et al., 1987). An equivalent shift to lighter carbon isotope values has

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>$\delta^{13}$C (‰)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td><strong>Land plants</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake Biwa watershed</td>
<td>$-25$ to $-30$</td>
<td>Nakai and Koyama (1991)</td>
</tr>
<tr>
<td>Willow leaves</td>
<td>$-26.7$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Cottonwood leaves</td>
<td>$-25.0$</td>
<td>Meyers (1990)</td>
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<tr>
<td>Aspen leaves</td>
<td>$-25.8$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Popular leaves</td>
<td>$-27.9$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Juniper needles</td>
<td>$-22.5$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Pinyon pine needles</td>
<td>$-24.8$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>White spruce needles</td>
<td>$-25.1$</td>
<td>Meyers, unpublished</td>
</tr>
<tr>
<td><strong>Lacustrine plants</strong></td>
<td></td>
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<tr>
<td>Walker Lake mixed plankton</td>
<td>$-28.8$</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Pyramid Lake mixed plankton</td>
<td>$-28.3 \pm 0.7$ ($N = 3$)</td>
<td>Meyers, unpublished</td>
</tr>
<tr>
<td>Lake Michigan mixed plankton</td>
<td>$-26.5 \pm 1.4$ ($N = 7$)</td>
<td>Meyers, unpublished</td>
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<tr>
<td><strong>Lacustrine sediments</strong></td>
<td></td>
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<tr>
<td>Lake Biwa surface sediment</td>
<td>$-25.3$</td>
<td>Meyers and Horie (1993)</td>
</tr>
<tr>
<td>Walker Lake surface sediment</td>
<td>$-24.2 \pm 0.8$ ($N = 30$)</td>
<td>Meyers (1990)</td>
</tr>
<tr>
<td>Coburn Pond surface sediment</td>
<td>$-28.4$</td>
<td>Ho and Meyers (1993)</td>
</tr>
<tr>
<td>Lake Bosumtwi surface sediment</td>
<td>$-26.4$</td>
<td>Talbot and Johannessen (1992)</td>
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<tr>
<td>Lake Michigan surface sediment</td>
<td>$-26.3$</td>
<td>Rea et al. (1980)</td>
</tr>
<tr>
<td>Lake Michigan settling sediment</td>
<td>$-27.5 \pm 0.9$ ($N = 6$)</td>
<td>Meyers and Eadie (1993)</td>
</tr>
<tr>
<td>Lake Baikal surface sediment</td>
<td>$-29.9$</td>
<td>Qiu et al. (1993)</td>
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</table>
been documented in an organic-carbon-rich sediment core from Mangrove Lake, Bermuda (Hatcher et al., 1982). The \( \delta^{13}C \) ratio of total organic carbon changes from \(-17\%\) in surface sediments to \(-21\%\) in sediments below 5 m, a depth corresponding to ca 4000 yr ago, as organic carbon concentrations increase from 20 to 28% (Fig. 1). This shift apparently is caused at least partly by selective loss of the isotopically heavy carbohydrate fraction of total organic matter (Spiker and Hatcher, 1984), but changes in the proportion of land-derived and marine-derived organic matter may also contribute to it.

Fig. 1. Organic carbon concentrations, isotope values, and compositions at different depths in a sediment core from Mangrove Lake, Bermuda. Isotope ratios are relative to the PDB standard. Organic carbon fractions are proteins (\( \bullet \)), lipids (\( \ast \)), carbohydrates (\( \Delta \)), and humin (\( \scriptstyle\circ \)). Concentrations of the different fractions are expressed as percentage contributions of carbon to the total organic carbon. The increasing contribution of humin carbon represents decreases in contributions of the other fractions with progressively greater sediment age, which is less than 4000 years old. Data are from Hatcher et al. (1982, 1984).

Organic carbon isotope ratios do not seem to display diagenetic shifts in lake sediments having more typical carbon concentrations. In a core from Lake Michigan, for example, \( \delta^{13}C \) values remained at \(-26\%\) from modern to 3500-yr old sediments in which organic carbon concentrations varied between 1 and 3% (Rea et al., 1980). If the possibility of diagenetic effects can be determined, then differences between \( \delta^{13}C \) values of sediments deposited at different times can provide paleoenvironmental information. The history of productivity enhancement of Lake Ontario is recorded by a shift in organic carbon \( \delta^{13}C \) values from \(-27\%\) in sediments deposited in the mid 1800s to \(-25\%\) in sediments from 1970 to 1980 (Schelske and Hodell, 1991). Periods of dessication of Walker Lake, Nevada, created shifts in the overall carbon isotopic contents of this saline lake which are preserved as heavier organic matter \( \delta^{13}C \) values in sediments from 2 and 5 Kya (Benson et al., 1991). Similarly, Talbot and Johannessen (1992) have documented organic carbon \( \delta^{13}C \) shifts to heavier values in sediments of Lake Bosumtwi, Ghana, that were deposited under the drier conditions that evidently existed near the end of the last glacial maximum 25–10 Kya. Organic matter synthesized by aquatic organisms records times when the waters of both Walker Lake and Lake Bosumtwi were concentrated by evaporation and consequently saltier. Episodes of extensive recycling of organic matter within the water column can produce algal organic matter which is isotopically light (e.g. Rau, 1978), again illustrating some of the potential paleolimnologic value of organic carbon isotopes.

Nitrogen stable isotopes

The nitrogen isotope contents of sediment organic matter have not been widely studied by organic geochemists, yet important paleolimnological information about organic matter source and diagenesis can be obtained from \( \delta^{15}N \) measurements. Inorganic nitrogen reservoirs available to land plants and aquatic plants differ in their isotopic contents: Dissolved nitrate has an isotope ratio of +7 to +10\%, whereas atmospheric molecular nitrogen has a \( \delta^{15}N \) of about 0\% (cf. Peters et al., 1978). This difference is preserved in the isotopic contents of plankton (\( \delta^{15}N \) of +8\%) and C3 land plants (\( \delta^{15}N \) of +1\%) and has been used to trace food chain relationships in a coastal marine marsh by Peterson et al. (1985).

The few investigations of the nitrogen isotope content of lake sediments show that the source information derived from the difference between atmospheric and dissolved forms of nitrogen appears to be preserved. The potential isotopic effects expected from preferential degradation of nitrogen-containing organic substances are minor or absent. In sediments from lakes Superior and Ontario, Pang and Nriagu (1976, 1977) found that areas receiving a large proportion of land-sourced organic matter have lighter \( \delta^{15}N \) values than areas where aquatic organic matter is dominant (+3.7\% vs +4.9\%). Significant amounts of downcore degradation of nitrogenous
matter occurred relative to total organic matter at all locations in these lakes, increasing the potential for diagenetic isotope shifts. Nevertheless, no differences are evident between $\delta^{15}N$ ratios in surface sediments and those at the bottom of half-meter cores. Most of the decomposition of organic matter that might cause nitrogen isotope shifts evidently occurs during sinking and prior to sedimentation in the Great Lakes. Meyers and Eadie (1993) note a change of $-1$ to $-2\%$ in the $\delta^{15}N$ values of sinking particulate organic matter between the near-surface and near-bottom of Lake Michigan. This shift is consistent with postulated microbial reprocessing of the sinking organic material.

The nitrogen isotope record from Lake Bosumtwi contains major changes to heavier organic $\delta^{15}N$ values in sediments interpreted to have been deposited during periods of dry glacial-age climate. Talbot and Johannessen (1992) suggest that evaporative losses of isotopically light ammonium nitrogen from the relatively saline and alkaline lake waters occurred during these periods. Land runoff would have been diminished in these intervals, hence the $\delta^{15}N$ excursions reflect aquatic production of organic matter from a modified nitrogen reservoir.

**Organic matter C/N ratio**

The presence or absence of cellulose in the plant sources of organic matter to lakes influences the C/N ratios of sediments. As shown by the examples in Table 3, nonvascular aquatic plants have low C/N ratios of sediments. As indicated in Table 3, nonvascular aquatic plants have low C/N ratios, typically between 4 and 10, whereas vascular land plants, which contain cellulose, have C/N ratios of 20 and greater. Lakes for which the contribution of organic matter from vascular land plants is small relative to water-column production, exemplified by Walker Lake and Lake Michigan, show lower C/N ratios in their sediments than do lakes receiving important amounts of vascular plant debris, such as Mangrove Lake and Lake Bosumtwi (Table 3). Ratios of 13–14 for surface sediments of the latter two lakes suggest a mixture of non-vascular and vascular contributions, which is expected for most lakes.

Selective degradation of organic matter components during early diagenesis can modify elemental compositions and hence C/N ratios of organic matter in sediments. C/N ratios of modern wood samples are consistently higher than those of wood that had been buried in sediments (Table 3). A similar change, although much more subtle, accompanies deposition of organic matter. Settling particles in Lake Michigan have a C/N value of 9; the ratio in resuspended bottom sediments is 8. A decrease in C/N ratios has also been observed in soils (e.g., Sollins et al., 1984), where it involves the microbial immobilization of nitrogenous material accompanied by the remineralization of carbon. These changes in the elemental composition of sedimentary organic matter are not commonly large enough, however, to erase the original C/N difference between vascular and non-vascular plants.

Burial in lake bottoms appears to stabilize organic matter C/N ratios to further diagenetic alteration. The C/N values of Quaternary sediment samples from the upper 10 m of a core from Mangrove Lake vary irregularly between 11 and 17 (Fig. 1). This variation resembles a similar downcore C/N profile from Lake Yunoko, Japan, which Ishiwatari (1977) interpreted as changes in the source mixture. Indication of preservation of the C/N source signal

| Table 3 A compilation of atomic C/N ratios of assorted biota and lacustrine samples |
|-----------------------------------------|---------|------------------|
| Type of sample                          | C/N     | Reference        |
| **Land plants**                         |         |                  |
| White oak, modern                       | 276     | Hedges et al. (1985) |
| White oak, 25 Kyr-old                   | 111     | Hedges et al. (1985) |
| Red alder, modern                       | 264     | Hedges et al. (1985) |
| Red alder, 2.5 Kyr-old                  | 106     | Hedges et al. (1985) |
| Spruce, modern                          | 546     | Hedges et al. (1985) |
| Spruce, 2.5 Kyr-old                     | 541     | Hedges et al. (1985) |
| White spruce, modern                    | 46      | Bourbonnere (1979) |
| White spruce, 10 Kyr-old                | 20      | Bourbonnere (1979) |
| Willow, modern                          | 38      | Meyers (1990)    |
| Cottonwood, modern                      | 22      | Meyers (1990)    |
| Pinyon pine, modern                     | 42      | Meyers (1990)    |
| **Lacustrine plants**                   |         |                  |
| Walker Lake plankton                    | 8       | Meyers (1990)    |
| Diatom, Asterionella formosa            | 9       | Bourbonnere (1979) |
| Green alga, Chlamydomonas sp            | 7       | Bourbonnere (1979) |
| Lake Bwa mixed plankton                | 6–7     | Nakai and Koyama (1991) |
| **Lacustrine samples**                  |         |                  |
| Surface sediment, Lake Bwa              | 6       | Meyers and Hone (1993) |
| Resuspended sediment, Lake Michigan     | 9       | Meyers et al. (1984a) |
| Surface sediment, Walker Lake           | 8       | Meyers and Benson (1988) |
| Surface sediment, Pyramid Lake          | 9       | Meyers, unpublished |
| Surface sediment, Lake Baikal           | 11      | Qiu et al (1993)  |
| Surface sediment, Coburn Pond           | 12      | Ho and Meyers (1993) |
| Surface sediment, Mangrove Lake         | 13      | Hatcher et al (1982) |
| Surface sediment, Lake Bosumtwi         | 14      | Talbot and Johannessen (1992) |
was also found by Ertel and Hedges (1985), who demonstrated that vascular plant debris isolated from a sediment sample having a bulk C/N of 15 retains the elevated C/N values characteristic of cellulosic plants. The sediment ratio indicates mixing of vascular and nonvascular plant debris rather than diagenetic alteration. Talbot and Johannessen (1992) similarly conclude that selective diagenesis has had no discernible effect on organic matter C/N ratios in sediments as old as 27,500 yr in Lake Bosumtwi.

Judicious interpretation of C/N ratios can yield information about past sources of organic matter to lake sediments. Ishiwatari and Uzaki (1987), for example, reported a sharp transition in atomic C/N values from an average of 9 to an average of 13 at the 250 m level in a drilled core of sediment from Lake Biwa, Japan. They interpreted this change as a shift in proportions of organic matter source from algal dominance in younger sediments to land plant dominance in deeper sediments. This interpretation is consistent with a change in sediment types from fine-grained deep-water sediment to shallow-water sands and gravels at the 250 m depth. Another example is from the sediments of Pleistocene Lake Karewa, India. Several marked increases to values of 10 or more occur in C/N ratios that typically remain below 4 in sediments deposited between 2.4 Myr and 400 Kyr (Krishnamurthy et al., 1986). Concomitant lighter δ13C values indicate that land plant contributions to sediment organic matter increased at these times.

**DIAGENESIS OF HUMIC SUBSTANCES**

Humic substances are operationally divided into fulvic acid (soluble in base and acid), humic acid (soluble in base but not acid), and humin (insoluble in base and acid). Between 60 and 70% of organic matter in young lacustrine sediments is constituted by humic substances; this percentage rises to over 90% in older sediments (Ishiwatari, 1985). In lithified sediments, the term “kerogen” is commonly used to describe the non-soluble fraction of organic matter; this material is equivalent to the humin of younger, non-lithified sediments. Because of this operational and probably geochemical equivalence, the term “protokerogen” has been used by some workers instead of humin.

The geochemical compounds grouped as humic substances are complex and diverse. As a consequence, studies of this organic matter fraction have traditionally employed general characterizations, such as elemental and spectroscopic analyses. These procedures show that humic substances, themselves products of diagenetic alteration of biogenic organic matter, evidently continue to undergo limited diagenesis in lake sediments. Bourbonniere and Meyers (1978) used infrared and visible spectroscopy to explore the possible condensation of fulvic acid into humic acid in a half-meter-long core of Lake Huron sediment. They found no evidence for this conversion. Furthermore, overall diagenetic effects are minor, inasmuch as H/C ratios of the fulvic acid (ca 2.2) and the humic acid (ca 1.6) do not change downcore.

The H/C values greater than one reflect the aliphatic nature of the Lake Huron humic substances and a probable origin from algal or bacterial organic matter, as opposed to vascular plant material. The 550-yr period represented in this core of Lake Huron sediment is inadequate for major diagenetic effects to appear in fulvic and humic acids.

Over multi-thousand-year periods of time, the effects of diagenesis of humic substances become evident in lake sediments. The humin fraction increases from 65% of the total humics at the surface to 85% of the total at the bottom of a 1 m core of Lake Michigan sediment (Fig. 2), a depth corresponding to ca 3500 yr ago (Rea et al., 1980). Some of this increase may arise from conversion of fulvic and humic acids to humin, but the overall decrease in total sediment organic carbon indicates that diagenetic loss of organic matter continues throughout the core and that preferential degradation of fulvic and humic acids occurs. Despite evidence of organic matter degradation in this core, the δ13C ratio of total organic carbon does not shift from −26.3‰ (Rea et al., 1980). The C/N ratios of both fulvic and humic acids remain ca 7 (Fig. 2) and suggest a common origin from aquatic or bacterial sources. In contrast, the humin fraction has a C/N ratio of ca 15. Humin typically has an atomic C/N value of 14–16 (Ishiwatari, 1985), and this ratio suggests an important component of cellulosic land plant material for humin.

![Fig. 2. Fulvic acid, humic acid, and humin C/N values and proportional contributions to total organic carbon in a core of Lake Michigan sediment. Sediment age is from modern to 3500 yr. B.P. The downcore decrease in organic carbon concentration is mostly from diagenetic losses of fulvic and humic acid concentrations, producing a proportional increase in the relative contribution of humin. Atomic C/N ratios are not affected by the diagenetic changes. Core location, sedimentology, and dating are described by Rea et al. (1980) and Bourbonniere (1979).](image-url)
Comparisons of samples of wood from modern trees and of wood that has been buried for thousands of years in sediments have been used as proxies for the kinds of chemical changes that can occur in humic substances (e.g., Meyers et al., 1980a; Hedges et al., 1985; Spiker and Hatcher, 1987). A consistent observation of such studies is that cellulose, made up of aliphatic monomeric units, decreases in abundance in relation to lignin, which is a polyaromatic macromolecule. Solid-state $^{13}$C nuclear magnetic resonance spectra have revealed that a trend from predominantly aliphatic character to predominantly aromatic character occurs in the humin fraction of progressively older sediments from Mangrove Lake, Bermuda. In this case, humic substances convert to less reactive, more aromatic material in a period of about 10 Kyr (Hatcher et al., 1982), largely through preferential destruction of their aliphatic components.

**LIPID BIOMARKERS AND THEIR ALTERATIONS**

The molecular composition of the lipid fraction of sediment organic matter provides particularly useful information about the sources and diagenetic alterations of organic matter. Lipids are operationally defined as that fraction of organic matter which can be isolated by extraction with an organic solvent. The term “geolipid” is sometimes used to describe the materials obtained from solvent extraction of sediments in recognition of the differences that exist between the molecular compositions of unaltered biological matter and the contents of geological samples. In older, lithified sediments where the distinction between unaltered and altered lipids becomes greater, the term “bitumen” is typically employed.

Lipid extraction of lake sediments yields hydrocarbons and the hydrocarbon-like carboxylic acids, alcohols, ketones, aldehydes, and related compounds commonly having 10 or more carbon atoms. Many of these compounds have specific biological origins; all of them reflect enzymatic control on their molecular structures. Retention of their biological heritage earns the name “biological marker”, commonly abbreviated to “biomarker”, for many of these compounds. This characteristic makes the lipid fraction especially important to geochemical studies, even though it typically constitutes only a few percent of the total sediment organic matter.

Several extensive reviews of the lipid biomarker contents of young, non-lithified sediments are available (e.g., Barnes and Barnes, 1978; Cranwell, 1982; Johns, 1986; Müller, 1987). We have selected examples of studies that illustrate the responses of geolipid biomarker compounds to paleolimnetic changes and to diagenetic alterations. The biomarker alterations can be used as proxies for the general processes affecting all forms of lacustrine organic matter.

**Alteration of lipids during sedimentation**

Studies of settling particles intercepted by sediment traps indicate that lipids undergo substantial amounts of degradative alteration during sinking to the bottoms of lakes, so that the geolipid compositions of sediments differ from their source compositions. The relative contributions of alkanoic acids and of alkanols become smaller, and distributions change, in settling sediment collected at progressively deeper depths in Lake Michigan (Meyers et al., 1980b, 1984a). The $n$-C$_{16}$ and $n$-C$_{18}$ acids and alcohols from algal material become less dominant, whereas the even-chain C$_{28}$-C$_{30}$ components from the waxy coatings of land plants become proportionally more important. Fatty acid decomposition rates calculated from sediment trap compositions show that $n$-C$_{16}$ degrades ca 10 times faster than $n$-C$_{30}$ (Meyers and Eadie, 1993). Similarly, Kawamura et al. (1987) found that distributions of $n$-alkanes in surficial sediments from Lake Haruna, Japan, were depleted in $n$-C$_{17}$, an algal biomarker, relative to the hydrocarbon contents of sediment trap material in this lake. Aquatic lipid matter is evidently preferentially degraded during the sinking of particulate material, probably 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.

Comparison of the lipid compositions of aquatic organisms with those of underlying sediments shows degradation trends similar to those found in sediment trap studies. Robinson et al., (1984a) analyzed the lipid contents of bacteria, rotifers, and protozoans from Priest Pot, a eutrophic lake in the English Lake District. They found that shorter carbon-chain $n$-alkanes degrade faster than their longer homologs and that sterols having more than two double bonds do not survive sinking to the lake bottom. Alteration of lipid compositions continues in the sediments of this lake, most intensely in the surface layer. In particular, solvent extractable lipids become less abundant, and “bound” lipids, those that can be isolated only after acid or base hydrolysis of sediment samples, increase. In several lakes, evidence of microbial oxidation of $n$-alkanes, the least reactive type of lipid, has been found in the appearance of sedimentary $n$-alkan-2-ones having chain-length distributions similar to those of their precursor hydrocarbons (Cranwell et al., 1987; Rieley et al., 1991a). Preferential degradation of algal components ultimately biases the geolipid record of organic matter sources retained in the sediments of most lakes. For example, Goossens et al. (1989) showed that land plant lipids dominate the biomarker content of modern sediment from Lake Vechten, The Netherlands, although carbon budgets indicate that land contributions comprise a small part of the total organic carbon input to the lake system.
Changes in geolipid sources vs selective diagenesis

Geolipid compositions reflect the combined effect of original source inputs and selective diagenesis during and after sedimentation. Within the range of geolipid molecular structures, some are less likely to be altered by diagenesis than are others. Comparisons between easily altered and less easily altered molecules help to distinguish diagenetic changes from source changes. Hydrocarbons are generally not as sensitive to diagenetic alteration as are oxygen-containing lipids. Within the $n$-alkane fraction of hydrocarbons, longer-chain-length molecules are less degradable than are their shorter-chain-length counterparts and can preserve evidence of source changes. As an illustration, the dominant $n$-alkane has shifted from $n$-$C_{31}$ in pre-1900 sediments to $n$-$C_{31}$ in modern sediments of Priest Pot, England, as marsh and shore grasses replaced trees as the major source of land-derived organic matter (Cranwell et al., 1987).

In contrast to the long-chain $n$-alkanes, the short-chain components from the algal contributions in this productive lake experience substantial diagenetic losses.

The relative contributions of organic matter from lake and watershed biota affect the biomarker compositions of lake sediments. $n$-Alkanoic acid distributions in sediments of eutrophic Esthwaite Water and Blelham Tarn, England, give similar bimodal patterns having maxima at $C_{16}$ and $C_{24}$ (Cranwell, 1974), representing combinations of aquatic and land-plant sources. In contrast, the distribution found in the sediments of oligotrophic Lake Grasmere has a single maximum at $C_{30}$ indicative of a dominance of land-plant wax lipid input. Furthermore, $n$-alkane distributions provide an approximate record of watershed plant types. In watersheds where grasses dominate, $n$-$C_{31}$ is the major sediment $n$-alkane, whereas $n$-$C_{27}$ and $n$-$C_{30}$ are more abundant in lake sediments where deciduous trees dominate, (Cranwell, 1973a). Measurements of the carbon isotopic contents of individual $n$-alkanes isolated from sediments and from leaf waxes allows source identifications to be more specific. Willow leaves appear to be the major source of the $n$-$C_{25}$ to $n$-$C_{28}$ hydrocarbons present in Ellesmere Lake, England (Rieley et al., 1991b).

Selective microbial utilization and replacement of biomarker components affects geolipid distributions in lake sediments. The $n$-alkane distributions of sediments in oligotrophic lakes Motosu and Biwa, Japan, are dominated by the $C_{30}$, $C_{31}$, and $C_{33}$ components diagnostic of land-plant waxes (Fig. 3; Kawamura and Ishiwatari, 1985). The $n$-alkanol distributions from these two low-productivity lakes contain dominant-to-large proportions of long-chain, plant-wax components as well. The $n$-alkanolic distributions, however, are not similarly dominated by long-chain, land plant components. 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 has 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 $C_{18}$ components. The relatively small contributions of long-chain acids and alcohols indicates that contributions of land-plant lipids are small in Lake Suwa compared to the algal contributions.

Some lipid compounds appear to be particularly resistant to diagenetic alteration in lake sediments. For example, Cranwell (1985) reported the presence of $C_{37}-C_{39}$ unsaturated ketones in the sediments of three lakes, but their absence in those of three others. These compounds have been found in marine locations, where they evidently can retain their molecular integrity in sediments as old as Eocene (Marlowe et al., 1984). Although the specific source of these ketones has not been identified in the lacustrine settings, it is probably from prymnesiophyte algae by analogy to the marine source.

Wax esters are also evidently resistant to diagenetic alteration. Fukushima and Ishiwatari (1984) compared the molecular distributions of the component fatty acids and alcohols comprising the wax esters in surface sediments of three lakes in Japan. Those from oligotrophic Lake Motosu are dominated by the $C_{24}$ $n$-alkanoic acids and $n$-alkanols characteristic of land.

![Fig. 3. 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).]
Lacustrine organic geochemistry

plant epicuticular waxes, whereas those from eutrophic Lake Shoji contain a predominance of the \( n-C_{16} \) components expected from aquatic plants and few of the long-chain, land-plant materials. The sediment from mesotrophic Lake Haruna displays an intermediate wax ester composition, having the \( n-C_{16} \) acid and the \( n-C_{24} \) alkanol as the major contributions to their respective distributions. The wax esters, because of their low solubilities and presumably low susceptibilities to microbial utilization, provide improved records of the original proportions of algal and watershed sources of sedimentary lipids.

Influence of sediment grain size on geolipid compositions

The relationship between sediment grain size and geolipid compositions was investigated by Thompson and Eglinton (1978), who isolated five sediment size fractions from Rostherne Mere, England. The lake is eutrophic, and bottom water anoxia limits benthic reworking of organic matter. \( n \)-Alkane distributions nonetheless contain small amounts of algal components and instead are dominated by \( n-C_{27}, n-C_{29}, \) and \( n-C_{31} \), as shown by long/short ratios significantly greater than one (Table 4). The \( n \)-alkanoic acids, however, are nearly equally made up of algal and land-plant components, giving long/short ratios of close to one. Relatively high carbon preference indices (CPI) indicate the biogenic characters of both the hydrocarbons and the acids are well preserved. Microbial reprocessing of organic matter has evidently degraded many of the short-chain \( n \)-alkanes and has probably replaced much of the original fatty acids with microbial acids. The degree to which these alterations have taken place vary with the sediment size-fractions. In general, land-plant lipid character and total extractable lipid concentrations decrease as particle size diminishes. This pattern is consistent with the decrease in abundance of intact plant detritus and accompanying decrease in C/N ratios in the sediment fractions. The trend towards decreasing concentra-

<table>
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</table>

*\((nC_{14} + nC_{16} + nC_{18})/(nC_{17} + nC_{19} + nC_{21})\).*
†\((n24:0 + n26:0 + n28:0)/(n14:0 + n16:0 + n18:0).\)

Table 4. Characteristics of organic matter associated with different size fractions of Rostherne Mere sediment. Data are from Thompson and Eglinton (1978)

Alkane source records in lake sediments

Because of their low susceptibility to microbial degradation compared with other types of organic matter, saturated hydrocarbons can record many aspects of the depositional history of organic matter which have the highest loadings of \( n \)-alkanes and of fatty acids. The larger surface area per unit weight and the likelihood of a greater abundance of clay minerals probably provide enhanced sorptive capacities for this size fraction.

Two other size-related changes in the lipid compositions are progressive decreases in the ratio of individual \( n \)-alkanes to the unresolved complex mixture (UCM) of hydrocarbons and in the proportion of unsaturated \( n-C_{18} \) acids to their saturated analog. These changes, combined with the decreases in CPI values, suggest that the lipid contents of the finer-sized particles of sediment have experienced more microbial reworking than those of the coarser particles. Finer-sized particles settle more slowly to lake bottoms than coarser ones, increasing the exposure time of their organic contents to such attack. Diminished aliphatic/UCM ratios, in particular, from the finer-sized particles indicate the presence of microbiologically degraded petroleum residues, presumably from run-off of lubricating oil from the roadways in the watershed (Thompson and Eglinton, 1978), although some amount of eolian contribution is also possible for the smaller particles. Similarly, Meyers and Takeuchi (1979) found that finer-grain-sized sediments generally contained higher concentrations of extractable aliphatic, aromatic and UCM hydrocarbons and of extractable fatty acids than did coarser sediments in Lake Huron. In addition, the size of the UCM component of sediment hydrocarbons decreased with distance from the mouth of the major river in Saginaw Bay of Lake Huron, verifying its principal origin from urban run-off.
Fig. 4. Concentrations of total extractable aliphatic hydrocarbons in sediment cores from Lake Washington in urban Seattle and Lake Quinault in rural Washington. Gas chromatographic traces illustrate hydrocarbon distributions in three of these core samples. Carbon numbers of \( n \)-alkanes are indicated on the traces; UCM represents the unresolved complex mixture of hydrocarbons underlying the individual aliphatic hydrocarbon peaks. Most of the increase in Lake Washington hydrocarbon concentrations since ca 1900 is due to the large addition of petroleum residues, indicated by the UCM, to a low background of land plant \( n \)-alkanes, typified by the Lake Quinault hydrocarbon contents. Core sediment ages shown are from \( ^{210}\)Pb dating. Data are from Wakeham (1976).

Fig. 5. Downcore concentrations of total fatty acids and of representative components of the total acids in parts per million of Lake Suwa, Japan, sediment. Ratios of total fatty acid carbon to total organic matter are given as FAC/TOC. Carbon preference indices of total alkanoic acids (CPI\(_H\)), of higher-molecular-weight acids (CPI\(_L\)), and of lower-molecular-weight acids (CPI\(_L\)) are shown. Composition Diversity Indices (CDI) of fatty acids at different core depths are presented. Major shifts in all parameters at a sediment depth of 20 cm record modern eutrophication of Lake Suwa. Microbial reprocessing of fatty acids in surface sediments is also evident from the distribution of \( C_{19} \) acids. Data are from Matsuda and Koyama (1977a, b).
sources in lake sediments. One such example compares hydrocarbon contents of sediment cores from lakes in the State of Washington. Sediments of Lake Quinalt, which is surrounded by a forested and virtually pristine watershed, contain low concentrations of hydrocarbons which are dominated by the C<sub>27</sub> n-alkane diagnostic of tree waxes (Fig. 4; Wakeham, 1976). No significant difference exists in the n-alkane contents of sediments deposited in the early 1800s and in the mid-1970s. In contrast, modern sediments of Lake Washington, which is surrounded by the city of Seattle and its suburbs, have hydrocarbon contents dominated by the unresolved complex mixture (UCM) indicative of petroleum residues (Fig. 4). Anomalously old radiocarbon ages of 15–20 Kyr for the aliphatic hydrocarbon extracts of modern sediments confirm large proportions of fossil hydrocarbons (Wakeham and Carpenter, 1976). Furthermore the contribution of short-chain-length n-alkanes derived from algae is equal to the land-plant n-alkane contributions, suggesting eutrophication of the waters of Lake Washington. In progressively older sediments, the contributions of UCM and short-chain hydrocarbons diminish, until in sediments deposited in the mid-1800s the concentrations and distributions resemble those of Lake Quinalt sediments (Fig. 4). Three sources of hydrocarbons can be identified in these sediments: (1) a natural, low contribution of land-plant n-alkanes as found throughout the sedimentary records of both lakes, (2) an input of petroleum residues from urban run-off, which first appears in the Lake Washington record around 1900 and becomes dominant in modern sediments, (3) algal input of C<sub>17</sub> and C<sub>18</sub> n-alkanes which is usually small in comparison to the land-plant contributions, probably because of selective diagenetic degradation. It becomes large only in the sediments of Lake Washington which were deposited starting ca 1500, when residential population growth led to a two-decade period of eutrophication of the lake and large increases in the algal production of n-C<sub>17</sub>.

**Fatty acid preservation and degradation in lake sediments**

Fatty acids are more sensitive to degradation and modification than most types of biogenic lipids. Some fatty acids are more susceptible to diagenesis than others; comparisons between different components can therefore help to distinguish diagenetic effects from source changes.

The results of a study by Matsuda and Koyama (1977a, b) illustrate some of the effects of diagenesis and of source change on the fatty acid contents of sediments. Concentrations of total fatty acids and of total organic carbon decrease rapidly over the top 25 cm of a 150-cm-long core from Lake Suwa, Japan (Fig. 5). The ratio of fatty acid carbon to total organic carbon also decreases, showing that fatty acids are degraded more readily than total organic matter. Long-chain components, represented by 24:0, 26:0, and 28:0 (number of carbon atoms:number of double bonds) change little with depth, but short-chain acids, such as 15:0, 16:0, and 18:0, decrease markedly. The degradation rates of these latter acids have been estimated in coastal marine sediments to be 6–7 times faster than for the long-chain acids (Haddad et al., 1992). Shorter-chain unsaturated acids, such as 16:1 and 18:1, have higher concentrations than saturated acids of the same carbon chain length in surficial Lake Suwa sediment, but disappear faster than their saturated analogs. In contrast, the concentration of the 24:1 acid appears to experience little change with depth (Fig. 5).

Fatty acids in lake sediments typically originate from several sources. The long-chain components in Lake Suwa sediments are probably from land plants and as such are the non-reactive survivors of transport of land-derived debris to the lake bottom. The shorter-chain components, particularly the alkanolic acids, are products of algal lipidsynthesis in the lake. These lipids are easily metabolized by sediment microbes. The n-15:0 and anteiso-15:0 fatty acids are indicators of microbial biomass (cf. Cranwell, 1973b), and they represent in situ production of secondary lipids at the expense of primary organic matter. Most of the concentration changes occur in the top 25 cm of these sediments, corresponding to ca 60 yr (Matsuda and Koyama, 1977a). Although the decrease in the contribution of fatty acids to total organic matter (FAC/TOC in Fig. 5) is compelling evidence for diagenetic losses of these lipids, it is also probable that there have been source changes as a result of the documented increasing algal productivity of Lake Suwa over this time. The lower concentrations of the C<sub>16</sub> and C<sub>18</sub> acids in deeper sediments may arise jointly from formerly lower production and from diagenetic removal. The similar pattern for the C<sub>17</sub> acids may reflect the presence of larger microbial populations in response to larger amounts of readily metabolized organic matter in younger sediments than in older deposits.

Matsuda and Koyama (1977b) examined the possibility that source changes as well as diagenetic changes impact the downcore fatty acid composition of Lake Suwa sediments. They compared the sediment contents to those of potential source materials, and they present several measures of source vs alteration effects. The Carbon Preference Index (CPI), devised by Bray and Evans (1961) to indicate the degree of diagenetic alteration of n-alkanes, can be modified for similar application to n-alkanoic acids. This index is essentially a numerical representation of how much of the original biological chainlength specificity is preserved in geological lipids. In fresh lipid material, odd-numbered carbon chains dominate hydrocarbon compositions and even-numbered chains dominate compositions of fatty acids and alcohols. This specificity diminishes as diagenesis proceeds.

Matsuda and Koyama (1977b) modified the Carbon Preference Index (Fig. 5) to test for the presence
of source changes as well as diagenetic effects. They separated fatty acids into their lower molecular weight (C₁₇-C₁₉) and higher molecular weight (C₂₂-C₃₂) groups as CPIₗ and CPIₜ, respectively. In the lipid content of most plants, CPIₗ values are high, ranging between 12 and 0.1; CPIₜ values are not as high, being between 0.9 and 8, because of the presence of long-chain odd-carbon acids in some land plants. Bacteria generally have low CPI values, and therefore bacterial reworking of sediment organic matter results in lowered CPI values.

The downcore CPI profiles in the sediments of Lake Suwa are variable (Fig. 5), and they are lower than CPI values of potential source materials. The variability indicates that a combination of source changes and of changes in the degree of microbial reworking is involved. The index for all n-alkanionic acids, CPI₁, is similar to CPIₗ in the upper ca 20 cm of sediment and becomes more like that of CPIₜ in sediments lower than 25 cm in the core. The generally lower CPI values below 25 cm imply that microbial resynthesis of fatty acids has been important in erasing the original compositions. Much of this resynthesis evidently occurred in the upper part of this core.

A Composition Diversity Index (CDI) was also employed by Matsuda and Koyama (1977b) to evaluate the possibility of changes in sources of fatty acid inputs to the Lake Suwa sediments. The downcore CDI values are shown in Fig. 5. Higher values below ca 20 cm indicate a greater diversity of sources. Matsuda and Koyama (1977b) interpreted this pattern to reflect the addition of microbial contributions to the sediment contents. This interpretation is consistent with the downcore CPIs, yet both patterns could also arise from increased algal production in modern times. Higher concentrations of C₁₆₀ between 75 and 100 cm in the core accompany higher percent FAC/TOC, higher CPIs, and lower CDIs (Fig. 5). These parameters suggest substantial preservation of the record of fatty acid contributions to the deeper sediments of this lake. On this basis, the CPI and CDI trends may record eutrophication as well as microbial inputs. Original fatty acid source indicators appear not to have been totally replaced by microbial components in this example, probably because of the relatively rapid sedimentation rate in Lake Suwa (ca 4 mm/yr: Matsuda and Koyama, 1977a).

Unsaturated fatty acids are generally more susceptible to alteration in sediments than are saturated acids of the same chainlengths. Unsaturated n-C₁₆ and n-C₁₈ acids are major constituents of the lipids of freshwater algae, and they are rapidly degraded by microbial attack (Cranwell, 1976). In a dated core of sediments from Lake Haruna, Japan, ratios of C₁₆₁, C₁₈₁, C₁₈₂, and C₁₈₃ to their corresponding alkanoic acids decrease by a factor of 10 in the upper 8 cm of sediment. Little unsaturated acid remained below this depth, corresponding to 120 yr of accumulation, and consequently the ratios decreased much more slowly (Kawamura et al., 1980). The change with depth found in Lake Haruna sediments is similar to the unsaturated-to-saturated change illustrated by Lake Suwa sediments (Fig. 5) and found in sediments of Lake Huron (Meyers et al., 1980c). The existence of carbon–carbon double bonds evidently facilitates microbial utilization of these lipids and enhances their degradability.

Variations in factors such as sedimentation rates and degree of lake water oxygenation impact the preservation of the relatively reactive fatty acids incorporated in sediments laid down at different times. Mendoza et al. (1987) reported fatty acid compositions of a core of sediment from Lake Leman, Switzerland, which illustrate the effects of changing sedimentation rates. Concentrations of lower-molecular-weight and higher-molecular-weight acids begin to decrease in the expected diagenetic pattern over the top meter of this core, but they increase in sediments between 2.5 and 3.5 m deep, presumably because of an interlude of higher sedimentation rate. Unsaturated n-C₁₆ and
Fig. 7. Representative sterol compounds which have been detected in lacustrine sediments. C27 compounds (e.g., cholesterol) generally dominate the sterol compositions of aquatic plants, whereas C29 compounds (e.g., sitosterols) constitute most of the sterols of land plants. Other sterols give greater source specificity. Dinosterol, for example, is indicative of dinoflagellate production.

Sources and diagenesis of sterols in lacustrine sediments

Sterols and their derivatives are important geochemical biomarker compounds. 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 C17 position, and the stereochemistry of the substituent bonds create a variety of geochemically useful compounds (Fig. 7). The structural diversity of sterols and their derivatives provides opportunities to infer sources and diagenetic pathways of organic matter in sediments. The same diversity, however, has presented analytical challenges which have limited the widespread application of sterol biomarkers in lacustrine organic geochemistry.

Sterols extracted from cores of lake sediments have revealed changes in the sources of these biomarker compounds in sediments deposited at different times. The sources of total organic matter to the sediment presumably also changed, although not necessarily exactly in the same fashion as the sterol sources. In a study of sediments of Lake Leman, Switzerland, Mermoud et al. (1985) noted that epicholestanol (Fig. 7) is present in surficial sections of a core from an 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 enabled anaerobic bacteria to produce this uncommon sterol. A 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 bacterial 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 source organism
is not known in freshwater systems. Both of the sterol precursors of the saturated stanols are commonly considered to be indicators of marine algae; freshwater algae evidently also synthesize the precursors. The absence of aplystanol in the upper parts of the core suggests that the unidentified freshwater organism that synthesizes the precursor compound no longer populates Motte Lake.

Sterol compositions have been used to distinguish aquatic sources of organic matter in sediments from land sources. Comparisons of algae and vascular plants from the Lake Suwa (Japan) area showed that cholesterol is the dominant algal sterol whereas 24-ethylcholesterol (β-sitosterol) is the major sterol in emergent water plants and in land plants (Nishimura and Koyama, 1977; Nishimura, 1977a). Similarly, Rieley et al., (1991a) reported that many leaf waxes contain C29 and C27 sterols but lack C27 sterols. This difference has been applied by Nishimura (1977b) to infer that the sediments of alpine, oligotrophic Lake Shirakome-ike contain largely land-derived organic matter, which is consistent with known sources of sediments.

The distinction between algal and higher plant sterol compositions has become blurred, however, as new sources of biomarker sterols are identified. Some marine phytoplankton can synthesize ethylcholesterols (e.g., de Leeuw and Baas, 1986; Volkman, 1986), and some lacustrine algae appear to have this capability. Matsumoto et al. (1982) have identified 24-ethylcholesterol as the dominant sterol in sediments and epibenthic blue-green algae from saline lakes in Victoria Land, Antarctica. Absence of land vegetation rules out contributions of organic matter from living vascular plants to the sediments of these lakes, yet the ratios of C29/C27 sterols (between 1.4 and 7.2) mimic those of temperate zone lakes known to receive terrigenous organic matter. Dinosterol (Fig. 7) is the major component of a group of 4α-methyl sterols present in freshwater dinoflagellate algae (e.g., Robinson et al., 1984b, 1987); closely related 4α-methyl sterols have also been identified in marine prymnesiophyte algae (Volkman et al., 1990) and in a submerged vascular plant from Motte Lake (Klink et al., 1993).

Several diagenetic changes occur to the sterol contents of lake sediments. The concentration of sterols decreases relative to total organic carbon (e.g., Nishimura, 1977a), although not as fast as the decreases of linear alcohols or fatty acids (Cranwell, 1981; Leenheer and Meyers, 1983). Another important change is the conversion of sterols, the unsaturated biological form of most sterols, into stanols, the hydrogenated analog. This conversion evidently begins in the water column (e.g., Robinson et al., 1984a, 1986; Wünsche et al., 1987), with the consequence that both sterols and derived stanols are common in surficial lacustrine sediments.

The rapid diagenetic alteration of biological sterols into their geochemical derivatives implies that microbes are responsible. A variety of steroid compounds have been identified in the surficial mixed layer of sediments in Lake Haruna, Japan (Meyers and Ishiwatari, 1993). Many of these compounds are intermediates in alteration pathways that will lead to either saturation or aromatization of the steroid carbon skeleton and hence improved geochemical stability. Evidence of both reductive and oxidative pathways is present, but simple chemical disproportionation is unlikely in view of the intermediate molecules. Instead, the coexistence of both pathways indicates that a complex microbial assemblage is present in the lake sediments. Nearly all of the Lake Haruna steroids are intermediates in the diagenetic pathways described by Mackenzie et al. (1982) and Brassell et al. (1983), except that a steroid diketone is a newly identified compound. Steranes are absent in the Lake Haruna sediments, and their absence indicates that these hydrocarbons are products of later diagenesis.

Conversion of stanols to sterols and the resulting enhanced stabilization of the sterol carbon skeleton continues after burial in lake sediments. The stanol/sterol ratio is ca 50 in diatoms from Lake Suwa, Japan, but drops to 5 in surficial sediments (Nishimura and Koyama, 1976). The stanol/sterol ratio decreases to 2 in the upper 30 cm of the 150 cm long sediment core and remains constant with greater depth. A similar total organic carbon pattern suggests that microbial reprocessing of organic matter is largely responsible for the decrease in the stanol/sterol ratio. Microbially mediated hydrogenation of sterols has been postulated to be part of this reprocessing (e.g., Gaskell and Eglinton, 1976; Nishimura and Koyama, 1977; Reed, 1977; Nishimura, 1977b; Rieley et al., 1991a). Hydrogenation of the Δ4 double bond (Fig. 7) yields sterols having 5α(H) and 5β(H) configurations. Hydrogenation in oxygenated sedimentary environments favors the 5α form (Reed, 1977), whereas the 5β form is favored in strongly anoxic sediments (Reed, 1977; Nishimura, 1982). An additional factor contributing to the decrease in stanol/sterol ratio is preferential preservation of the small amount of stanols synthesized by organisms (Nishimura and Koyama, 1977; Nishimura, 1977b; Reed et al., 1984b). Preferential preservation may also explain why stanol/sterol ratios of aquatic C27 sterols decrease more rapidly in sediments than do those of land-derived C29 sterols (Nishimura, 1978; Leenheer and Meyers, 1983).

Sterols and sterol derivatives in sediments provide information about lake conditions of the past. Surface sediments from Rostherne Mere, England, are dominated by cholesterol, campesterol, and β-sitosterol (Gaskell and Eglinton, 1976). In deeper sections, the contribution of cholesterol diminishes, indicating that the aquatic productivity was formerly less than the modern, high level. Sterol and stanol distributions are the same at each sediment depth horizon, although total sterol concentrations decrease with
Fig. 8. Concentrations of total organic matter (T.O.M.), perylene, and three pyrolytic polycyclic aromatic hydrocarbons (PAH) in a dated sediment core from Coburn Mountain Pond, Maine. The progressive increase in perylene concentration as sediment age increases indicates diagenetic formation of this PAH. The concentration maxima of the three pyrolytically formed PAHs coincides with the time of peak coal combustion. Data are compiled from Norton et al. (1981), Gschwend and Hites (1981), and Gschwend et al. (1983).

Sources and diagenesis of polycyclic aromatic hydrocarbons in lake sediments

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous components of both marine and lacustrine sediments (e.g., Laflamme and Hites, 1978; Hites et al., 1980), yet these compounds do not occur naturally in organisms. PAHs are produced by diagenesis and not by biosynthesis. Individual PAHs are created by one of three processes: (1) early diagenesis from biogenic precursors, (2) later diagenesis over long periods of geological time, and (3) high-temperature processes which reconstitute organic matter fragments into characteristic PAH distributions. Nearly all PAH molecules fit into one of these three categories (e.g., Wakeham et al., 1980a, b; Tan and Heit, 1981; Furlong et al., 1987), making these compounds especially useful as indicators of geochemical transport and transformation processes.

Sedimentary PAH accumulations record contributions from the different source categories. The sediments of Coburn Mountain Pond, Maine, record two types of PAH input (Gschwend and Hites, 1981;
Gschwend et al., 1983). The concentration of perylene increases regularly with depth in a half-meter core, which corresponds to about 200 yr of deposition (Fig. 8). Perylene is the diagenetic product of some unknown biogenic precursor, possibly an erythraophin plant pigment (e.g., Aizenshstat, 1973). Its increase with depth reflects relatively slow in situ formation via either a first-order or a second-order reaction requiring anoxic conditions (Gschwend et al., 1983). Surficial sediments consequently contain no perylene. In contrast to the perylene profile, concentrations of pyrolytically-derived benzo(a)pyrene, chrysene, and pyrene decrease with depth after peaking at a depositional horizon corresponding to ca 1958 (Fig. 8). This pattern records the history of coal combustion in the northern United States and air-borne transport of combustion products to isolated depositional sites, such as Mountain Pond (Gschwend and Hites, 1981; Furlong et al., 1987). The preservation of this record attests to the low reactivity of aromatic hydrocarbons once they have been formed and deposited.

Sediments of Sagamore Lake in Adirondack Park of northern New York State contain three types of downcore PAH patterns (Tan and Heit, 1981). Perylene increases in concentration to a core depth of 35 cm, corresponding to a sediment age of about 85 yr, and then decreases to the bottom of the 75 cm core (Fig. 9). The decrease in concentration indicates that its older sediments contained less of the unknown precursor. Diagenetic degradation of perylene is unlikely inasmuch as a similar decrease does not occur in the older Mountain Pond sediments. The concentrations of the pyrolytic PAHs fluoranthene and benzo(a)pyrene are highest at the surface of this 1978 core and drop to low and nearly constant values by a core depth of 15 cm. The pyrolytic PAH patterns reflect greater fossil fuel combustion in more modern times. Non-alkylated forms dominate the fluoranthene and pyrene PAH families, clearly identifying a high-temperature source, as opposed to a geologically older, low-temperature source (Tan and Heit, 1981).
Concentrations of retene, dimethyl octahydrochrysene, and trimethyl tetrahydropicene vary little over the Sagamore Lake sedimentary record (Fig. 9), suggesting that these compounds are produced quickly in sediments and are the relatively stable products of diagenesis. The postulated precursor of retene is abietic acid, a component of pine resin (Simoniet, 1977; Wakeham et al., 1980a). The biogenic precursors for chrysene and picene are not confirmed; \( \alpha \)-amyrin, present in woody plants, is a possible source (Spyckereille et al., 1977). Postulated diagenetic pathways for the three types of biogenic PAHs found in Sagamore Lake sediments are summarized in Fig. 10. Many of the intermediate compounds have been identified (Tan and Heit, 1981), giving credence to these hypothetical transformations. \( \beta \)-Amyrin can be an additional precursor for hydrochrysene, especially in lakes having a large fraction of deciduous trees in their watersheds. \( \beta \)-Amyrin is abundant in the sediments of Lake Biwa, Japan, and is the major source of hydrochrysene in this lake (Ishiwatari, unpublished). Hydropicene cannot be derived from \( \beta \)-amyrin, however, because the positions of the two methyl groups on its saturated E-ring clearly reflect an origin from \( \alpha \)-amyrin.

**Source information in “free” and “bound” geolipid fractions of lake sediments**

Many of the lipid components of biological organic matter are biochemically bound into the structural matrices of the cells and cell walls of organisms. Geochemical studies generally ignore such bonds.

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Fig. 11. Chromatograms of total free and bound lipids isolated from a section of sediment core from Heart Lake, New York. \( n \)-Alkanoic acids are identified as 16:0, 18:0, etc., where the carbon chainlengths are given by 16, 18, etc. \( n \)-Alkanes are identified as \( C_{17}, C_{29}, \) etc. The free lipid fraction contains a greater proportion of long-chain, land-plant components than does the bound fraction. (Meyers, unpublished.)
and instead concentrate on the molecules released by hydrolysis of sediment extracts. Important geochemical information potentially can be obtained from geolipids in which the original biochemical bonds are not destroyed during isolation and analysis.

A two-step sediment extraction procedure is commonly employed to preserve some of the original biochemical associations of geolipids. In the first step, solvent extraction is done to obtain the soluble geolipid components. These include truly free molecules having no bonds with other compounds and also molecules which are chemically combined with others, yet can be dissolved in the solvents. This fraction is called the “free” or “solvent-extractable” lipids. The second step uses hot acid or base to break hydrolyzable bonds, followed by a second solvent extraction. These lipids are normally called the “bound” or “non-solvent-extractable” fraction. The additional lipids obtained by the hydrolysis procedure include materials incorporated into humic substances, retained in biological detritus, and associated with minerals.

The free and bound geolipid fractions of sediment organic matter generally have different sources. The free fraction contains a large proportion of land-plant biomarker material, whereas the bound fraction is constituted mostly of algal and bacterial components (Cranwell, 1978, 1984; Ishiwatari et al., 1980; Cranwell et al., 1987; Wünsche et al., 1988). A comparison of the n-alkanoic acid and n-alkane contents in sediment from Heart Lake, New York, shows that the free geolipids are dominated by long-chain components diagnostic of land-plant epicuticular waxes (Fig. 11; Meyers, unpublished). The bound geolipids are dominated by short-chain, algal biomarkers.

The ratio of free-to-bound geolipids commonly decreases with depth in lake sediments, indicating either that free components become diagenetically converted into bound forms (e.g., Cranwell et al., 1987) or that components of the free fraction are preferentially destroyed. This pattern is not universally found, however (e.g., Meyers et al., 1984b; Wünsche et al., 1988). Complicated source and preservation effects appear to influence sediment geolipid fractions. Free and bound geolipids in sediments from

Fig. 12. Concentrations of free (—) and bound (---) n-alkanes, n-alkanols, n-alkanoic acids, and total organic matter (T.O.M.) in sediments of Heart Lake, New York Postglacial pollen zones and changes in diatom abundance are shown with radiocarbon ages. The lack of correlation between the lipid fractions and the microfossil components indicates that complicated source and preservation changes impact the lipid compositions of the organic-carbon-rich sediments. Data are from Meyers et al. (1984b).

![Chlorophyll a](image)

Chlorophyll a

**Tetapyrrole Ring**

**Phytol Sidechain**

 ![β-Carotene](image)

β-Carotene

![Lutein](image)

Lutein

![Fucanxanthin](image)

Fucanxanthin

Fig. 13. Molecular structures of representative types of pigments found in lake sediments. The chlorophylls are the primary photosynthetic pigments.
Heart Lake do not show progressive downcore decreases (Fig. 12). Bound hydrocarbons are nearly always present in this example, even though hydrocarbons cannot be chemically bonded to other compounds. As suggested by Cranwell (1978), the bound materials may represent the contents of intact biological debris and therefore may be strongly influenced by fluctuations in preservational conditions.

Intact esterified geolipids are a specific type of bound material that has been studied for biomarker source information. Compositions of fatty acid esters of alkanols, sterols, and triterpenols isolated from lake sediments as old as 50 Kyr indicate that the ester linkage, combined with the high molecular weights of the esters, enhances the resistance of bound lipids to microbial attack (Cranwell, 1986; Cranwell and Volkman, 1981). These ester-linked biomarker compounds consequently retain evidence of their respective algal or vascular plant origins. Bacterial biomarkers constitute little of the ester fraction, principally because these organisms do not synthesize large amounts of esters. Selective losses of lower-molecular-weight esters have nonetheless been inferred from surprisingly low contributions of algal ester biomarkers in sediments of Tokyo Bay (Fukushima and Ishiwatari, 1984).

**SOURCES AND ALTERATIONS OF PIGMENTS IN LAKE SEDIMENTS**

Higher plants and algae synthesize a variety of pigmented organic compounds, principally for use in photosynthesis. Some of these molecules serve as biomarkers specific to various types of plants. 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. 13). The double bonds and functional groups provide sites for microbial attack, making these compounds especially susceptible to diagenetic alterations. Despite this lability, a portion of the pigment input to lakes can become diagenetically more stable. The major types of stabilizing alterations are complete aromatization of the chlorophyll tetrapyrrole ring leading to porphyrins and hydrogenation of carotenoid chains to form isoprenoid alkanes. These stabilized products of diagenesis are found in ancient lake sediments, but not in young sediments. The transformations proceed slowly.

The principal photosynthetic pigments used by plants are the chlorophylls, of which chlorophyll a (Fig. 13) is the most common. The various chlorophylls differ principally in the alkyl sidechains attached to the central tetrapyrrole ring; chlorophyll a has the diterpenoid alcohol, phytol, attached by an ester linkage. 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 which they utilize as accessory pigments to broaden the range of wavelengths useful for photosynthesis (Table 5).

**Table 5. Selected pigments indicative of different types of freshwater algae (compiled from Schwendener, 1969; Züllig, 1981, and Leavitt et al., 1989)**

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Taxa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorophyll a</td>
<td>Plantae</td>
</tr>
<tr>
<td>Chlorophyll b</td>
<td>Trachophyta, Chlorophyta, Euglenophyta</td>
</tr>
<tr>
<td>Chlorophyll c</td>
<td>Chrysophyta, Pyrrophyta</td>
</tr>
<tr>
<td>Alloxanthin</td>
<td>Cryptophyta</td>
</tr>
<tr>
<td>Fucoxanthin</td>
<td>Chrysophyta</td>
</tr>
<tr>
<td>Lutein</td>
<td>Chlorophyta, Charophyta, Euglenophyta</td>
</tr>
<tr>
<td>Peridinin</td>
<td>Pyrrophyta</td>
</tr>
<tr>
<td>β-Carotene</td>
<td>Plantae</td>
</tr>
<tr>
<td>Myxoxanthophyll</td>
<td>Cyanophyta</td>
</tr>
<tr>
<td>Canthexanthin</td>
<td>Cyanophyta</td>
</tr>
<tr>
<td>Oscillaxanthin</td>
<td>Cyanophyta</td>
</tr>
</tbody>
</table>
Both source changes and the effects of diagenesis are recorded in the pigment contents of lake sediments. Sanger (1988) reviewed the factors important to the accumulation of pigments in lacustrine sediments. In general, lakes having higher aquatic productivities contain greater proportions of pigments in their sedimented organic matter (e.g., Gorham et al., 1974; Gorham and Sanger, 1976). Land-derived pigments do not typically survive transport to lakes. Even lake-derived pigments are rapidly degraded if they are not quickly carried to the lake bottom; Carpenter et al. (1986) found that photodegradation of chlorophyll derivatives was virtually complete after only three days in the photic zones of three lakes in southern Michigan. 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 lacustrine sediments (e.g., Leavitt et al., 1989). After incorporation in lake 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. The interaction of source and preservation factors is complex. Similar changes in the proportions of chlorophyll and carotenoid components of total organic matter in sediments from Brown Pond, Ohio, suggest that both production and preservation are linked (Fig. 14), although a progressive diagenetic effect for these reactive materials is not obvious.

Changes in algal populations can be recorded in pigment compositions. 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. 15). Diminished concentrations in the uppermost, most eutrophic sediments may result from replacement of cyanophytes by other algae (Griffiths, 1978), or this decrease may be due to a preservational effect. A related history of the development of eutrophication in Zürichsee, Switzerland, has been described from the pigments contained in a century-long core of sediment (Züllig, 1981). In this case, 10 different pigment groups were utilized 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 paleolimnological conditions extending back thousands of years. Pigments in the sediments of Kirchner Bog, Minnesota, for example, contain a history of postglacial plant succession spanning nearly 14 Kyr (Sanger and Gorham, 1972).

### SOURCE INFORMATION AND DIAGENESIS OF LIGNINS AND THEIR DERIVATIVES

Lignins are phenolic polymers synthesized by higher plants as part of their vascular systems. Nearly
all vascular plants grow on land, and therefore these compounds record contributions of land-derived organic matter to sediments. Gymnosperms (non-flowering plants) and angiosperms (flowering plants) synthesize different types of lignin, so past changes in watershed vegetation can be inferred from the lignin contents of sediments. Lignin is relatively resistant to diagenesis, making its sedimentary record longer-lived than many other forms of primary organic matter.

Because lignin is a polymer, its characterization typically involves oxidative depolymerization to release various phenolic aldehyde, ketone, and acid monomers like those illustrated in Fig. 16. Monomers have been grouped by Hedges and Mann (1979) to identify the general vascular plant sources of sedimentary lignins (Fig. 17). The sum of p-coumaric acid plus ferulic acid concentrations divided by the sum of the three vanillyl phenols gives the C/V ratio, a measure of the relative contributions of woody and non-woody plant tissues. The sum of the amounts of the three syringyl phenols divided by the sum of the vanillyl phenols is the S/V ratio, which distinguishes between gymnosperm and angiosperm sources of plant tissues. 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, 1984).

A drilled core of sediment from Lake Biwa, Japan, has provided a unique opportunity to investigate the record of lignin source and diagenetic changes over a long period of time. The core was obtained during 1982–1983, and 430 Kya is the extrapolated basal age of the T Bed, a continuous sedimentary unit representing lake conditions similar to the present (Meyers et al., 1993). Lignin contents were characterized in the T Bed and the underlying S and R Beds by Ishiwatari and Uzaki (1987). The latter two beds are discontinuous and represent shallow-water or fluvial conditions; a fission-track age at 681 m in the R Bed is 2.4 My (Takemura, 1990).

Accumulation of organic matter was fairly uniform over the entire history of the T Bed; organic carbon concentrations are generally between 0.5 and 1%, and C/N ratios remain about 10 (Fig. 18). In the coarser S and R Beds, organic carbon values are slightly lower, and the higher C/N ratios indicate a greater proportion of land-plant matter. The contribution of lignin to the total organic matter drops steadily with depth in the T Bed, evidently because of diagenesis, inasmuch as the S/V and C/V ratios indicate that the lignin composition does not change. Ishiwatari and Uzaki (1987) calculated a lignin half-life of 400 Kyr on the assumption that in situ degradation is responsible for this decrease. Their value is based on an earlier estimate of a basal age of 600 Kyr for the T Bed; a recalculated half-life is 300 Kyr. These values indicate the potential longevity of lignins in lacustrine sediments.

An increase in the ratio of vanillic acid to vanillin (Ad/Al), indicates that selective diagenesis of lignin components occurs in Lake Biwa sediments (Fig. 18). Vanillic acid is the more oxidized component in this ratio; its increase suggests continued oxidative degradation of lignins. Furthermore, the (Ad/Al), ratio is above 0.5 throughout the core, which is substantially higher than in fresh plant material (0.15; Hedges et al., 1982). The elevated (Ad/Al), values indicate that the lignins delivered to Lake Biwa have been extensively oxidized prior to deposition. In wood buried in sediments for up to 25 Kyr, as much as 30% of the original syringyl phenols can be lost from lignins, whereas vanillyl components are preserved better (Hedges et al., 1985). Although these types of selective diagenesis can jeopardize source identification, the low S/V ratios in Lake Biwa sediments agree with pollen data.

Fig. 17. The relationships between the lignin parameters S/V, C/V, and their general plant source assignments. S/V is the sum of syringyl phenols divided by the sum of vanillyl phenols; C/V is the sum of p-coumaric acid and ferulic acid divided by the sum of vanillyl phenols. Data adapted from Hedges and Mann (1979).

Fig. 18. Downcore comparisons of organic carbon (TOC), atomic C/N ratios, total lignin derivatives, S/V, C/V, and the Ad/Al ratio for vanillyl phenols from sediments of Lake Biwa, Japan. The T Bed is a continuously deposited deepwater clay layer representing the last 430 Kyr of lake history. Increase in the lignin/TOC ratio indicates gradual degradation of lignin. Variations in organic matter parameters in the S and R Beds reflect varying inputs under shallow-water depositional conditions. The sediment is dated at 2.4 Myr at a core depth of 681 m. Data are from Ishiwatari and Uzaki (1987).
and indicate a dominance of gymnosperm sources of organic matter to these sediments (Ishiwatari and Uzaki, 1987).

**DIAGENESIS OF CARBOHYDRATES AND PROTEINS IN LAKE SEDIMENTS**

Carbohydrates and proteins are two important types of biologically synthesized organic matter. Carbohydrates encompass simple sugars, which are water-soluble and reactive compounds, and complex sugars having high molecular weights, which are consequently relatively insoluble and less reactive. The simple sugars are both produced and destroyed rapidly within sediment microcosms, with the result that the source and alteration pathways of these carbohydrate forms are difficult to decipher. Proteins, made up of amino acid units, can be similarly reactive. Interconversion between different amino acids is common, again obscuring information about source and diagenesis. Both carbohydrate and protein compounds decrease relative to total organic carbon in sediments of Mangrove Lake (Fig. 1) and in general appear to decompose rapidly in lacustrine sediments (cf. Kemp and Johnston, 1979; Hatcher et al., 1982).

Attempts to link amino acid compositions of sediments to those of likely plant sources have not been successful. Casagrande and Given (1980) compared amino acids contained in peat deposits with compounds obtained from swamp grass and mangrove trees. Their conclusion was that the bulk of the peat amino acids were produced by microbes. Primary source patterns had been erased. The secondary amino acids, however, were produced as part of the sedimentation process and were approximately the same age as the peat deposits.

The contemporary formation of amino acids by benthic biota permits their use to date sediments through the racemization of the stereochernical specificity of biosynthesized amino acids. The slow-acting process, by which the original L-amino acids are converted to an equal mixture of L- and D-forms, is usually not applicable to lake sediments because of their geologically limited ages. In some situations, however, it can be useful. For example, McCoy (1987) employed epimerization of L-isoleucine to D-alloisoleucine in fossil gastropod shells to conclude that some Lake Bonneville sediments date from before 2 Mya, confirming the antiquity of this lake.

Monosaccharide compositions of potential source organisms have been explored for their potential as tracers of organic matter inputs to sediments. Cowie and Hedges (1984) examined plankton, bacteria, and land plants for distinctive sugar compositions. They found that aquatic and land sources could be distinguished in coastal marine sediments. A similar source study in two Minnesota lakes found, however, that no correlation existed between the monosaccharides of dominant aquatic plants and those of sediments (Rogers, 1965). Concentrations of total sugars in the lake sediments appeared to reflect the amount of post-depositional degradation rather than initial contributions. The reactivity of even complex carbohydrates is shown by losses of 90–98% of the original polysaccharide contents of wood buried in sediments for ca 2500 yr (Hedges et al., 1985).

**PALEOLIMNOLOGICAL ORGANIC GEOCHEMISTRY**

The amounts and types of organic matter in lake sediments provide an integrated history of past life and conditions in and around each lake. Multi-dimensional organic geochemical studies have been

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Fig. 19. Concentrations of total organic carbon (TOC), δ¹³C_organic, total pollen, total n-alkanes, lower-molecular-weight fatty acids (LFA), and higher-molecular-weight fatty acids (HFA) in the 200 m core of Lake Biwa sediment. Organic carbon isotope values are included. LFA and HFA are given as μg of n-alkanoic acid per g total organic matter (TOM), which is estimated as TOC × 1.67. Enhanced contributions of HFA suggest larger amounts of land-plant lipids were delivered to the lake sediments at times in the past which were coincident with enhanced pollen inputs. Enhanced contributions of LFA, in contrast, suggest larger amounts of lake-derived lipids, most notably during the past 15 Kyr. Data are from Kawamura and Ishiwatari (1984) and Ishiwatari and Uzaki (1987).
done on sediments from a number of lakes. Indications of changes in the trophic status of these lakes and of changes in the watersheds around them have emerged from the organic matter records documented by these studies. Lake Biwa, Lake Greifen, Lake Washington, and the North American Great Lakes are examples of lakes that have been the subjects of a large number of organic geochemical determinations.

The record of organic matter accumulation in Lake Biwa (Biwa-ko)

Lake Biwa, the largest lake in Japan, has been the subject of paleolimnological studies for over 4 decades. Much of the watershed is forest or farmland, but the fraction containing human settlement has grown greatly since the 1950s. The maximum water depth is 102 m, and the surface area of the lake is 674 km². The lake has existed for ca 6 Myr, although major tectonic reorganizations of its basin have evidently occurred (e.g., Takemura, 1990), which have interrupted the sedimentary record. Organic geochemical studies have concentrated on the upper 250 m of sediments, which is an apparently continuous sedimentary record of the past ca 430 Kyr (Meyers et al., 1993). The results of a number of these investigations are reviewed by Ishiwatari and Ogura (1984) and Ishiwatari (1991).

Organic carbon δ¹³C values change from −25.5%o in near-surface sediments to ca −28%o at 200 m (Fig. 19). A progressive change in organic matter source or diagenesis is not evident from organic carbon concentrations, C/N ratios, or C/V and S/V ratios, all of which remain virtually unchanged (Fig. 18). Nakai (1972) postulated that the local climate has become progressively warmer over the past 400 Kyr, warming the surface waters of the lake and decreasing the kinetic isotopic fractionation by algae, but the pollen record does not confirm this suggestion. The carbon isotope shift is nonetheless intriguing and suggests that some sort of progressive paleoenvironmental change has occurred.

Several episodes of comparatively short-term paleolimnological change are recorded in Lake Biwa sediments. Organic carbon concentrations are typically ca 1% but rise to ca 2% at two core intervals, between 3–15 m and 80–90 m (Fig. 19). Maximum pollen concentrations and heavier carbon isotope values also occur at the 80–90 m depth (Fig. 19). Total n-alkane concentrations similarly increase with depth to a maximum between 3 and 15 m and increase again at 80–90 m. n-Alkane distributions are dominated by C₃₀ or C₃₁ (Kawamura and Ishiwatari, 1984), which are diagnostic of land-plant waxes from trees or shrubs (C₃₀) or grasses (C₃₁).

Possible changes in the sources of the n-alkanoic acids in these sediments have been explored by dividing them into two groups (Kawamura and Ishiwatari, 1984). The lower-molecular-weight fatty acids indicative of algae (C₁₂–C₁₈) are the first group (LFA), and the higher-molecular-weight acids (C₂₀–C₃₂) corresponding to land-plant contributions are the second group (HFA). Concentrations of the LFAs decrease with depth relative to total organic matter, whereas the HFA concentrations peak at about 100 m. The agreement between pollen concentrations and land-plant contributions of n-alkanes and n-alkanoic acids in sediments between 80 and 90 m indicates that inputs of organic matter from watershed vegetation were elevated during this time. Meyers et al. (1993) have concluded that this sediment interval corresponds to the interglacial episode ca 120 Kya and a wetter climate than during the subsequent glacial period.

Important features of the upper 20 m of Lake Biwa sediments include peak values of organic carbon and LFAs (Fig. 19) and the maximum concentration of diatom frustules (Mori and Horie, 1975). These features, combined with C/N values averaging 8.5 in this interval (Kawamura and Ishiwatari, 1981), indicate that aquatic production has been the principal source of sediment organic matter. Long-chain n-alkanoic acids (HFA) change little relative to total organic matter, but the C₁₂-C₁₅ acids (LFA) decrease by a factor of four (Fig. 19), indicating that diagenetic losses are severe for the LFAs. Kawamura and Ishiwatari (1981) noted that some oxidation of n-alkanoic acids to hydroxy acids and dicarboxylic acids may occur over the top 5 m of this core, but most of the loss of LFAs is from microbial alteration to non-fatty-acid forms of carbon. Conversion of fatty acids from free to bound forms does not occur during the 20–30 Kyr period represented by the upper 20 m of these sediments.

Despite the evidence for major losses of short-chain saturated fatty acids, unsaturated acids exist throughout the upper 20 m of Lake Biwa sediment. The proportion of polyunsaturated acids commonly increases in algae as water temperatures decrease as a biochemical response to maintain fluidity of cell membranes. Kawamura and Ishiwatari (1981)
proposed that variations in the ratio of sedimentary $n$-$C_{18}$ and $n$-$C_{16}$ acids may provide a lake paleotemperature record. This ratio compares well to the proportion of boreal conifer pollen in the sediments (Fig. 20). If diagenesis were the dominant factor, then a continual decrease in the unsaturated/saturated ratio would be present. The fluctuations evident in Fig. 20 indicate that source changes contribute to the relative concentrations of these fatty acids. The $C_{18}/C_{16}$ ratio appears to record periods of cooler surface water in the history of Lake Biwa, but the ratio is progressively diminished by preferential degradation of the unsaturated acid with greater age of the sediment.

The record of organic matter accumulation in Lake Greifen (Greifensee)

Lake Greifen is a small eutrophic lake which is located in a heavily populated region 12 km east of Zürich, Switzerland. It has a surface area of 8.6 km$^2$ and a maximum depth of 32 m. A 6.4 m-long core from near the center of Lake Greifen contains three main stratigraphic units: a sapropelic mud from 0 to 60 cm, a carbonate ooze from 60 to 350 cm, and a postglacial clay from 350 to 640 cm.

Concentrations of organic carbon generally decrease with depth in this core, but the most significant downcore changes are found in the compositions of the hydrocarbons in each of the three layers (Fig. 21). In the upper sediment unit, $n$-$C_{17}$ is the dominant alkane and reflects the high rates of algal production in this eutrophic lake. Concentrations of this algal biomarker decrease in deeper sediments and record times when the lake evidently was oligotrophic. Part of the decrease in contributions of $n$-$C_{17}$, however, is due to diageneric loss of this algal biomarker relative to the long-chain plant-wax hydrocarbons (Giger et al., 1980). Important contributions of long-chain $n$-alkanes, represented by $n$-$C_{29}$ in Fig. 21, are present throughout the 6.4 m core. High CPI values (Bray and Evans, 1961) of the long-chain hydrocarbons verifies that their origin is from contemporary watershed plants, inasmuch as ancient $n$-alkanes would have lost much of their odd/even predominance. The dominance of $n$-$C_{29}$ at all sediment levels except the topmost, most eutrophic one indicates that deciduous trees have been the major watershed plant type (cf. Cranwell, 1973a), which is consistent with what is known of the historical record.

The isoprenoid hydrocarbon phytane, derived through diageneric from the phytol sidechain of chlorophyll $a$ (Fig. 13), is found at all sediment depths, but pristane, a related isoprenoid, is present only in the postglacial clays and in small amounts in some samples of the sapropelic mud. Pristane is common in most modern sediments and 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). Both phytane and pristane are produced from slow-acting diageneric reworking of phytol and become common constituents of the hydrocarbon contents of ancient sedimentary rocks. Giger et al. (1980) interpreted the pristane in the postglacial clays to indicate that hydrocarbons from erosion of Miocene sedimentary rocks in the watershed were incorporated into the lake bottom at this time. With the development of forests in the watershed after about 11 Kya, erosion became negligible, and pristane inputs essentially disappeared.

The downcore profiles of the diageneically formed polycyclic aromatic hydrocarbon perylene and the $C_{29}$ $n$-alkane are very similar (Fig. 21). The principal difference is in the topmost portion of the core, where perylene concentrations are low and increase with depth, whereas the $C_{29}$ $n$-alkane concentrations decrease from their maximum value. Most of this

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**Fig. 21.** Downcore concentrations of organic carbon and of two biomarker $n$-alkanes in sediments of Greifensee, Switzerland. Perylene concentrations and unresolved mixture of aliphatic hydrocarbons (UCM) are shown at different core depths. Changes in the whole lake environment, recorded in changes in the sediment types, appear also in the hydrocarbon molecular compositions. Data are from Giger et al. (1980) and Wakeham et al. (1980a).
difference results from the time lag in the diagenetic production of perylene (cf. Gschwend et al., 1983), and the overall similarities support the hypothesis of a land-plant precursor for perylene (cf. Aisenshtat, 1973).

An unresolved complex mixture of hydrocarbons (UCM) is a major component of the sapropelic muds and the postglacial muds, but not the carbonate oozes (Fig. 21). UCMs are common in geologically old hydrocarbon distributions, such as those found in petroleum and in ancient sedimentary rocks, and represent a huge variety of diagenetically formed hydrocarbons. The UCM hydrocarbons in the postglacial clays originate from erosion of Miocene watershed rocks, like the pristane in these sediments (Giger et al., 1980). Deposition of ancient hydrocarbons is also evident in the lack of odd/even predominance of C17-C19 n-alkanes in the postglacial muds, as represented by the C19/C18 ratios. The predominance is high in the surface sediment where algal inputs are large, but much lower deep in the sediments where geologically old n-alkanes are major contributors (Fig. 21).

The hydrocarbon compositions of the three major sedimentary units record differences in the sources of organic matter to Lake Greifen. Sediments deposited in this century contain a mixture of plant-wax n-alkanes, algal biomarkers, and a complex mixture of geologically old hydrocarbons. These components derive in turn from watershed biotic input, modern eutrophication of the lake waters, and a combination of enhanced land erosion and petroleum residues from urbanization of the watershed. Sediments laid down between the year 1800 and about 11,000 years ago are dominated by hydrocarbons produced by plants in and around the lake. Their n-alkane distributions show evidence of selective degradation of shorter-chain components (Giger et al., 1980). Prior to 11 Kya, sediments are postglacial clays in which geologically old hydrocarbon mixtures from erosion of surrounding rock formations are major components.

The progressive modern eutrophication of Lake Greifen is recorded in the concentration and isotopic composition of sedimentary organic matter. High nutrient/CO₂ ratios in the lake water have lead to enhanced preservation of aquatic matter as bottom water anoxia has become more strongly developed. At the same time, organic matter δ¹³C values have become heavier as the availability of dissolved CO₂ has been diminished by algal uptake (Hollander et al., 1992).

The record of organic matter accumulation in Lake Washington

Lake Washington is surrounded by the Seattle, Washington, metropolitan area. It is larger (surface area 87.6 km²) and deeper (60 m maximum) than Lake Greifen and is presently oligotrophic, but it was eutrophic in the 1950s and early 1960s. An 11 m-long core from northern Lake Washington contains several layers of different types of fine-sized gyttja deposited over a 1.5 m-thick layer of glaciolacustrine clay (Fig. 22). Pollen and lignin compositions record a 14 Kyr postglacial watershed plant succession (Leopold et al., 1982; Hedges et al., 1982). Pollen compositions indicate that an early pine-dominated forest was replaced ca 10 Kya by an alder and fern bracken mixture. Since ca 7 Kya, 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
Concentration, ng/g

- Perylene
- Retene

Approximate Time of Deposition

- 1920
- 1975
- 3000 BP

Fig. 23. Downcore concentrations of three types of diagenetically produced polycyclic aromatic hydrocarbons in sediments of Lake Washington. Perylene is gradually formed in sediments until the unknown precursor material is depleted. Retene is formed from abietic acid, a component of conifer sap, and the pence and chrysene hydrocarbons are formed from amyrin precursors, found in conifer bark. Widespread logging temporarily enhanced the availability of the conifer precursors. Data are from Wakeham et al. (1980a).

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 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 (Fig. 22) 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 which suggests an approximately equal mixture of land and algal material; these elemental ratios are less specific than the lignin parameters. Between 10 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. The lignin plant reconstruction in this interval contradicts the pollen data, leading Leopold et al. (1982) to conclude that the pine pollen dominance results from eolian transport from regions outside the watershed. High S/V and low C/V ratios from 7 to 4 m suggest large contributions of angiosperm wood, a conclusion which is consistent with the abundance of alder pollen (Fig. 22). The decrease in the S/V ratio while the C/V ratio holds constant between 4 m to the core top indicates a gradual

Fig. 24. Concentrations of total polycyclic aromatic hydrocarbons (PAH) deposited at different times in the sediments of Greifensee, Switzerland, and Lake Washington. Both total concentrations and sums of major components are shown. Increased erosion of watershed areas and increased urban pollution are responsible for the 50- to 100-fold magnifications of concentrations. Data are from Wakeham et al. (1980b).
replacement of deciduous trees by conifers. This interpretation also agrees with the pollen reconstruction. Hydrocarbon compositions from a core from near the center of Lake Washington record a variety of environmental changes in organic matter sources. Modern eutrophication of the lake and introduction of land runoff petroleum residues are evident in aliphatic hydrocarbon distributions (Fig. 4). Deforestation of the watershed during the past century is recorded in peaks in polycyclic aromatic hydrocarbons (Fig. 23). The diterpenoid PAH retene is derived from abietic acid (Fig. 10), a common constituent of conifer sap (Simoneit, 1977). Accelerated erosion of soil during logging of the conifer-covered watershed of Lake Washington since the early 1900s created a pulse of abietic acid to the lake sediments (Wakeham et al., 1980a). Concentration profiles of several triterpenoid PAHs are similar to the retene profile (Fig. 23). Probable precursors of these PAHs are α-amarin and β-amarin (Fig. 10), which are found in conifer bark. Logging and associated enhanced erosion of forest soil has evidently increased the delivery of these PAH precursors to Lake Washington sediments, too.

Concentrations of the pentacyclic aromatic hydrocarbon perylene change in a different way than those of the four PAH molecules derived from conifer precursors (Fig. 23). The typical delay (e.g. Figs 8 and 9) between addition of the unknown precursor and the diagenetic production of this PAH is evident. Absence of further change with core depth indicates that the input of the unspecified precursor to Lake Washington has remained constant over the past 3000 yr.

Comparison of PAH contents of Lake Greifen and Lake Washington sediments

Lake Greifen and Lake Washington are temperate-zone lakes that have experienced similar postglacial changes in watershed vegetation and aquatic productivity over the past 14 Kya. The PAH contents of their sediments record both similarities and differences in source inputs. In both lakes, PAH compositions increase markedly in concentration and complexity in sediments deposited since about 1900 (Fig. 24). These changes arise from a combination of street runoff of petroleum residues and airborne input of combustion-derived PAH (Wakeham et al., 1980b). Both of these anthropogenic sources have increased in magnitude during the last century and have overwhelmed the contributions of PAHs derived from biogenic precursors.

Natural differences in watershed biota also affect the sedimentary diagenetic PAH contents of these two lakes. Sediments of Lake Washington contain large concentrations of retene, whereas those of Lake Greifen contain negligible amounts (Wakeham et al., 1980a). Similarly, pimanthrene, for which resin-derived primaric acid is the probable precursor, and a wide range of triterpenoid hydrocarbons derived from amyrin precursors are abundant in the sediments of Lake Washington but not in those of Lake Greifen.

Fig. 25. The lower four Great Lakes, showing some of the locations of sediment studies described in the text. ST4 and ST11 are sediment trap stations in Lake Michigan. Lake Superior, the largest and deepest of the Great Lakes, is out of the figure and to the north of Lake Michigan; few organic geochemical studies have been conducted in Lake Superior.
Lake Greifen. These differences reflect the fact that conifers are abundant around Lake Washington, but not around Lake Greifen. The perylene profiles also differ in the two lakes. After the initial diagenetic lag, sedimentary concentrations are constant in Lake Washington, but variable in Lake Greifen (Figs 21 and 23). This contrast may indicate that the types of watershed vegetation and therefore the sources of the perylene precursor have varied more around Lake Greifen than around Lake Washington.

**Organic matter sources and diagenesis in sediments of Lake Huron and Lake Michigan**

The North American Great Lakes have large surface areas and volumes, but relatively shallow depths and small watersheds. Lake Huron and Lake Michigan (Fig. 25) are the second and third largest of the Great Lakes. Although Lake Huron is larger than Lake Michigan (59,530 km² vs 57,780 km²), the greater depth of Lake Michigan (85 m average) gives it a larger volume than Lake Huron (60 m average). The two lakes share a common water mass, have similarly oligotrophic ecosystems, and are similar in sedimentation processes (cf. Rea et al., 1981; Leenheer and Meyers, 1984).

The large size of Lake Michigan allows study of short-term changes during settling of organic matter to lake bottoms at locations distant from land (e.g., Eadie et al., 1984; Meyers et al., 1980b, 1984a; Meyers and Eadie, 1993). Organic carbon concentrations of settling particles collected in sediment traps decrease with depth while the organic matter bulk character changes little (Table 6). The concentration decreases found agree with the estimates of substantial oxidation of organic matter during sinking through the epilimnion and hypolimnion (Table 1). C/N ratios fluctuate with depth, suggesting that land-derived and algal organic matter have different rates of diagenesis and that lateral inputs of organic matter may occur. In contrast, carbon isotope ratios show little diagenetic or source change effect. The ratios of long/short n-alkanes indicate more land-derived hydrocarbons in the contents of the upper traps at Station 4 and in all traps at Station 11 in the northern portion of the lake, which has a forested watershed. Estimates of downward fluxes of n-alkanoic acids and n-alkanes in traps at two depths indicates that degradation of the acids occurs ten times faster than for hydrocarbons (Meyers and Eadie, 1993). As concluded by Meyers et al. (1984a), the changes occurring to the organic matter contents of settling particles are complex, yet information about sources remains evident.

The sedimentary record in the Great Lakes dates from the retreat of the Laurentian ice sheet about 12 Kya. Although continuous at some locations, the record is often punctuated by hiatuses due to slumping, underlake erosion, and changes in lake

<table>
<thead>
<tr>
<th>Sediment trap</th>
<th>TOC (%)</th>
<th>Atomic C/N</th>
<th>δ13C (%)</th>
<th>Long/short n-alkanes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Station 4—southern Lake Michigan</strong></td>
<td></td>
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<td></td>
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</tr>
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<td>15 m</td>
<td>16.0</td>
<td>20</td>
<td>−27.7</td>
<td>5.6</td>
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<tr>
<td>35 m</td>
<td>14.2</td>
<td>23</td>
<td>−28.8</td>
<td>6.2</td>
</tr>
<tr>
<td>80 m</td>
<td>6.4</td>
<td>9</td>
<td>−26.8</td>
<td>5.0</td>
</tr>
<tr>
<td>120 m</td>
<td>4.8</td>
<td>11</td>
<td>−26.2</td>
<td>1.3</td>
</tr>
<tr>
<td>140 m</td>
<td>8.8</td>
<td>21</td>
<td>−26.6</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>Station 11—northern Lake Michigan</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 m</td>
<td>38.1</td>
<td>13</td>
<td>−29.2</td>
<td>6.0</td>
</tr>
<tr>
<td>31 m</td>
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<td>166 m</td>
<td>5.7</td>
<td>13</td>
<td>−27.8</td>
<td>7.1</td>
</tr>
</tbody>
</table>

**Table 6. Organic matter characteristics in sediment traps from Lake Michigan.** Long/short n-alkane ratios represent the sum of C27 + C29 + C31 divided by the sum of C27, C29, + C31.
Fig. 27. Downcore changes in total organic carbon (TOC) concentration and in lipid characteristics in a core of Saginaw Bay sediment. Modern eutrophication of this bay is evident from increases in TOC, phytol/dihydrophytol, and \( \text{C}_{29}/\text{C}_{17} \) alkane inputs since 1955. Impact of petroleum pollution is recorded by dominance of unresolved complex mixture (UCM) of hydrocarbons since the late 1800s. Core location is shown in Fig. 25. Dates are extrapolated from \(^{210}\text{Pb} \) dating. Adapted from Meyers and Takeuchi (1981).

level resulting from isostatic rebound and drainage channel downcutting (cf. Rea et al., 1980, 1981). Sediment cores from sites located close to each other (Fig. 25) often contain very different spans of lake history and therefore allow interesting comparisons. Station 12 in southern Lake Huron, for example, provides a continuous record of the most recent 400 yr of sediment accumulation, whereas Station 58, less than 7 km distant, is made up almost entirely of glaciolacustrine clay deposited over 12 Kya (Meyers et al., 1980c). In general, fine-sized sediments contain higher concentrations of organic carbon, \( n \)-alkanoic acids, and \( n \)-alkanes than found in coarser sediments (cf. Thompson and Eglinton, 1978; Meyers and Takeuchi, 1979). The glaciolacustrine clays of Core 58 are nonetheless poorer in organic carbon, fatty acids, and hydrocarbons than the silty clays of Core 12 (Fig. 26). Dilution of organic matter by high sedimentation rates of the glaciolacustrine clays probably caused the low concentrations. In addition, the productivity of the surrounding land areas immediately following glacial retreat was probably lower than in subsequent periods. Indeed, the low \( \text{C}_{29}/\text{C}_{17} \) \( n \)-alkane ratio in Core 58 indicates little land-derived hydrocarbon material reached this site. In contrast, variations in the \( \text{C}_{29}/\text{C}_{17} \) ratios in Core 12 show that the proportions of land-plant and algal hydrocarbons have fluctuated repeatedly over the past 400 yr and that land-derived hydrocarbons have often been dominant. Diagenesis of Core 12 fatty acids is indicated by downcore decreases in their total concentration and in the proportion of unsaturated acids (Fig. 26). Both of these parameters are low in Core 58 because diagenesis is further advanced in these much older sediments.

Over the past 200 yr, sources of organic matter to the Great Lakes have been successively modified by replacement of native watershed vegetation by farmland, urbanization of the near-lake areas, industrialization of the region, and eutrophication of some nearshore areas of the lakes. These changes are recorded in the organic matter contents of lake sediments. A shift in organic carbon \( \delta^{13} \text{C} \) values from \(-27\% \) in Lake Ontario sediments deposited before ca 1830 to values of \(-24\% \) in younger sediments has been interpreted by Sackett et al. (1986) as a record of the replacement of native \( \text{C}_3 \) plants by agricultural \( \text{C}_4 \) plants in the watershed of this lake. The carbon isotope change is accompanied by the appearance of Ambrosia (ragweed) pollen in the sediment record, which indicates deforestation of the surrounding land area. A subsequent interpretation of the shift to heavier organic carbon isotopic ratios in sediments from Station E30 in Lake Ontario (Fig. 25) is that enhanced algal productivity is the principal cause (Schelske and Hodell, 1991), even though a change in watershed vegetation has occurred.

Sediments of Saginaw Bay, Lake Huron, contain a geolipid record of both urbanization of the local land area and eutrophication of the bay. Contributions of aquatic geolipid biomarkers have increased since ca 1900 (Meyers and Takeuchi, 1981), and the relative proportions of land-plant \( n \)-alkanols, sterols, and \( n \)-alkanes have consequently become smaller (Fig. 27). Phytol concentrations correlate with chlorophyll and hence with algal biomass (Schultz and Quinn, 1974), whereas dihydrophytol is eroded from land and has a constant concentration in Saginaw Bay sediments. The increase in phytol/dihydrophytol ratio indicates enhanced algal inputs (Fig. 27). These changes record progressive eutrophication of the waters of Saginaw Bay.

Petroleum residues at the same time become the dominant hydrocarbons in the bay sediments. The unresolved complex mixture (UCM) changes from a minor to the major part of the total aliphatic hydrocarbon concentrations (Fig. 27). UCM concentrations diminish as distance from land increases (Meyers
and Takeuchi, 1979; Meyers, 1984), indicating fluvial sources for the petroleum residues. The heavily industrialized and urbanized watershed of the Saginaw River is the most likely origin of these contaminants.

Petroleum hydrocarbons appear in general to be transported in association with suspended sediment particles in Lakes St. Clair, Erie, and Ontario. Highest concentrations are found in sediments close to major cities and in areas where fine-sized sediment particles can settle to the lake bottoms (Nagy et al., 1984). Western Lake Erie, which receives the discharge from the heavily industrialized and urbanized Detroit River, has the largest accumulation of petroleum hydrocarbons. The sediments of shallow Lake St. Clair (ca 6 m) contain low concentrations of petroleum hydrocarbons (Nagy et al., 1984), yet Meyers (1984) notes that UCM components constitute nearly 80% of the total hydrocarbons in a 20 cm core of sediment from this lake. The organic matter characteristics of this core closely resemble those of Core 58 from southern Lake Huron, which is made up of glaciolacustrine clay estimated to be 12 Kyr old. Radiocarbon dating of organic matter in the Lake St. Clair core gives an age of 24 Kyr, indicating the presence of a sizable fraction of geologically ancient organic matter. Meyers (1984) suggests that the bulk of the sediments in this shallow lake are relict postglacial clays and that they incorporated petroleum hydrocarbons long ago from natural oil seeps in nearby Canada. Little modern sediment accumulates under the shallow, wind-mixed, and turbulent waters of Lake St. Clair.

TRENDS AND FUTURE PERSPECTIVES

This overview of the organic geochemistry of lake sediments 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 and have become more quantitative and more inquisitive. The question that has always been important is “Why are these organic substances here?”

From a principally analytical perspective, three areas deserve particular attention in organic geochemical studies of lake sediments:

1. The types of compounds that are analyzed should be expanded from the predominantly low-molecular-weight fractions to include many more of the higher-molecular-weight materials that constitute the bulk of biological and sedimentary organic matter. It is now feasible to analyze by gas chromatography intact molecules containing up to 80 carbon atoms, corresponding to a molecular weight of over 1100. Larger molecules can be disassembled by controlled procedures such as hydrolysis, ozonolysis, and pyrolysis to yield analyzable fragments.

2. The isotopic contents of organic matter are generally underutilized in organic geochemistry. Carbon isotopes of bulk organic matter are regularly measured, yet the different components comprising this material have characteristic isotope ratios that are not commonly investigated. Precursor–product relationships have been successfully explored using carbon isotope signatures of specific compounds isolated from the Eocene Messel shale (e.g. Hayes et al., 1987; Freeman et al., 1990), and this approach has potential application to early diagenesis of lacustrine organic matter. The isotopes of hydrogen, nitrogen, and sulfur also contain biochemical and geochemical information that is seldom determined. Instruments are now sufficiently sensitive to perform these analyses.

3. Analyses need to become more quantitative and to be linked with other limnological parameters. Measurements of primary production rates, transport fluxes, and mass accumulation rates of organic matter in lacustrine settings are important for evaluating the relative significances of input, recycling, and preservation. Calculations of mass balances are important and attainable goals.

On a conceptual level, several areas merit special attention for future organic geochemical research in lake settings:

1. Better descriptions of paleolimnological conditions can be obtained by wider use of the information provided by the organic matter contained in lake sediments. Evidence about paleoproductivity, changes in aquatic communities, transport processes, and watershed vegetation is available.

2. The collection of useful biomarker compounds needs to be expanded. Paleolimnologists can define questions that organic geochemists can help answer. Indicator organisms, characteristic of different types of lacustrine environments, can be identified and their molecular and isotopic compositions can be scanned for new biomarker information.

3. 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.

4. Diagenetic interactions between different individual compounds and different classes of compounds should be investigated. Most studies have concentrated on the changes which occur to single compounds or to single types of compounds. Dynamic diagenetic interrelationships may exist which are important to interpreting the organic geochemical record in sediments.

5. The different roles played by high-molecular-weight forms of sediment organic matter are not
understood well and need clarification. Progress in determining the molecular structure of humic substances, for example, has been slow. This information is critical to defining the significance of humics in lake sediments. Does the structure of humin/kerogen incorporate and enhance preservation of biomarker molecules, or are there systematic alterations of these useful compounds?

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