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Geolipid, pollen and diatom stratigraphy in postglacial lacustrine sediments

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Abstract—As part of our continuing investigation of specific compounds as organic matter indicators in lake bottoms, we have examined geolipids, pollen and diatoms in sediments from different periods in the postglacial history of Heart Lake, New York. Sediment core sections representing the major watershed vegetation periods were extracted for unbound and bound fatty acids, hydrocarbons and alcohols. Fatty acids constitute most of the extracted material. Minor decreases in unsaturated acids with depth indicate little degradation of organic matter in these sediments. The dominant unbound *n*-alkanoic acid in the core sections is either C_{22} or C_{24}, but bound fractions contain few long chain acids and are dominated by *n*-C_{16}. Nearly all the hydrocarbons are found in the unbound fraction. The ratio of C_{29}/C_{17} *n*-alkanes increases from the bottom of the core to near the top as watershed forests have matured and lake productivity has diminished, but drops since European settlement of the region. Organic degradation in this lake bottom is mild, and input indicators appear to be well preserved.

Key words: lake sediments, alkanoic acids, *n*-alkanes, alkanols, sterols, geolipids

INTRODUCTION

Organic matter in lake sediments represents the residue remaining after the degradation and alteration of aquatic and watershed biota. Local environments determine the relative importance of the many possible sources of organic matter, so that changes in local conditions over time and in postdepositional alterations may be reflected in the organic character of sediments deposited at different times.

Geolipid compositions have been widely employed in geographical and temporal comparisons of subaqueous sediments. Organic matter inputs over long periods of depositional history have been characterized using distributions of fatty acids, alkanes, and sterols in sediments of Mono Lake (Reed, 1977) and of Cam Loch (Cranwell, 1977). Based upon studies of geolipid compositions of sediments from oligotrophic and eutrophic lakes (Cranwell, 1978; 1981; Cranwell and Volkman, 1981), it appears that the trophic status of lakes is important to both the types of material incorporated into sediments and the extent of organic matter preservation.

As part of our continuing investigation of indicators of organic matter input and alteration in lake sediments, we have determined geolipid distributions in sediments deposited during different segments of the postglacial history of Heart Lake, New York. Trophic status of this lake and watershed forest cover are inferred from diatom and pollen assemblages present in the sediments, thus providing information about sources of organic matter.

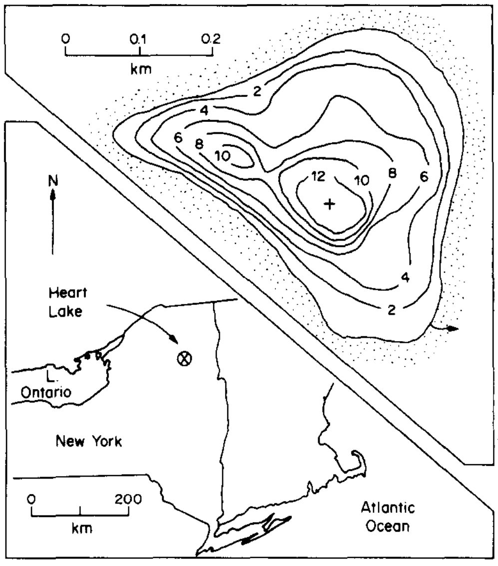

Fig. 1. Location of sediment core from Heart Lake. General siting of Adirondacks area and this lake shown in inset. Bathymetric contours in metres.

EXPERIMENTAL

Sampling

Heart Lake is situated at an elevation of 661 m in Adirondack State Park of New York State (Fig. 1).

The area of the lake is 11.2 ha, and its maximum depth is 14 m. The watershed is forested and has an area of 56 ha. On the basis of nutrient concentrations in surface waters, the lake is oligotrophic, but a subsurface chlorophyll maximum is present and indicates mesotrophy.

A 6.7m core of sediment was obtained from the central, deepest part of Heart Lake in July 1976. One meter sections were carefully wrapped in aluminum foil and Saran wrap and stored at 4°C. Samples for organic geochemical analysis were selected from the core sections after pollen and diatom analyses had been completed and radiocarbon dating had been done. When geochemical sampling was done in November 1979 and April 1980, the core sections showed no evidence of dessication or fungal growth and seemed to be well preserved.

Organic matter

Concentration of organic matter was estimated by combustion of dried sediment at 500°C and determination of the resulting weight loss.

Extraction

An extraction procedure was used which provided extractable lipids and those released by alkaline hydrolysis of the extracted sediment. These fractions are called unbound and bound, respectively, in this report, but no implications about the presence or absence of chemical bonds are intended. Unbound lipids were obtained from samples of wet sediment by Soxhlet extraction with toluene/methanol, 1:1, for 48 h. Bound lipids were released by refluxing the extracted sediment in 0.5 N methanolic KOH/ toluene/water, 6:3:1, for 1 h after which the cooled mixture was adjusted to pH 7 with 3 N HCl. The extracts were partitioned into aqueous and organic phases in separatory flasks by addition of water and dichloromethane, and the aqueous phases were extracted repeatedly with dichloromethane until the solvent remained colorless. After being concentrated, unbound lipids were saponified and methylated as described by Leenheer (1981), and the bound lipids were methylated with methanolic boron trifluoride.

Separation into lipid components

The extracts were split to ease further handling. Twenty percent of the unbound and 50% of the bound fractions were removed from each sample for use in column chromatography separations. Internal standards of C_{36} *n*-alkane and of methylheptadecanoate were added to each subsample. Column chromatography of each sample on a column packed with aluminum oxide over silica gel as detailed by Leenheer (1981) provided four fractions: hydrocarbons (saturated plus aromatic), fatty acid methyl esters, a sterol–alcohol fraction, and a column wash. The sterol/alcohol fractions were derivatized with BSTFA and an internal standard of 5α-cholestane was added for quantification by gas chromatography.

Analysis

Hydrocarbon, fatty acid methyl ester, and sterol–alcohol fractions of sediment lipids were analyzed using a Hewlett Packard 5830A FID gas chromatograph equipped with a 20 m SE-54 capillary column and fitted with a splitless injection system. Hydrogen was used as the carrier gas and nitrogen as the make-up gas. Quantitative results were obtained using the internal standard amounts after corrections were made with response factors calculated from standard mixes. The reported results have been further corrected for small amounts of laboratory contamination as determined from blank analyses.

RESULTS AND DISCUSSION

Pollen and diatom stratigraphy

Pollen and macrofossil studies of the Heart Lake core indicate that the late-glacial and Holocene vegetational changes in the watershed have been comparable to those described elsewhere in the North-east (e.g. Whitehead, 1979; Davis *et al.*, 1980; Davis 1981b). The vegetation was initially treeless, probably tundra (zone T). Between 11,000 and 9700 years B.P. a spruce-dominated open boreal forest developed (zone A); this was followed by mixed coniferous (with much white pine) and deciduous forests (zone B; 9700–7000 B.P.). Hemlock-dominated northern hardwoods forests were prevalent between 7000 and 4800 B.P. (zone C1). The dramatic hemlock decline (Davis, 1981a) occurs at 4800 B.P., causing a shift from a conifer-dominated northern hardwoods forest to one with mostly hardwoods (zone C2; 4800–2000 B.P.). Spruce reimmigrated about 2000 years ago and once again became an important tree in the High Peaks region (zone C3).

The diatom stratigraphy also indicates significant changes in Heart Lake from the late-glacial to the present. The lake was initially moderately alkaline (pH 7.5–8.0) and productive with many planktonic taxa present. The diatom assemblages shift in the early Holocene to more benthic species, and there is indication of an acidification trend and low primary production. The lake stabilized at about pH 6.0 at 6000 B.P. There were two minor shifts to lower pH in the later Holocene. These were apparently influenced by the expansion of specific conifers in the watershed (e.g. a recovery and expansion of hemlock beginning at 3400 B.P. and reappearance of spruce beginning at 2000 B.P.). Planktonic diatoms have again become more common in the recent sediments. In addition to diatoms, other types of algae must have lived in the waters of Heart Lake but have left no fossil record of their community composition.

Concentrations of geolipids and organic matter

The concentrations of unbound and bound geolipid material released from samples of Heart Lake sediment are shown in relation to sediment depth, radiocarbon age and pollen zones in Fig. 2. Concentration of total organic matter is also presented. This remains *ca* 40% in most of the samples, and the decrease with depth common to many lacustrine sediments (Nishimura and Koyama, 1976; Cranwell, 1977; Meyers *et al.*, 1980a,b; Leenheer and Meyers, 1983) is not present. This observation, plus the high concentrations of organic matter, indicates exceptional preservation of biotic materials in the sediments of this lake. As noted by Leenheer and Meyers (1983), high sedimentation rates estimated to range up to 5.5 mm yr^{-1} are probably responsible, inasmuch as lake waters undergo normal seasonal overturn and are not permanently anoxic.

Concentrations of total alkanes, total alcohols, and total fatty acids are high relative to sediments of the Great Lakes and of marine areas (e.g. Leenheer and Meyers, 1983) and instead resemble those reported for surficial sediments of English lakes (Cranwell, 1977, 1978, 1981). Unlike most lacustrine sediments (e.g. Cranwell, 1977; Nishimura, 1977; Matsuda and Koyama, 1977; Meyers *et al.*, 1980a), geolipid concentrations do not decrease with increasing sediment depth. They are variable and do not have an obvious relationship to the amount of total organic matter, although peak concentrations of some geolipid components do coincide with organic matter peaks at the pollen zone boundaries A–B and C2–C3 (Fig. 2).

Unbound geolipids released by solvent extraction of the sediment consistently have higher concentrations than do the bound materials released by alkaline hydrolysis, most notably in the case of aliphatic hydrocarbons. Downcore patterns of total alcohol and total fatty acid concentrations are similar in both unbound and bound fractions, thus ruling out variations in extraction efficiencies as a significant factor in the concentrations found at each depth. Fatty acid compositions are dominated by C_{22} and C_{24} *n*-alkanoic acids in the unbound fraction and C_{16} acids in the bound portion. C_{27} and C_{29} *n*-alkanes are the major components of unbound hydrocarbons, whereas *n*-C_{17} comprises most of the bound fraction. Similar contrasts exist between the unbound and bound fractions of alcohols and agree with the findings in sediments of other lakes (e.g. Cranwell, 1978, 1981).

Geolipid alteration indicators

The concentration data summarized in Fig. 2 imply relatively good preservation of organic matter in the sediments of Heart Lake. Several ratios of geolipid components were used to investigate this possibility in more detail. One indicator of organic matter alteration is the proportion of unsaturated components in a geolipid fraction, and another is the ratio of unbound and bound geolipid fractions.

The contribution of unsaturated acids to the total fatty acid content of lacustrine sediments commonly decreases with depth of burial (e.g. Matsuda, 1978; Meyers *et al.*, 1980a; Kawamura *et al.*, 1980; Cardoso

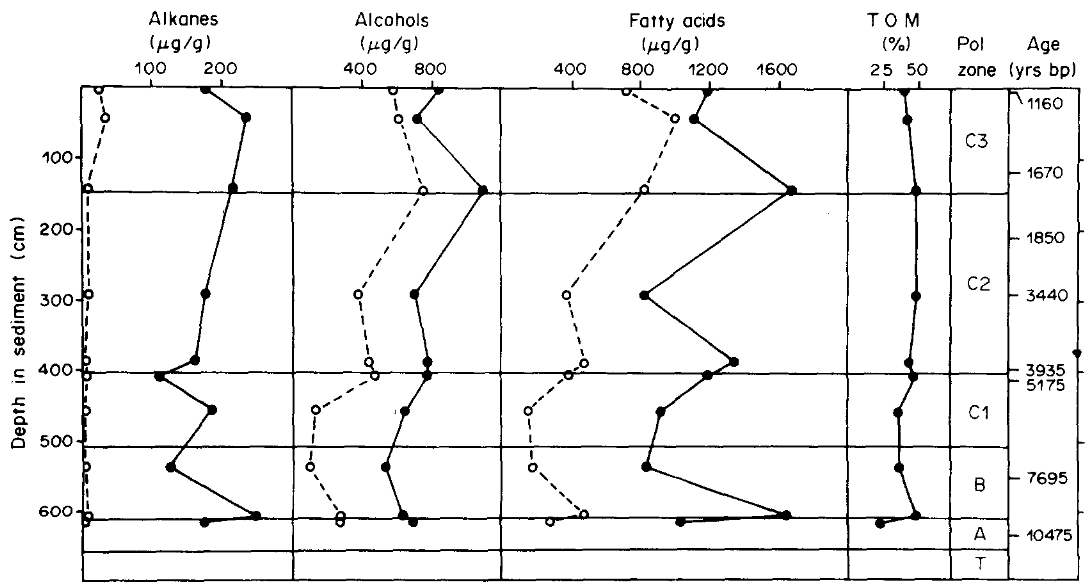

Fig. 2. Downcore concentrations of total alkanes, total fatty acids, and total alcohols plus sterols in unbound (solid lines) and bound (broken lines) lipid extracts of Heart Lake sediments. Percent total organic matter (TOM), pollen zones and radiocarbon ages are included.

et al., 1983). Possible factors involved in this pattern include preferential destruction of unsaturated molecules and reduction of double bonds, as well as a depth-related decrease in viable microflora, which are a potential source of lipids to subaqueous sediments. The palmitoleic/palmitic acid ratio (16.1:16.0) plotted in Fig. 3 shows a small general decrease with depth in both the unbound and bound fractions, and this suggests that some postdepositional alteration of organic matter occurs in Heart Lake sediments. The surficial contribution of palmitoleic acid is small relative to its saturated analog, however, and this may indicate that microbial populations are not large in these sediments.

The stenol/stanol ratio is another unsaturated-to-saturated ratio that has been found to decrease with depth in lacustrine sediments (e.g. Gaskell and Eglinton, 1976; Nishimura and Koyama, 1976, 1977; Leenheer and Meyers, 1983). As shown in Fig. 3, the ratio of C_{29} stenols to C_{29} stanols changes little with depth in the unbound fraction from Heart Lake and displays several increases in the bound fraction. The C_{27} stenol/stanol ratio is not plotted but has a similar pattern.

Nishimura (1978) has suggested that C_{29} stenols are resistant to conversion to stanols, relative to C_{27} stenols, in sediments of lakes in which land-derived organic matter is the dominant form. If this is true, then the lack of major decrease in the C_{29} stenol/stanol ratio in Heart Lake sediments is understandable, yet the similar absence of downcore change in the C_{27} ratio remains surprising. It may be that an abundance of lignaceous phenolic compounds retards microbial degradation of organic matter in these sediments and, hence, better preserves source indicators. Moreover, if bound components are more resistant than unbound components to microbial alteration as suggested by Nishimura (1977) and Cardoso et al. (1983), then the downcore increases in bound C_{29} stenol/stanol ratio may record changes in sources of organic matter to these sediments. Because the highest bound C_{29} ratio occurs in pollen zone B, where white pine is important, this type of tree may be an important source of bound stenols.

Unbound materials constitute the greater fraction of total geolipids in most surficial lacustrine sediments, but this proportion commonly decreases with sediment depth (e.g. Nishimura, 1977; Cranwell, 1981) due to better stabilization of bound material. As a result, the ratio of unbound-to-bound material commonly decreases. In sediments of Heart Lake, however, unbound-to-bound ratios of total alkane, alcohol and fatty acid fractions increase with depth and have maximum values in pollen zones B or C1 at times corresponding to 5500 to 7500 yr B.P. (Fig. 3). These increases reflect the proportionately greater amounts of unbound geolipids deeper in the sediments (Fig. 2) and may record both changes in the types of organic matter buried in lake sediments and changing degrees of organic matter alteration at different times in the history of Heart Lake.

Geolipid source indicators

Relative contributions of allochthonous and autochthonous components to the unbound and bound fractions of geolipids were investigated in Heart Lake sediments. Ratios of terrigenous-to-aquatic components in these fractions are plotted in Fig. 4 in relation to diatom inputs and pollen zones. Although shorter chain length *n*-alkanoic acids and *n*-alkanols are not accurate indicators of biotic sources due to their ubiquity, the longer chain length homologues seem valid land-plant indicators. The C_{26}/C_{16} ratio of unbound *n*-alkanols is 10 or greater throughout this sediment profile and indicates major contributions of land-derived alkanols. In contrast, the bound C_{26}/C_{16} ratio is low, supporting the suggestion that autochthonous sources provide much of the bound materials (Cranwell, 1978). Maxima in both unbound and bound C_{26}/C_{16} ratios at 535 cm coincide with peaks in the unbound C_{26}/C_{16} *n*-acid ratio, the diatom flux, and unbound-to-bound ratios of alkanes and fatty acids. The lack of similar changes in the C_{29}/C_{27} sterol and C_{29}/C_{17} *n*-alkane ratios, combined with somewhat lower concentrations of alcohols, fatty acids and total organic matter (Fig. 2) suggests that an interlude of higher burial rate and accompanying enhanced preservation of waxy lipids probably occurred, rather than a change in organic matter sources.

As in the case of the *n*-alkanols, the unbound C_{26}/C_{16} *n*-acid ratio is much greater than the bound acid ratio. Furthermore, the downcore patterns of the *n*-alkanol and *n*-acid ratios are similar (Fig. 4). A major difference exists, however, in the magnitude of the ratios. The unbound C_{26}/C_{16} acid ratio is small, changing from *ca* 0.4 at the sediment surface to *ca* 1.2 at 607 cm. Because the relatively high C_{29}/C_{17} *n*-alkane, C_{26}/C_{16} *n*-alkanol, and C_{29}/C_{27} sterol ratios (Fig. 4) indicate important amounts of allochthonous lipids and the relatively low values of the fatty acid 16.1:16.0 ratio (Fig. 3) suggest limited microbial biomass, the low C_{26}/C_{16} *n*-acid ratio implies the possibility of good preservation of allochthonous shorter chain length fatty acids in this lake which has moderate-to-low aquatic productivity.

Evidence that the productivity of Heart Lake has changed over its postglacial history is preserved in its sediments. Ratios of C_{29}/C_{17} *n*-alkanes and of C_{29}/C_{27} sterols are *ca* 1 in sediments deposited early in the lake's history. As the flux of diatom frustules decreases toward modern times, these ratios become larger, reflecting a possible shift toward decreased aquatic production of hydrocarbons and sterols and increased importance of terrigenous sources of organic matter. In recent times, the *n*-alkane C_{29}/C_{17} ratio has dropped and the contribution of planktonic diatoms has increased to become as important to the

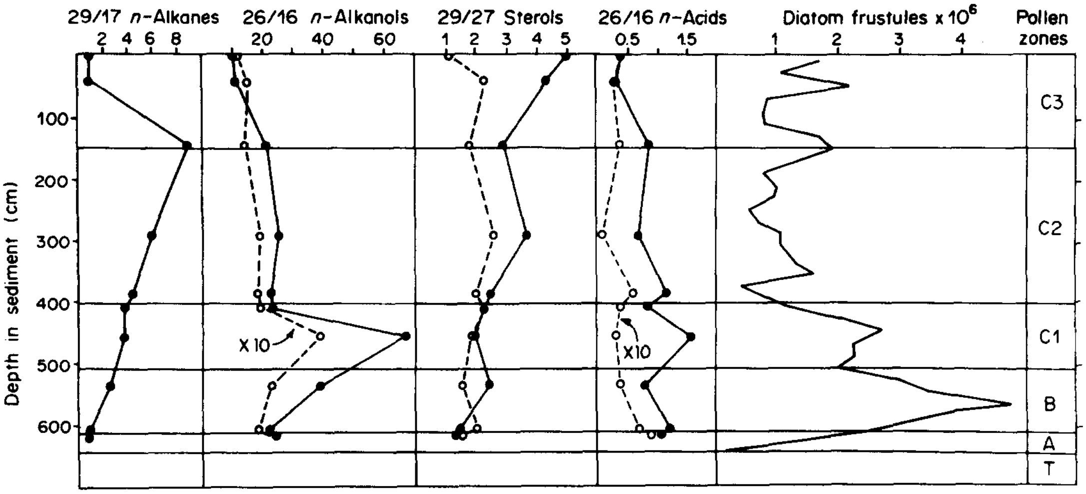

Fig. 3. Ratios of terrigenous/aquatic indicators in unbound (solid lines) and bound (broken lines) lipid extracts of Heart Lake sediment samples. Diatom abundances are expressed as fluxes (10^6 cells cm^{-2} yr^{-1}).

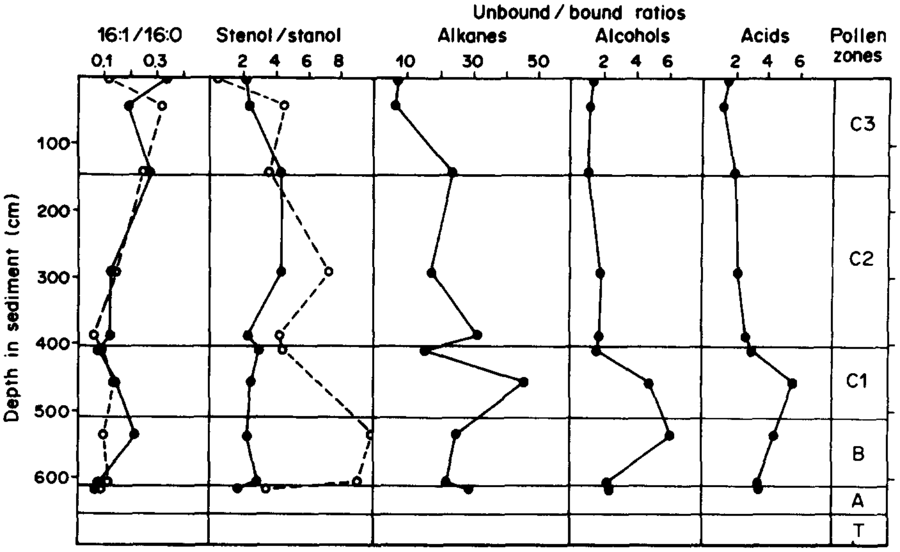

Fig. 4. Ratios of diagenesis indicators in lipid extracts of Heart Lake sediment samples. Relative contributions of monounsaturated and saturated C_{16} n-acids and of 5-unsaturated and saturated C_{29} sterols in unbound (solid lines) and bound (broken lines) extracts, and of total unbound and bound alkanes, alcohols plus sterols and fatty acids are given.

total flux of frustules as it was during the early history of this lake. Although the watershed of the lake has not been seriously modified by man's activities, atmospheric inputs into the lake have enhanced nutrient levels and have decreased pH levels, thus changing the aquatic environment. Such changes may be recorded in the geolipid contents of the sediments.

CONCLUSIONS

The purpose of this study was to identify and describe the molecular constitutions of geolipid fractions extracted from sediments deposited during different parts of the postglacial history of Heart Lake, New York. The hope of this investigation was to find significant geolipid differences between the various pollen and diatom zones in the lake's sediments; this hope has not been realized. Athough no significant changes in molecular character which clearly relate to diatom or pollen stratigraphy were found, the results of this study do permit several general conclusions.

(1) Organic matter is well preserved in the sediments of Heart Lake. Sedimentation rates seem to be sufficiently high to protect biotic debris from exten-

sive degradation. The source of much of the sediments, as well as much of the organic materials, is run off from the hilly watershed surrounding the lake. It is possible that lignaceous components of this land run off contribute to preserving organic matter by retarding microbial activity.

(2) Progressive changes in *n*-alkane and sterol compositions indicate a decrease in the relative contribution of aquatic lipid material to the sediments from early parts of the lake's history to near-recent times. This trend has reversed in the last several hundred years in hydrocarbon compositions, but not in those of sterols. These patterns probably signify changes in the amount of aquatic productivity and in the structure of aquatic communities.

(3) No obvious correlations could be found between the molecular compositions of unbound or bound geolipids and pollen zones in the sediments. Fluctuations in concentration often occur near pollen zone boundaries and may be related to changes in watershed biotic communities; however, the relationship remains elusive.

(4) This study was limited by lack of adequate characterization of source materials. It is clear that more information is needed about the biochemical compositions of biotic communities and of their component organisms. This need exists for the general, chain length approach used in this study, as well as for specific biomarkers.

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