

Reprinted from

# CHEMICAL GEOLOGY

INCLUDING  
**ISOTOPE GEOSCIENCE**

---

Chemical Geology 152 (1998) 163–179

## Changes in the trophic state of Lake Erie: discordance between molecular $\delta^{13}\text{C}$ and bulk $\delta^{13}\text{C}$ sedimentary records

P.H. Ostrom <sup>a,\*</sup>, N.E. Ostrom <sup>a</sup>, J. Henry <sup>a</sup>, B.J. Eadie <sup>b</sup>, P.A. Meyers <sup>c</sup>,  
J.A. Robbins <sup>b</sup>

<sup>a</sup> Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115, USA

<sup>b</sup> Great Lakes Environmental Research Laboratory, Ann Arbor, MI 48105, USA

<sup>c</sup> Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA



ELSEVIER



## Changes in the trophic state of Lake Erie: discordance between molecular $\delta^{13}\text{C}$ and bulk $\delta^{13}\text{C}$ sedimentary records

P.H. Ostrom<sup>a,\*</sup>, N.E. Ostrom<sup>a</sup>, J. Henry<sup>a</sup>, B.J. Eadie<sup>b</sup>, P.A. Meyers<sup>c</sup>,  
J.A. Robbins<sup>b</sup>

<sup>a</sup> Department of Geological Sciences, 206 Natural Science Building, Michigan State University, East Lansing, MI 48824-1115, USA

<sup>b</sup> Great Lakes Environmental Research Laboratory, Ann Arbor, MI 48105, USA

<sup>c</sup> Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063, USA

### Abstract

Prior to 1980, anthropogenic phosphorus (P) loadings resulted in increased algal productivity and the deterioration of water quality within Lake Erie. We measured C and N elemental compositions, geolipid concentrations, and  $\delta^{13}\text{C}$  values for bulk organic material and individual alkanes in samples taken from a 40-cm sediment core from the eastern basin of Lake Erie to infer recent trends in primary productivity and diagenesis. The predominance of autochthonous algal-derived C throughout the core is evidenced by low C/N values (9–10) and the persistent abundance of *n*-C<sub>15</sub> to *n*-C<sub>17</sub> alkanes throughout the core. The  $\delta^{13}\text{C}$  values of bulk organic C from Lake Erie vary between  $-25.9$  and  $-24.9\text{‰}$  with a maximum corresponding to the period of elevated historical P loading. Within Lake Erie,  $\delta^{13}\text{C}$  values of short-chained algal-derived alkanes ( $< n\text{-C}_{18}$ ) are lower (approximately  $1.0\text{‰}$ ) than their terrestrial-derived homologs ( $> n\text{-C}_{25}$ ). Down-core variations in the  $\delta^{13}\text{C}$  composition of algal-derived short-chained alkanes do not exhibit the same trend as that observed for bulk organic C. Down-core variation in  $\delta^{13}\text{C}$  values of individual alkanes likely reflect multiple diagenetic effects including kinetic fractionation effects, variations in the relative contributions of isotopically unique *n*-alkanes to the sediments, and/or temporal changes in  $^{13}\text{C}$  enrichments of *n*-alkanes associated with a single source. High sedimentation rates characteristic of this core emphasize temporal variations in molecular  $\delta^{13}\text{C}$  values that might not otherwise be observed. Whereas  $\delta^{13}\text{C}$  data for bulk sedimentary organic C appear to reflect variation in trophic state, the isotopic record for algal-derived *n*-alkanes (e.g., *n*-C<sub>17</sub> and pristane) from Lake Erie must be considered from the perspective of molecular transformations. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Lake Erie; Molecular  $\delta^{13}\text{C}$ ; Anthropogenic P loadings; Carbon isotopes; Sediment cores

### 1. Introduction

Algal productivity and water quality of the Great Lakes, have varied with the amount of anthropogenic

phosphorus (P) loading. Lake Erie, the smallest of the five Great Lakes has been especially sensitive to variations in the delivery of anthropogenic P over the past century. In particular, high P loadings between 1960 and 1975 resulted in increased sediment oxygen demand, widespread anoxia in the hypolimnion of the central basin during stratification, and the decline of one of the world's largest freshwater

\* Corresponding author. Tel.: +1 517 355 4626; fax: +1 517 353 8787; e-mail: 22381pho@msu.edu

fisheries (Burns, 1985; Rosa and Burns, 1987). Subsequent declines in phytoplankton biomass and recovery of the fishery in the mid-1970s occurred concomitantly with P abatement practices. These fluctuations in trophic state of the lower Great Lakes are recorded in the carbon isotope ( $\delta^{13}\text{C}$ ) values of sedimentary organic matter (Schelske and Hodell, 1991, 1995).

The relationship between  $\delta^{13}\text{C}$  of primary photosynthate and the extent of production reflects the response of isotopic fractionation during carbon fixation to variations in aqueous  $\text{CO}_2$  concentrations (Rau et al., 1989; Fogel et al., 1992; Fogel and Cifuentes, 1993; Goericke et al., 1994). Early models of photosynthetic fractionation recognized that isotopic discrimination occurs during diffusion of  $\text{CO}_2$  into the cell and, to a greater extent, during carboxylation of ribulose diphosphate by the enzyme RuBP

carboxylase (O'Leary, 1981; Roeske and O'Leary, 1984). During periods of high productivity when aqueous  $\text{CO}_2$  concentrations are low, discrimination against  $^{13}\text{C}$  by the enzyme RuBP carboxylase is effectively reduced. This may result in an increase in the  $\delta^{13}\text{C}$  of the primary photosynthate relative to periods of low productivity. Current work, however, recognizes that additional factors, such as pH, temperature, degree of nitrogen limitation, and growth rate, can influence the  $\delta^{13}\text{C}$  of phytoplankton (Beardall et al., 1982; Takahashi et al., 1990; Fogel and Cifuentes, 1993; Hinga et al., 1994; Laws et al., 1995).

Clearly, the ability of  $\delta^{13}\text{C}$  values to provide an indication of variations in trophic state within the Great Lakes is dependent on the degree to which C isotopic discrimination is dependent on  $p\text{CO}_2$ . Additionally, temporal variation in the contribution of

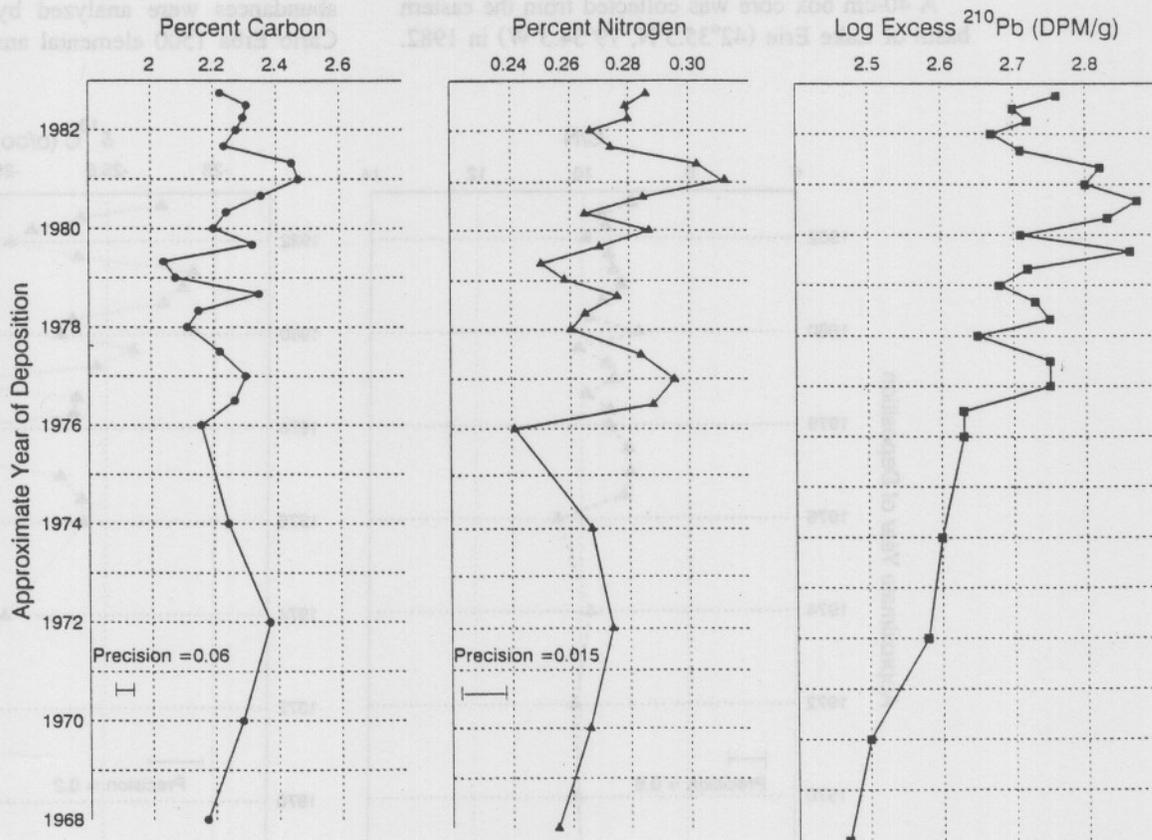


Fig. 1. Percent C, percent N, and log excess  $^{210}\text{Pb}$  data for the organic component of sediments from the eastern Lake Erie.

allochthonous material and diagenesis may confound  $\delta^{13}\text{C}$  records of bulk organic carbon. Carbon isotopic values of algal-derived molecules, however, should not be influenced by terrigenous inputs and, thus, provide a better indication of trophic state than  $\delta^{13}\text{C}$  data on bulk sediments. We compare  $\delta^{13}\text{C}$  data for bulk sedimentary organic matter and individual *n*-alkanes (*n*-C<sub>16</sub> to *n*-C<sub>29</sub>) obtained from a core taken from Lake Erie. To identify variations in allochthonous inputs and diagenesis, C and N elemental abundances and concentrations of individual *n*-alkanes are also presented.

## 2. Methods

### 2.1. Core material

A 40-cm box core was collected from the eastern basin of Lake Erie (42°35.3' N, 79°34.3' W) in 1982.

A sub-core was sectioned at 1-cm intervals for the top 20 cm and at 5-cm intervals for the lower 20 cm for this research. Sediment samples were immediately frozen and stored in glass containers until 1994 when they were freeze-dried for geochemical analyses associated with the current study. Each sample contained approximately 10 g dry sediment. Approximate ages from a companion sub-core were previously calculated using  $^{210}\text{Pb}$  dating techniques (Robbins et al., 1989).

### 2.2. Elemental and isotopic analyses

Prior to elemental and isotopic analyses, inorganic carbon was removed from a 500-mg aliquot of dried sediment sample by acidification (2 N HCl). The acidified samples were subsequently dried at 45°C and homogenized. Carbon and nitrogen elemental abundances were analyzed by combustion with a Carlo Erba 1500 elemental analyzer. The  $\delta^{13}\text{C}$  val-

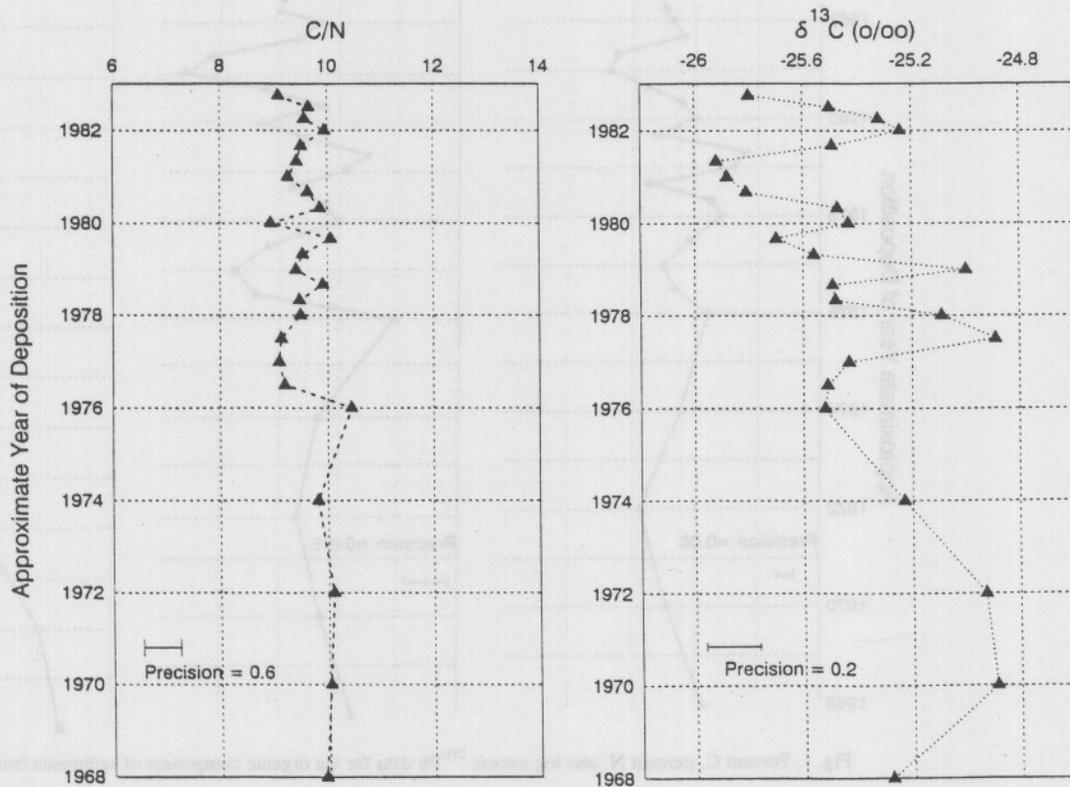


Fig. 2. Atomic C/N and  $\delta^{13}\text{C}$  data for the organic component of sediments from sediments obtained from the eastern basin of Lake Erie.

ues of the bulk sediment samples were determined using a PRISM stable isotope mass spectrometer (VG Isotech) interfaced with the Carlo Erba elemental analyzer, following the method of Wong et al. (1992).

### 2.3. Isolation and analysis of lipid concentrations

The lipid component of an aliquot (8 g) of each sediment sample was extracted in quartz distilled dichloromethane (DCM, Sigma, HPLC grade) in a soxhlet apparatus for 7 h. Separation of individual hydrocarbon classes was accomplished by column chromatography using activated (305°C) silica and alumina and high purity solvents (quartz distilled, HPLC grade) of increasing polarity (*n*-hexane, 2:1 *n*-hexane/DCM and methanol, for aliphatic, aromatic and polar compounds, respectively). After rotoevaporation, each hydrocarbon fraction was evaporated to dryness under a stream of filtered air and weighed.

Identification and quantification of the abundance of individual *n*-alkanes contained within the aliphatic

fraction was accomplished using a gas chromatograph (Hewlett-Packard 5890) fitted with a DB-5 column (32  $\mu\text{m}$  i.d.  $\times$  25 m; J&W Scientific) and interfaced to a mass selective detector (Hewlett-Packard 5971). Samples were separated within the gas chromatograph using a temperature program of 100°C for 5 min, 5°C  $\text{min}^{-1}$  to 305°C, and 305°C for 10 min. The mass selective detector was operated in scan mode ( $m/z$  30 to 500). An internal standard (phenanthrene) was added to each sample prior to injection for quantification of individual components. Compound identification was based on the abundance and mass of molecular ion and fragment ions produced during the scan and by comparison with literature mass spectra (Giger et al., 1980; Kvenvolden et al., 1987; Schoell et al., 1994).

### 2.4. GC / IRMS of *n*-alkanes

Carbon isotope values of *n*-C<sub>16</sub> to *n*-C<sub>29</sub> alkanes, pristane and phytane were determined from an aliquot of the aliphatic fraction obtained from 10 of the sediment samples. Phenanthrene and deuterated *n*-

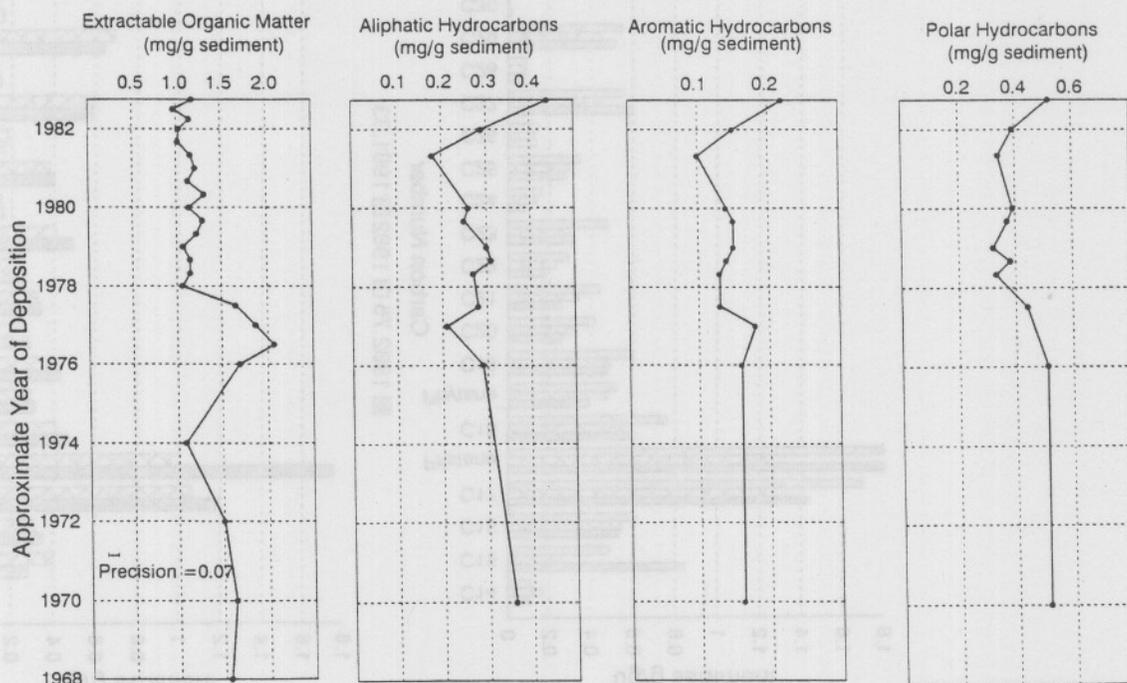


Fig. 3. Concentrations of extractable organic matter and aliphatic, aromatic, and the polar hydrocarbons ( $\mu\text{g g}^{-1}$  sediment) isolated from sediments from the eastern basin of Lake Erie.

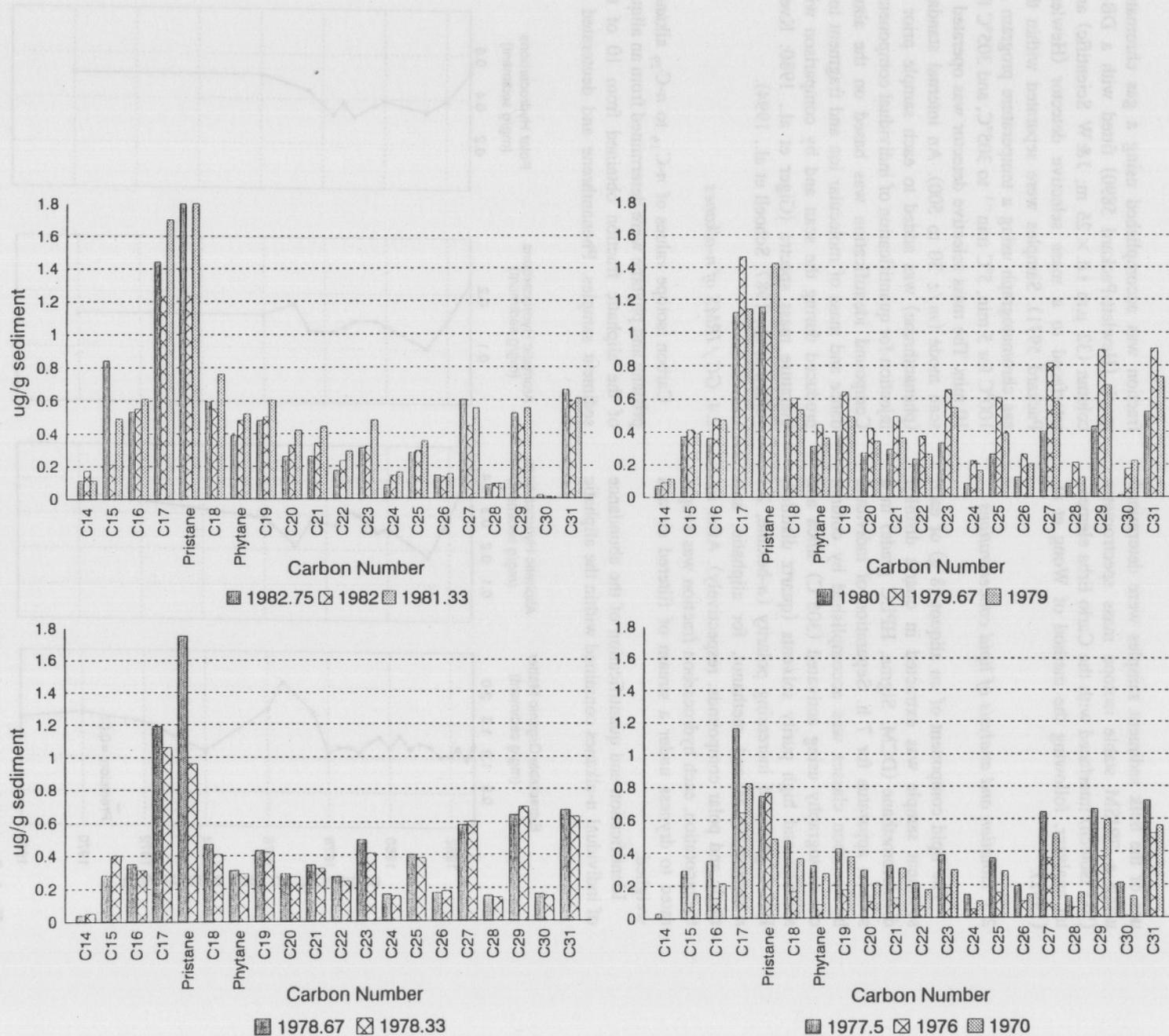


Fig. 4. Absolute abundances of *n*-alkanes (*n*-C<sub>15</sub> to *n*-C<sub>31</sub>), pristane, and phytane ( $\mu\text{g g}^{-1}$  sediment) from sediments from the eastern basin of Lake Erie sediments.

C<sub>24</sub> were isotopically characterized and used as an internal standard for each of the samples. Isotope values for several alkanes quantified by gas chromatography with mass selective detection are not reported owing to their low abundance (e.g., *n*-C<sub>14</sub> and *n*-C<sub>30</sub>) or co-elution (e.g., *n*-C<sub>31</sub>). The  $\delta^{13}\text{C}$  values of individual *n*-alkanes were analyzed on a VG Isochrom I (Hewlett-Packard 5890 gas chromatograph interfaced by a combustion furnace and water trap to a VG PRISM isotope ratio mass spectrometer). Samples (1  $\mu\text{l}$ ) were injected (splitless) onto a DB-5 fused silica column (32  $\mu\text{m}$  i.d.  $\times$  25 m; J&W Scientific) and the following temperature program was used during chromatography: 70°C for 3 min, 70°C to 120°C at 1°C min<sup>-1</sup>, 130°C to 300°C at 20°C min<sup>-1</sup> and 300°C for 5 min. The injector was maintained at 280°C, the combustion furnace interface at 400°C, and the combustion furnace at 850°C.

Reference CO<sub>2</sub> was introduced into the mass spectrometer before and after elution of the *n*-alkanes while column eluent was diverted. The slow ramp in the chromatographic program between 70 and 120°C provided for near base-line separation between *n*-C<sub>17</sub> and pristane and between *n*-C<sub>18</sub> and phytane.

### 3. Results

#### 3.1. Sedimentation rate and mixed depth

The age-depth relationship of the core was estimated using <sup>210</sup>Pb dating techniques (Fig. 1; Robbins and Edgington, 1975; Eisenreich et al., 1989). The approximate year of deposition for the bottom of the 40-cm core is 1968. The <sup>210</sup>Pb data reveal a mixed depth of 10.5 cm that is equivalent to 3.7 years of

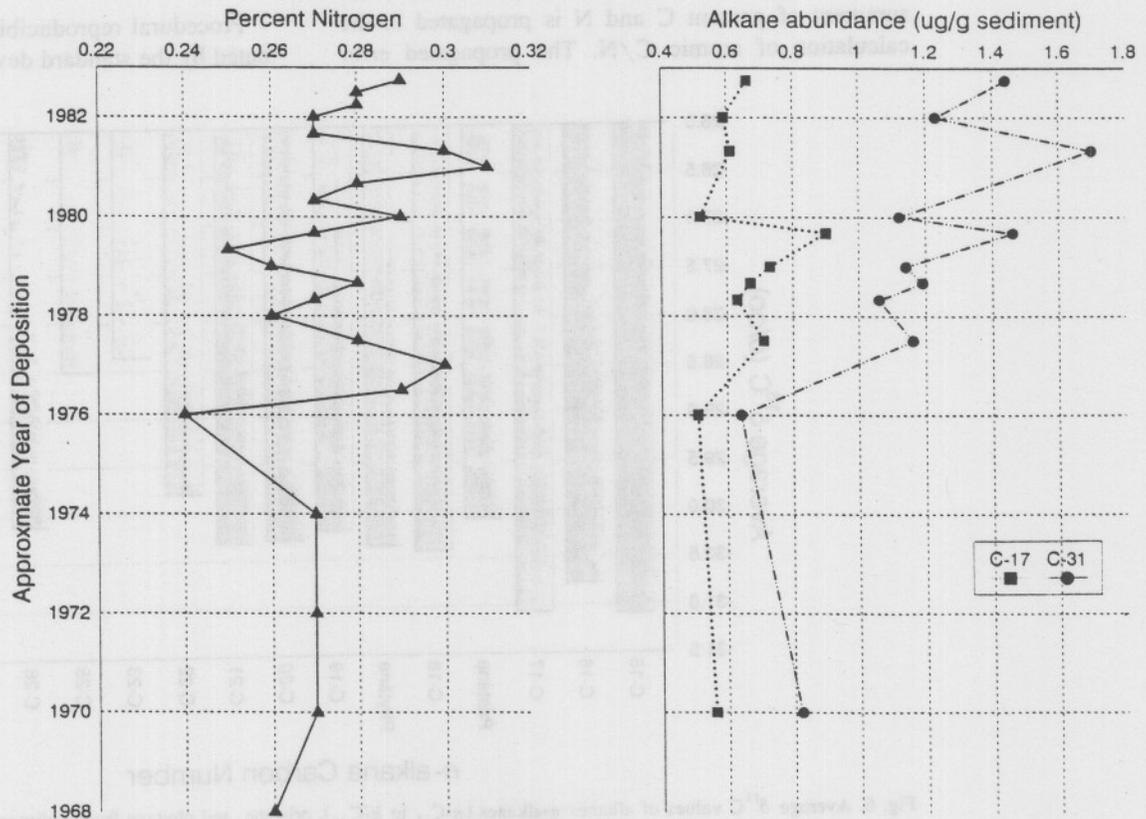


Fig. 5. Temporal variation in percent N and the absolute abundance of *n*-C<sub>17</sub> and *n*-C<sub>31</sub> ( $\mu\text{g g}^{-1}$  sediment) from sediments from the eastern basin of Lake Erie.

sedimentation and a cumulative weight of  $2.84 \text{ g cm}^{-2}$ . The mass sedimentation rate is  $0.88 \text{ g cm}^{-2} \text{ year}^{-1}$  and is much higher than previously reported estimates from the eastern basin of Lake Erie (Mortimer, 1987; Robbins et al., 1989).

### 3.2. Elemental abundance

Organic C and N elemental abundances are reported as percentages relative to dry sediment weight, and as atomic C/N (Figs. 1 and 2). The range in percent C is small (2.04 to 2.47%), with an average of  $2.26 \pm 0.11\%$ . Percent N ranges between 0.241 and 0.311%, with an average of  $0.274 \pm 0.016\%$ . The ratio of organic carbon to organic nitrogen averages  $9.60 \pm 0.38$  (Fig. 2).

Procedural reproducibility for elemental analysis, estimated as the standard deviation of triplicate analyses (sample preparation and elemental abundance determination), is  $\pm 0.06$  and  $\pm 0.02$  for percent C and N, respectively. Error associated with the measurement of percent C and N is propagated in the calculation of atomic C/N. The propagated error

associated with C/N, determined by the method of Taylor (1982), is  $\pm 0.58$ .

Net depletion of organic matter with depth in sediments can be an indicator of microbial remineralization of organic matter. There is no depletion in C abundance with depth in the core. Percent N decreases slightly from the top to the bottom of the core. The most salient feature of the data is the repetitive series of maxima and minima in both percent C and percent N. Comparison of the trends in percent C and percent N shows that maxima and minima co-occur in most instances. The observation that differences in percent C or N between two successive maxima and minima are, in many cases, two times greater than the procedural reproducibility indicates that these differences are not an artifact of analytical error and instead record actual variations in sedimentary organic matter content.

### 3.3. Carbon isotopic composition of the total sedimentary organic C

Procedural reproducibility for  $\delta^{13}\text{C}$  analysis, estimated by the standard deviation of triplicate analyses

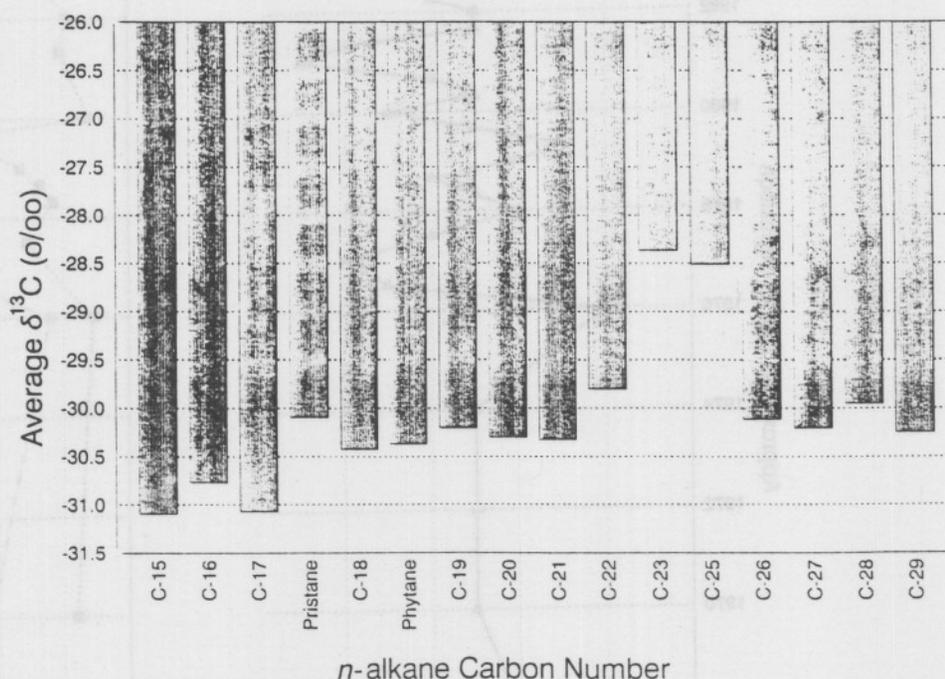


Fig. 6. Average  $\delta^{13}\text{C}$  values of alkanes  $n$ -alkanes ( $n$ -C<sub>15</sub> to  $n$ -C<sub>31</sub>), pristane, and phytane from sediments from the eastern basin of Lake Erie.

(sample preparation and isotopic determination) of a single sediment, is 0.2‰. The  $\delta^{13}\text{C}$  composition of sedimentary organic matter extracted from Lake Erie generally exhibits a trend of  $^{12}\text{C}$  enrichment between 1968 and 1970 (Fig. 2). The maximum  $\delta^{13}\text{C}$  value of  $-24.9\text{‰}$  is recorded in sediments deposited in 1970 and again in 1977. The minimum  $\delta^{13}\text{C}$  value of  $-25.9\text{‰}$  is recorded in sediments deposited in 1981.

The  $\delta^{13}\text{C}$  depth profile is characterized by a series of maxima and minima at intervals of 3 to 4 cm. These variations differ from the pattern of repeating maxima and minima exhibited by C and N abundances. The observation that differences in  $\delta^{13}\text{C}$  values between two successive maxima and minima are, in many cases, two times greater than the procedural reproducibility suggests that these differences are not an artifact of analytical error and record

actual variations in the isotopic composition of bulk organic carbon.

### 3.4. Concentrations of lipids

The analytical reproducibility for the amount of extractable organic material (EOM) determined by triplicate analysis of a surficial sediment is  $1.15 \pm 0.07 \mu\text{g g}^{-1}$  dry sediment. Sediments deposited during 1976–1977 contained  $2.07 \mu\text{g EOM g}^{-1}$  dry sediment, nearly twice the amount extracted from the most recent sediments. With the exception of these sediments, the total EOM ranges between 0.97 and  $1.70 \mu\text{g g}^{-1}$  and does not exhibit major variation with time (Fig. 3).

Each of the individual subfractions of EOM (aliphatic hydrocarbons, aromatic hydrocarbons, and

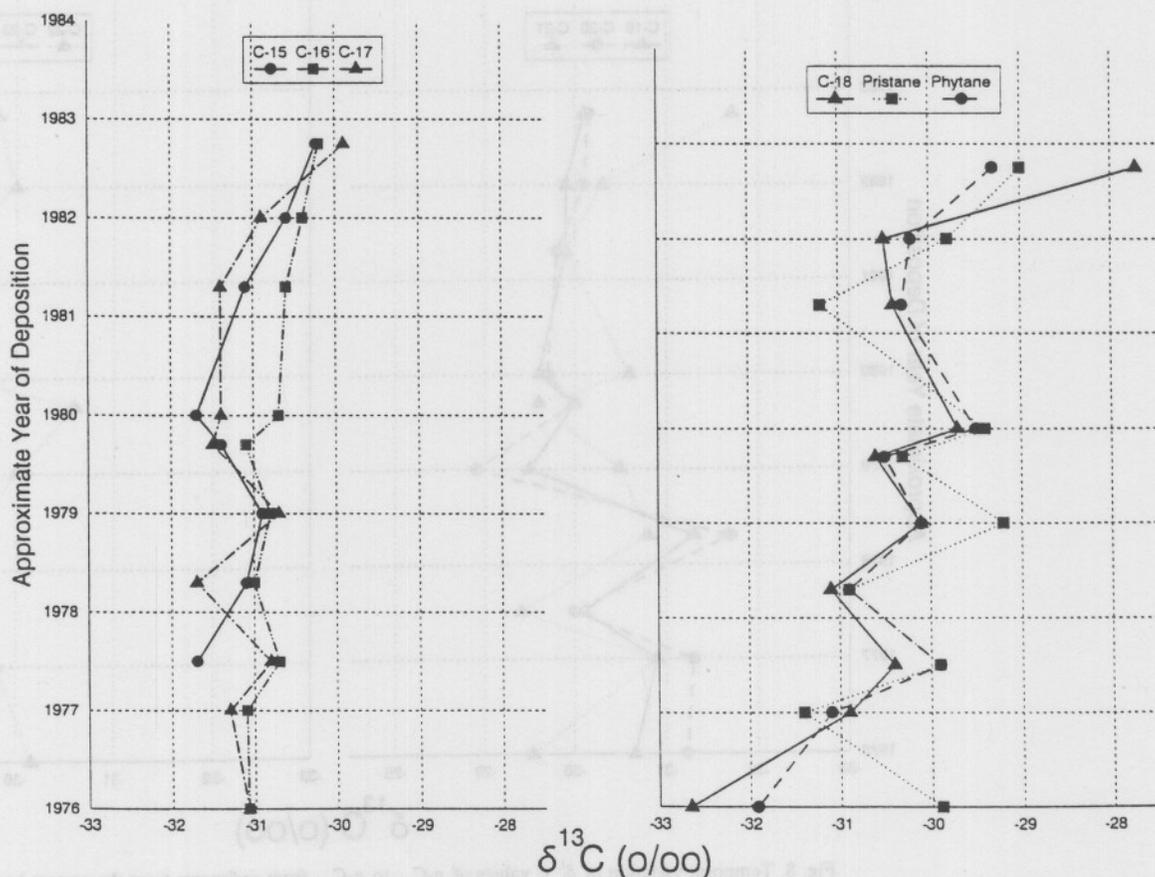


Fig. 7. Temporal variation in  $\delta^{13}\text{C}$  values of  $n\text{-C}_{15}$  to  $n\text{-C}_{18}$ , pristane, and phytane from sediments from the eastern basin of Lake Erie.

polar compounds) exhibits a decrease in concentration with depth in the upper 5 cm of the core (within sediments younger than 1981) that is likely due to early diagenetic degradation (Fig. 3). The aliphatic, aromatic and polar fractions contain an average of  $0.29 \pm 0.07$ ,  $0.15 \pm 0.03$  and  $0.41 \pm 0.07$  mg g<sup>-1</sup> dry sediment, respectively.

Concentrations for eighteen *n*-alkanes (C<sub>14</sub>–C<sub>31</sub>) and two branched alkanes (pristane and phytane; Fig. 4) have bimodal distributions that are typical of sediments with mixed terrestrial and algal sources of hydrocarbons (Giger et al., 1980; Ho and Meyers, 1994). Heptadecane (C<sub>17</sub>) is the most abundant *n*-alkane in the distribution, and either C<sub>29</sub> or C<sub>31</sub> is the major component in the secondary mode (Fig. 4).

The absolute abundances of short-chain *n*-alkanes (C<sub>14</sub>–C<sub>20</sub>) tend to decrease down core, but the abundances of mid (C<sub>21</sub>–C<sub>24</sub>) and long (C<sub>25</sub>–C<sub>31</sub>) chain *n*-alkanes remain relatively constant. Within the upper 10 cm (sediments younger than 1981), the abundance of *n*-C<sub>17</sub> is characterized by a series of variations that closely corresponds to the trend in percent N (Fig. 5). In contrast, variations in abundance of *n*-C<sub>31</sub> within the upper 10 cm are small.

### 3.5. $\delta^{13}\text{C}$ values of *n*-alkanes

Reproducibility for  $\delta^{13}\text{C}$  analysis of individual alkanes based on triplicate analyses of a single sample is  $\pm 0.3\text{‰}$ . Individual carbon isotope values of *n*-C<sub>15</sub> to *n*-C<sub>29</sub>, pristane and phytane in all samples

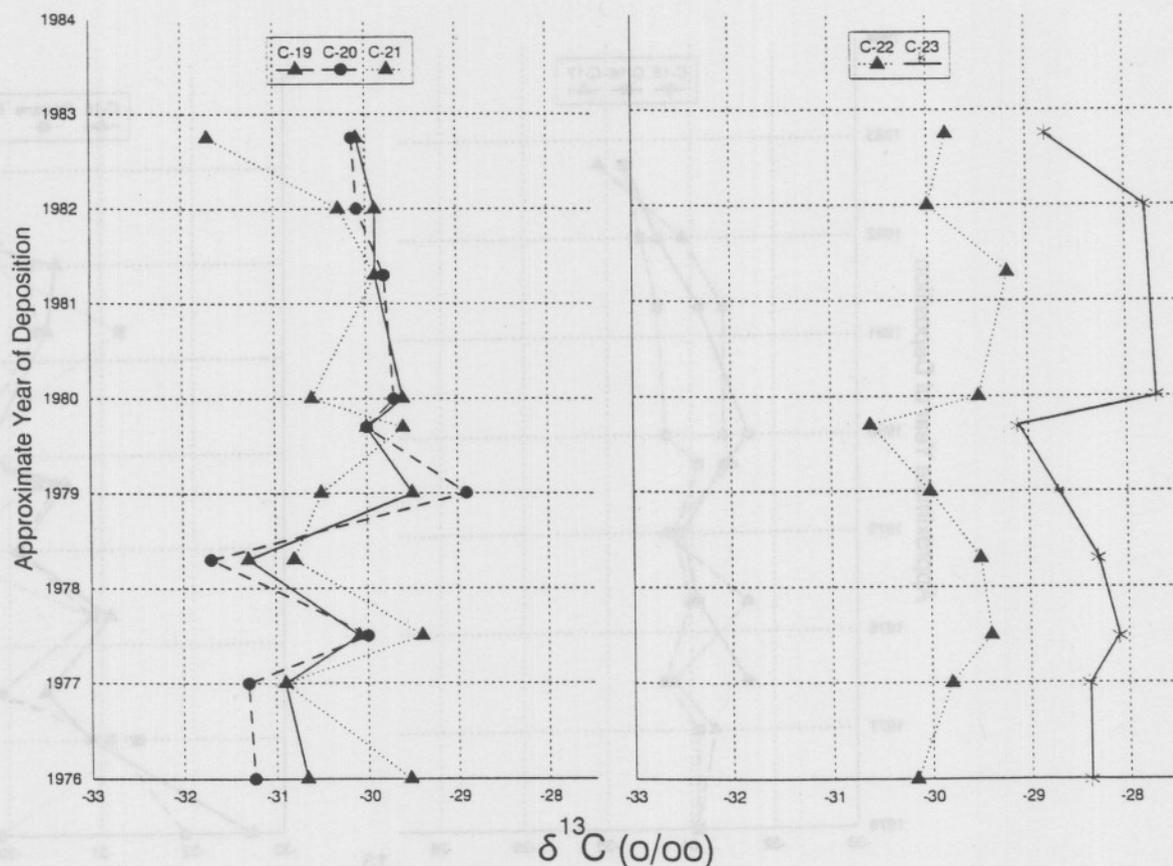


Fig. 8. Temporal variation in  $\delta^{13}\text{C}$  values of *n*-C<sub>19</sub> to *n*-C<sub>23</sub> from sediments from the eastern basin of Lake Erie.

analyzed ranged between  $-32.7$  and  $-27.8$ ‰. The average  $\delta^{13}\text{C}$  values of  $n\text{-C}_{15}$ ,  $n\text{-C}_{16}$ , and  $n\text{-C}_{17}$  are lower (at least  $1.0$ ‰) than those of alkanes with a longer C chain length (Fig. 6).

The highest  $\delta^{13}\text{C}$  values for  $n\text{-C}_{15}$ ,  $n\text{-C}_{16}$ ,  $n\text{-C}_{17}$ ,  $n\text{-C}_{18}$ , pristane, and phytane ( $-30.2$ ,  $-30.2$ ,  $-29.9$ ,  $-27.7$ ,  $-29$ ‰, and  $-29.3$ , respectively) are from the surface sediments of the core (Fig. 7). Within sediments deposited since 1981, there is a decrease in the  $\delta^{13}\text{C}$  values of these alkanes ( $0.5$  to  $2.9$ ‰) with depth. Within sediments older than 1981, the  $\delta^{13}\text{C}$  values of  $n\text{-C}_{16}$  to  $n\text{-C}_{17}$  range between  $-30.7$  and  $-31.7$ ‰ and exhibit coincident maxima and minima. With the exception of the 1976 sample (bottom of the core),  $\delta^{13}\text{C}$  values of pristane and  $n\text{-C}_{18}$  deposited prior to 1981, range between  $-31.4$

and  $-29.2$ ‰ and exhibit corresponding maxima and minima.

The  $\delta^{13}\text{C}$  values of  $n\text{-C}_{19}$  and  $n\text{-C}_{20}$  vary in a similar manner (Fig. 8). Between 1983 and 1980,  $\delta^{13}\text{C}$  values of these alkanes increase slightly down-core from approximately  $-30.2$  to  $-29.7$ ‰. In older sediments, large shifts in  $\delta^{13}\text{C}$  (as much as  $2.8$ ‰) occur between consecutive samples down-core. Similarly,  $\delta^{13}\text{C}$  values of  $n\text{-C}_{21}$  initially increase down-core and prior to 1979, exhibit maxima and minima that often coincide with those observed for  $n\text{-C}_{19}$  and  $n\text{-C}_{20}$ .

The down-core variations in  $\delta^{13}\text{C}$  values of  $n\text{-C}_{22}$  and  $n\text{-C}_{23}$  are similar but offset by approximately  $1.5$ ‰ ( $n\text{-C}_{23}$  is enriched in  $^{13}\text{C}$  relative to  $n\text{-C}_{22}$ ; Fig. 8). The most salient trend in the isotopic compo-

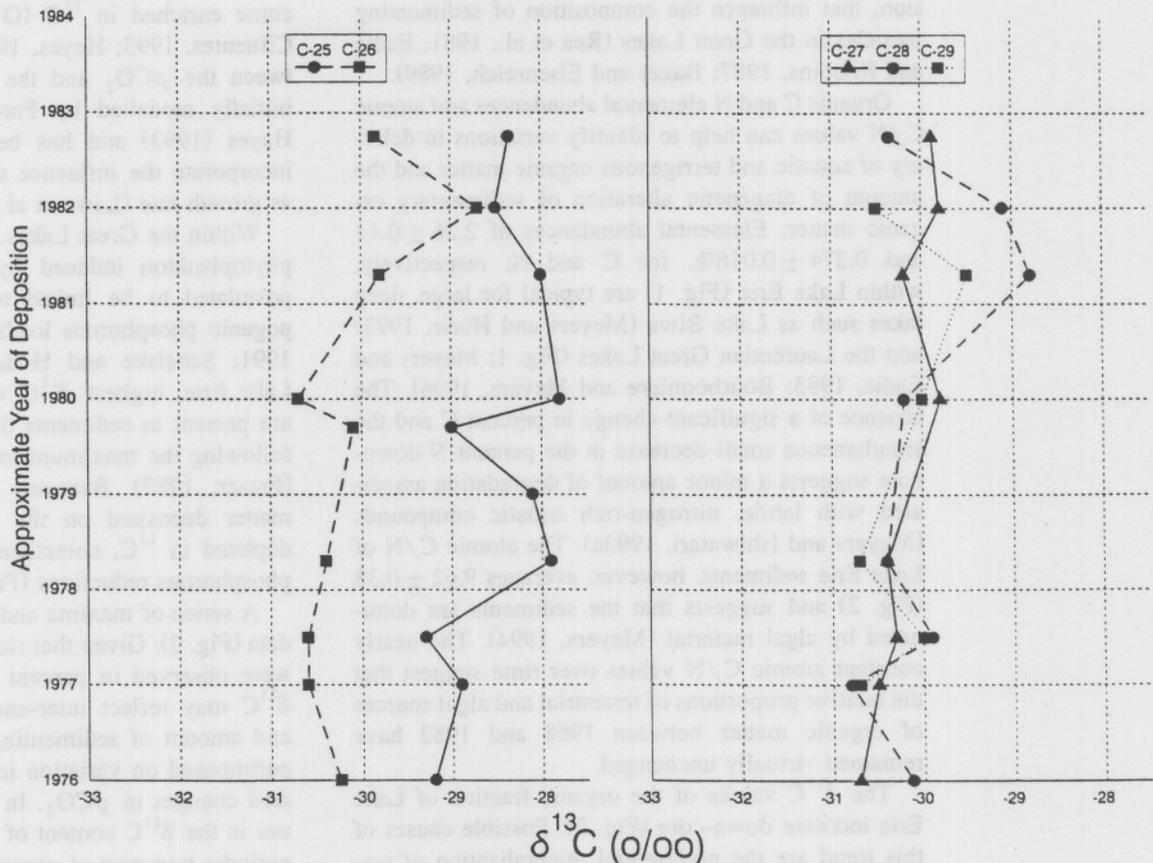


Fig. 9. Temporal variation in  $\delta^{13}\text{C}$  values of  $n\text{-C}_{25}$  to  $n\text{-C}_{29}$  from sediments from the eastern basin of Lake Erie.

sition of all alkanes from  $n\text{-C}_{25}$  to  $n\text{-C}_{29}$  is a decrease in  $\delta^{13}\text{C}$  values down-core (Fig. 9).

#### 4. Discussion

The high sedimentation rate in the eastern basin of Lake Erie (3 to 4 cm year<sup>-1</sup>) permits resolution of short-term variations in the geochemical characteristics of the sediments, despite a <sup>210</sup>Pb mixed depth of approximately 10.5 cm (Robbins et al., 1989). For example, large differences between maximum and minimum values for percent C, percent N, and  $\delta^{13}\text{C}$  data and variations in <sup>210</sup>Pb within this interval indicate that this portion of the sediment core has not been entirely homogenized by bioturbation and physical mixing (Fig. 1). These short-term variations reflect the complex interactions between the physical, chemical, and biological processes, such as shoreline erosion, biotic production and resuspension, that influence the composition of sedimenting particles in the Great Lakes (Rea et al., 1981; Eadie and Robbins, 1987; Baker and Eisenreich, 1989).

Organic C and N elemental abundances and atomic C/N values can help to identify variations in delivery of aquatic and terrigenous organic matter and the amount of diagenetic alteration of sedimentary organic matter. Elemental abundances of  $2.26 \pm 0.11$  and  $0.274 \pm 0.016\%$ , for C and N, respectively, within Lake Erie (Fig. 1) are typical for large, deep lakes such as Lake Biwa (Meyers and Horie, 1993) and the Laurentian Great Lakes (Fig. 1; Meyers and Eadie, 1993; Bourbonniere and Meyers, 1996). The absence of a significant change in percent C and the simultaneous small decrease in the percent N down-core suggests a minor amount of degradation associated with labile, nitrogen-rich aquatic compounds (Meyers and Ishiwatari, 1993a). The atomic C/N of Lake Erie sediments, however, averages  $9.62 \pm 0.38$  (Fig. 2) and suggests that the sediments are dominated by algal material (Meyers, 1994). The nearly constant atomic C/N values over time suggest that the relative proportions of terrestrial and algal sources of organic matter between 1968 and 1982 have remained virtually unchanged.

The  $\delta^{13}\text{C}$  values of the organic fraction of Lake Erie increase down-core (Fig. 2). Possible causes of this trend are the preferential mineralization of iso-

topically light carbon compounds, a change in the relative contribution of algal and terrestrial materials to the sediments, or variation in the  $\delta^{13}\text{C}$  of phytoplankton. Isotopic discrimination associated with mineralization appears to have a minor influence on the  $\delta^{13}\text{C}$  of organic sediments like those of Lake Erie that contain low concentrations of organic carbon (< 2–3%; Jasper and Hayes, 1990; Fontugne and Calvert, 1992; Meyers and Horie, 1993; Meyers, 1994). The lack of variation in atomic C/N argues against an increase in terrestrial organic matter. Consequently, the shift in  $\delta^{13}\text{C}$  values suggests that the  $\delta^{13}\text{C}$  content of autochthonous production has changed between 1970 and 1982.

The  $\delta^{13}\text{C}$  of phytoplankton has been observed to vary inversely with aqueous CO<sub>2</sub> concentrations (Rau et al., 1989; Fogel et al., 1992; Fogel and Cifuentes, 1993). Under CO<sub>2</sub> limitation, isotopic discrimination during fixation of C by the enzyme RuBP carboxylase is effectively diminished and aquatic algae become enriched in <sup>13</sup>C (O'Leary, 1981; Fogel and Cifuentes, 1993; Hayes, 1993). The relationship between the  $p\text{CO}_2$  and the  $\delta^{13}\text{C}$  of autotrophs was initially modelled by Farquhar et al. (1982) and Hayes (1993) and has been recently modified to incorporate the influence of additional factors such as growth rate (Laws et al., 1995).

Within the Great Lakes, variations in the  $\delta^{13}\text{C}$  of phytoplankton induced by changes in  $p\text{CO}_2$  are postulated to be linked to fluctuations in anthropogenic phosphorous loadings (Bourbonniere et al., 1991; Schelske and Hodell, 1991, 1995). Within Lake Erie, highest  $\delta^{13}\text{C}$  values for organic carbon are present in sediments deposited in 1970, 2 years following the maximum loading of anthropogenic P (Fraser, 1987). Between 1970 and 1982, organic matter deposited on the bottom of Lake Erie is depleted in <sup>13</sup>C, coincident with known records of phosphorous reductions (Fraser, 1987; Rosa, 1987).

A series of maxima and minima exist in the  $\delta^{13}\text{C}$  data (Fig. 2). Given that similar large scale variations were observed in percent C and N, these shifts in  $\delta^{13}\text{C}$  may reflect inter-annual changes in the type and amount of sedimenting particles, which are superimposed on variation in trophic state and associated changes in  $p\text{CO}_2$ . In particular, maximum values in the  $\delta^{13}\text{C}$  content of the sediments may reflect periodic transport of organic matter from the central

basin of the lake, which is more eutrophic than the eastern basin (Burns, 1985). Concentrations of specific subfractions of extractable organic matter and of individual hydrocarbons offer additional information about diagenesis and variations in organic matter sources (Matsuda and Koyama, 1977a,b; Ishiwatari et al., 1980; Giger et al., 1980; Cranwell, 1984a,b; Kawamura et al., 1987; Rieley et al., 1991). Between the top of the core and sediments deposited in 1978 (upper 16 cm), concentrations of total extractable hydrocarbons remain essentially constant ( $1.14 \pm 0.09 \text{ mg g}^{-1}$  dry sediment; Fig. 3). Concentrations of extractable organic matter in sediments deposited between 1976 and 1977 peak at  $2.07 \text{ mg g}^{-1}$  dry sediment. The peak in total extractable hydrocarbons does not coincide with an increase in the aliphatic, aromatic, or polar fractions (Fig. 3) and, therefore, reflects an increase in some extractable, yet refractory, component that is not represented in these three groups. An increase in highly weathered terrestrial material in 1976 could have been derived from shoreline erosion associated with high water levels in Lake Erie at this time (Stevens and Neilson, 1987).

With the exception of the upper three samples, the concentrations of aliphatic, aromatic, and polar compounds are nearly constant throughout the core (Fig. 3). The concentration of each of these compound classes in the upper three samples decreases with depth and suggests the diagenetic loss of labile, predominantly aquatic compounds in the near-surface sediments.

The relative abundance of pristane and phytane in sediments has previously been interpreted as an indicator of oxic/anoxic deposition (Didyk et al., 1978). One of the primary biosynthetic pathways of these molecules is through the oxic or anoxic decomposition of phytol, the alcohol side-chain of chlorophyll *a*, during later diagenesis (Peters and Moldowan, 1993; Ho and Meyers, 1994). In recent sediments, however, the presence of pristane reflects the decomposition of chlorophyll *a* in the digestive tract of copepods (Blumer et al., 1963; Ho and Meyers, 1994). Large fluctuations in pristane concentration throughout the sediment core indicate the annual variability of zooplankton grazing communities (Fig. 4). The concentration of phytane remains relatively constant with depth, indicating a different formative

process, which has varied little during the 14 years of sediment deposition (Fig. 4).

The bimodal distribution of *n*-alkanes with peaks at *n*-C<sub>17</sub>, and at *n*-C<sub>29</sub> or *n*-C<sub>31</sub> is characteristic of sedimentary environments having dual sources of organic matter (Giger et al., 1980; Ho and Meyers, 1994; Fig. 4). Heptadecane (*n*-C<sub>17</sub>) is the most abundant *n*-alkane in phytoplankton (Gelpi et al., 1970; Giger et al., 1980) and its dominance throughout the core supports interpretations of atomic C/N data that identify algae as the primary source of organic matter in Lake Erie (Fig. 4). The observation that within sediments deposited prior to 1979, down-core variations in percent N are similar to those for *n*-C<sub>17</sub> abundance but not *n*-C<sub>31</sub> abundance (Fig. 5) suggests the influence of algal material on the labile component of the bulk organic fraction of these sediments. The high concentrations of *n*-C<sub>29</sub> and *n*-C<sub>31</sub>, however, indicate that a large terrestrial component is also present in the EOM.

Although C<sub>17</sub> remains the dominant *n*-alkane throughout the sediment core, the ratio of algal to terrestrial *n*-alkanes (aquatic/terrestrial *n*-alkane index =  $(n\text{-C}_{15} + n\text{-C}_{17} + n\text{-C}_{19}) / (n\text{-C}_{27} + n\text{-C}_{29} + n\text{-C}_{31})$ ; Bourbonniere and Meyers, 1996) changes down-core (Fig. 10). The decrease of at least 0.5 in the short/long *n*-alkane index for sediments younger than 1980 relative to older sediments suggests that short-chained algal *n*-alkanes may be preferentially respired by heterotrophs in the mixed layer of the sediments. A similar loss of autochthonous material was not observed in atomic C/N data for bulk organic material. The distinction is important because it emphasizes that individual compounds are much more sensitive to diagenetic alteration than is bulk organic matter.

The prevalence of algal *n*-alkanes (*n*-C<sub>15</sub> to *n*-C<sub>19</sub>) throughout the core provides an opportunity to evaluate relationships between variations in trophic state and  $\delta^{13}\text{C}$  values of individual compounds derived specifically from algae. Despite evidence that the total organic carbon is predominantly autochthonous, the down-core trend in  $\delta^{13}\text{C}$  values for the algal alkanes and bulk sedimentary organic matter interestingly differs (Figs. 2 and 7). In contrast to the general decrease in  $\delta^{13}\text{C}$  values from the bottom to the top of the core observed for bulk sediments, algal alkanes show little variation for sediments older

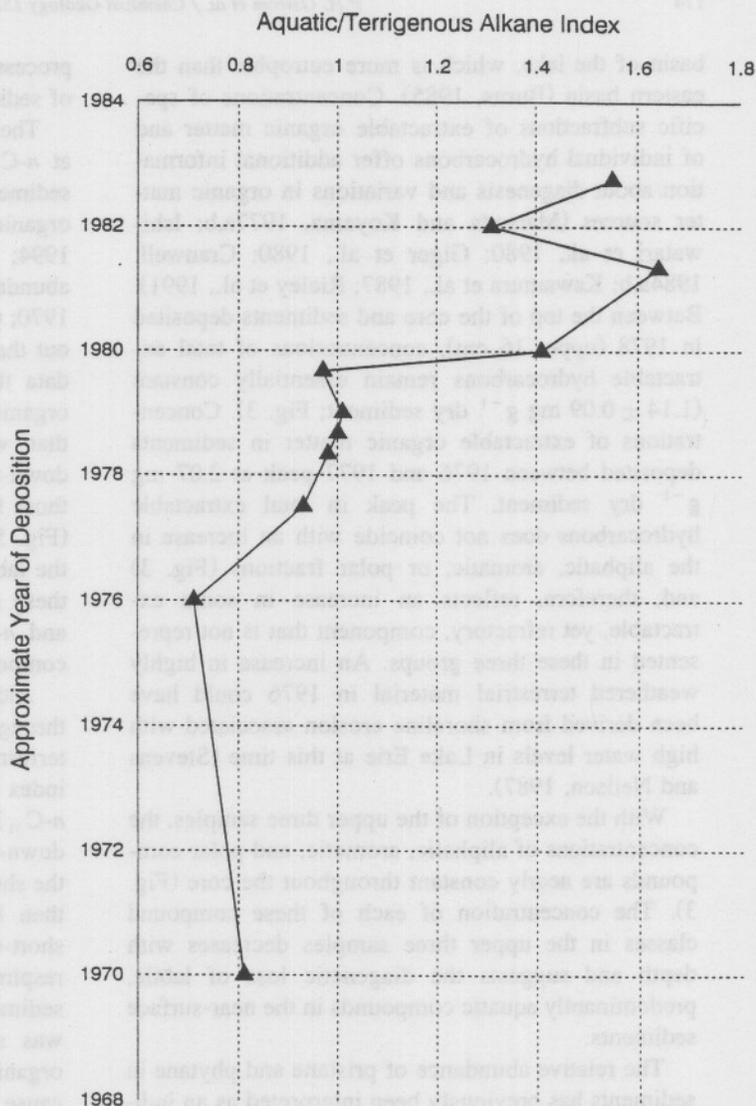


Fig. 10. Short/long *n*-alkane index =  $(n-C_{15} + n-C_{17} + n-C_{19}) / (n-C_{27} + n-C_{29} + n-C_{31})$  for sediments from the eastern basin of Lake Erie.

than 1980 and an increase between 1980 and 1983. Whereas  $\delta^{13}C$  value of bulk organic C is influenced by diverse reactions associated with multiple sources and processes, isotopic compositions of individual sedimentary hydrocarbons are determined by isotope effects associated with specific reactions of biosynthesis and diagenesis that are unique to the molecule. For example, the  $^{13}C$  depletion of the lipids relative to bulk organic carbon (1.7 to 5.7‰ based on com-

parison of average  $\delta^{13}C$  between sediments and individual alkanes) reflects isotopic fractionation during the oxidation of pyruvate to acetyl coenzyme-A (DeNiro and Epstein, 1977; Monson and Hayes, 1982) and hydrolysis of the thioester bond attaching the acyl chain to the carrier protein during elongation (Monson and Hayes, 1980). Molecular isotopic data may not be directly comparable to  $\delta^{13}C$  values of bulk organic carbon. Consequently, we discuss our

molecular data by comparing it to published  $\delta^{13}\text{C}$  data for *n*-alkanes and by considering factors that can affect variations in  $^{13}\text{C}$  enrichment of individual compounds.

The  $\delta^{13}\text{C}$  values of *n*-alkanes from Lake Erie sediments ( $-32.7$  to  $-27.8\text{‰}$ ) are generally similar to those reported for marine sediments from the Black Sea and Cariaco Trench ( $-31.6$  to  $-29.7\text{‰}$  and  $-32.8$  to  $-26.7$ , respectively; Freeman et al., 1994), Tokyo Bay ( $-32.9$  to  $-28.2$ ; Ishiwatari et al., 1994), New Zealand ( $-33.0$  to  $-27.0\text{‰}$ ; Kennicutt and Brooks, 1990) and coastal Newfoundland ( $-31.3$  to  $-26.0\text{‰}$ ; Bakel et al., 1994), but are enriched in  $^{13}\text{C}$  relative to those of Ellesmere Lake sediments ( $-35.9$  to  $-30.3\text{‰}$ ; Rieley et al., 1991). The low  $\delta^{13}\text{C}$  values of hydrocarbons from Ellesmere Lake sediments are similar to those of deciduous trees that surround the lake and likely reflect a greater contribution of allochthonous material relative to that which occurs in Lake Erie.

Within Lake Erie sediments, large variations in  $\delta^{13}\text{C}$  values (as much as  $5\text{‰}$  among different alkanes) exist among algal *n*-alkanes ( $n\text{-C}_{15}$  to  $n\text{-C}_{19}$ ) and for a single alkane (e.g.,  $n\text{-C}_{18}$ ) obtained from different sediment samples (Fig. 7). Such large variation is not unusual. Carbon isotope values of *n*-alkanes obtained from a single plant can differ by as much as  $6\text{‰}$  (Collister et al., 1994a). This was suggested to have been related to differences in the amount of homologs produced during the growth cycle under unique water and nutrient availability. Differences in  $\delta^{13}\text{C}$  values of *n*-alkanes of the same chain length obtained from sediments from similar depositional environments are as great as  $3.6\text{‰}$  (Freeman et al., 1994). Clearly, the expectation should be that the  $\delta^{13}\text{C}$  composition of sedimentary alkanes will differ between ecosystems as a consequence of the complex set of reactions that occur during biosynthesis and diagenesis.

The current study reports a pattern of  $^{13}\text{C}$  enrichment wherein the  $\delta^{13}\text{C}$  of  $n\text{-C}_{15}$  to  $n\text{-C}_{17} < n\text{-C}_{18}$  to  $n\text{-C}_{25}$  and  $n\text{-C}_{27}$  to  $n\text{-C}_{29} <$  than  $n\text{-C}_{23}$  and  $n\text{-C}_{25}$  (Fig. 6). These results differ from those of Spooner et al., 1994, who did not observe a difference in  $\delta^{13}\text{C}$  between low molecular weight alkanes ( $n\text{-C}_{17}$  and  $n\text{-C}_{19}$ ) and their homologs with a longer C chain length. Other studies, however, have observed depletions of  $^{13}\text{C}$  among short chained *n*-alkanes believed

to be of phytoplankton origin relative to the higher molecular weight alkane components (Hollander et al., 1993; Bakel et al., 1994; Collister et al., 1994b). Low  $\delta^{13}\text{C}$  values (e.g.,  $-31.7\text{‰}$ ) of sedimentary alkanes should not be unexpected given the observation of low  $\delta^{13}\text{C}$  values for sinking particles and near-surface sediments in lacustrine systems ( $-38$  to  $-25\text{‰}$ ) (Hollander and McKenzie, 1991; Schelske and Hodell, 1991; Meyers and Eadie, 1993; Schelske and Hodell, 1995) and the further  $^{13}\text{C}$  depletion that is typical of lipids relative to the material from which they are derived (Abelson and Hoering, 1961). Within Lake Erie, short chained *n*-alkanes are likely derived from phytoplankton ( $n\text{-C}_{15}$  to  $n\text{-C}_{17}$ ) and have lower average  $\delta^{13}\text{C}$  values than long chained homologs of terrestrial origin ( $n\text{-C}_{26}$  to  $n\text{-C}_{29}$ ; Fig. 6). The origins of the  $^{13}\text{C}$  enriched alkanes,  $n\text{-C}_{23}$  and  $n\text{-C}_{25}$ , remains unclear.

Down-core variation in the  $\delta^{13}\text{C}$  values of an individual *n*-alkane reflects kinetic isotope effects associated with a diverse series of reactions occurring during diagenesis. Kinetic isotopic discrimination typically results in preferential incorporation of  $^{12}\text{C}$  into the product, leaving the residual substrate enriched in  $^{13}\text{C}$  (Mariotti et al., 1981). Decreases in  $\delta^{13}\text{C}$  values of  $n\text{-C}_{15}$ ,  $n\text{-C}_{16}$ ,  $n\text{-C}_{17}$ , and  $n\text{-C}_{18}$  (Fig. 7) with depth between 1983 and 1980 may reflect the incorporation of isotopically light alkanes produced from defunctionalization of acids, alcohols, or esters during diagenesis. Long chained hydrocarbons of terrestrial origin are typically the survivors of extensive organic matter alteration prior to entering lake sediments (Meyers and Ishiwatari, 1993b) and, therefore, are not likely to be influenced by the same processes as algal hydrocarbons. This might explain why the  $\delta^{13}\text{C}$  values of long chained alkanes ( $n\text{-C}_{26}$  to  $n\text{-C}_{29}$ ) in the sediments deposited prior to 1980 do not exhibit the same pattern of variation as their short chain homologs (Figs. 7–9). In addition to kinetic isotope effects, variations in the relative contributions of isotopically unique *n*-alkanes to the sediments and temporal changes in  $^{13}\text{C}$  enrichments of *n*-alkanes associated with a single source can contribute to the down-core variation in  $\delta^{13}\text{C}$  values of single *n*-alkanes. For example, alkanes derived from *n*-alkanoic acids occurring in eukaryotes and eubacteria as triglyceride esters have not been isotopically characterized and are an unknown source of

variance in the data. At this point, the relative importance of different factors on the  $\delta^{13}\text{C}$  of individual hydrocarbons including kinetic isotope effects, variation in the relative abundance of *n*-alkanes from different sources or changes in the characteristics of a single source cannot be evaluated.

## 5. Conclusions

The isotopic composition of the bulk organic C in sediments from Lake Erie exhibits a significant decrease in  $^{13}\text{C}$  content between 1968 and 1982. Based on C and N elemental data and *n*-alkane distributions, this decrease in  $^{13}\text{C}$  is related neither to a change in diagenetic activity nor to a change in the relative distribution of terrestrial and aquatic sources of organic matter. Therefore, it is likely that the isotopic shift is due to a decrease in the algal productivity, a response related to diminished P loadings to Lake Erie since the mid-1970s.

Series of maxima and minima in percent C, percent N, and organic  $\delta^{13}\text{C}$  content occur in the sediment record. These variations and those in  $^{210}\text{Pb}$  activity indicate that sediments were not completely homogenized, despite a  $^{210}\text{Pb}$  mixed depth of 10.5 cm. The fluctuations in geochemical characteristics of Lake Erie sediments appear to reflect short term variations in the relative abundance of different types of particles settling to the lake bottom.

The diagenetic alteration and variations in the relative contributions of different sources of organic matter affect individual molecules, compound classes, and the bulk organic fraction differently. Early diagenetic alteration of the organic sediments is apparent in variations of the concentrations of *n*-alkanes, compound classes, and, possibly, the  $\delta^{13}\text{C}$  composition of short chained *n*-alkanes. The absence of significant change in the percent C content of the sediments, however, suggests that diagenetic alteration alone is insufficient to affect the  $\delta^{13}\text{C}$  of the bulk organic fraction.

Whereas  $\delta^{13}\text{C}$  values of bulk organic material appear to present an integrated history of the trophic state of Lake Erie, temporal variations in the C isotopic composition of individual *n*-alkanes appears to be largely influenced by a complex set of factors associated with diagenesis. The molecular isotopic

data for this core emphasize temporal variability that might not otherwise be apparent in sediments from environments that are characterized by low rates of deposition.

Bradshaw et al. (1991) suggested the possibility that little bulk organic material would survive the effects of heterotrophy but that a selection of algal biomarkers would. Our study demonstrates that isotopic analysis of bulk organic matter and of individual molecules has the potential to offer two distinct yet important sets of information. Furthermore, our results clearly emphasize that the retrieval of information relating to ecosystem level processes (e.g., trophic state or variations in  $p\text{CO}_2$ ) from molecular  $\delta^{13}\text{C}$  data will require careful selection of compounds whose  $\delta^{13}\text{C}$  values express this type of information rather than having isotopic compositions that are controlled by biosynthetic and diagenetic reactions that are unique to the molecule.

## Acknowledgements

Support for analyses was provided by a fellowship from the GE Foundation to PHO and the National Science Foundation (BIR9120006 to the Center for Microbial Ecology, Michigan State University). The sediment core was provided by the Great Lakes Environmental Research Laboratory, US National Oceanic and Atmospheric Administration.

## References

- Abelson, P.H., Hoering, T.C., 1961. Carbon isotope fractionation in formation of amino acids by photosynthetic organisms. *Proc. Natl. Acad. Sci. U.S.A.* 7, 623–632.
- Bakel, A.J., Ostrom, P.H., Ostrom, N.E., 1994. Carbon isotopic analysis of individual *n*-alkanes: evaluation of accuracy and application to marine particulate organic material. *Org. Geochem.* 21, 595–602.
- Baker, J.E., Eisenreich, S.J., 1989. PCBs and PAHs as tracers of particulate dynamics in large lakes. *J. Great Lakes Res.* 15, 84–103.
- Beardall, J., Griffiths, H., Raven, J.A., 1982. Carbon isotopic discrimination and the  $\text{CO}_2$  accumulating mechanisms in *Chlorella emersonii*. *J. Exp. Bot.* 33, 729–737.
- Blumer, M., Mullin, M.M., Thomas, D.S., 1963. Pristane in zooplankton. *Science* 140, 974.
- Bourbonniere, J.A., Meyers, P.A., 1996. Sedimentary geolipid

- records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnol. Oceanogr.*
- Bourbonniere, R.A., Meyers, P.A., Eadie, B.J., Robbins, J.A., 1991. Environmental and diagenetic effects on geolipid compositions of sediments in Lakes Erie and Ontario. In: Manning, D.A.C. (Ed.), *Organic Geochemistry: Advances and Applications in the Natural Environment*. Manchester Univ. Press, Manchester, pp. 498–501.
- Bradshaw, S.A., Eglinton, G., O'Hara, S.C.M., Corner, 1991. Biogeochemical changes in lipids in a model marine food chain. *Dev. Environ. Biogeochem.* 6, 49–58.
- Burns, 1985. *Erie: The Lake That Survived*. Rowman and Allanheld, Totowa, NJ.
- Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994a. Compound-specific  $^{13}\text{C}$  analysis of leaf lipids from plants with differing carbon dioxide metabolisms. *Org. Geochem.* 21, 619–627.
- Collister, J.W., Lichtfouse, G., Hieshima, G., Hayes, J.M., 1994b. Partial resolution of sources of *n*-alkanes in the saline portion of the Parachute Creek Member, Green River Formation (Piceance Creek Basin, Colorado). *Org. Geochem.* 21, 645–659.
- Cranwell, P.A., 1984a. Lipids of aquatic sediments and sedimenting particles. *Prog. Lipid Res.* 21, 271–308.
- Cranwell, P.A., 1984b. Lipid geochemistry of sediments from Upton Broad, a small productive lake. *Org. Geochem.* 7, 25–37.
- DeNiro, M.J., Epstein, S., 1977. Mechanism of carbon isotope fractionation associated with lipid synthesis. *Science* 197, 261–263.
- Didyk, B.M., Simoneit, B.R.T., Brassell, S.C., Eglinton, G., 1978. Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature* 272, 216–222.
- Eadie, B.J., Robbins, J.A., 1987. The role of particulate matter in the movement of contaminants in the Great Lakes. In: Hites, R.A., Eisenreich, S.J. (Eds.), *Sources and Fates of Aquatic Pollutants*. Am. Chem. Soc., Adv. Chem., Ser. No. 216, pp. 319–364.
- Eisenreich, S.J., Capel, P.D., Robbins, J.A., Bourbonniere, R., 1989. Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. *Environ. Sci. Technol.* 23, 1116–1126.
- Farquhar, G.D., O'Leary, M.H., Berry, J.A., 1982. On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Aust. J. Plant Physiol.* 9, 121–137.
- Fogel, M.L., Cifuentes, L.A., 1993. Isotope fractionation during primary production. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry*. Plenum, New York, pp. 73–97.
- Fogel, M.L., Cifuentes, L.A., Velinsky, D.J., Sharp, J.H., 1992. Relationship of carbon availability in estuarine phytoplankton to isotopic composition. *Mar. Ecol. Prog. Ser.* 82, 291–300.
- Fontugne, M.R., Calvert, S.E., 1992. Late Pleistocene variability of the carbon isotopic composition of organic matter in the eastern Mediterranean: monitor of changes in carbon sources and atmospheric  $\text{CO}_2$  concentrations. *Paleoceanography* 7, 1–20.
- Fraser, A.S., 1987. Tributary and point source total phosphorus loading to Lake Erie. *J. Great Lakes Res.* 13, 659–666.
- Freeman, K.H., Wakeham, S.G., Hayes, J.M., 1994. Predictive isotopic biogeochemistry: hydrocarbons from anoxic marine basins. *Org. Geochem.* 21, 629–644.
- Gelpi, E., Schneider, H., Mann, J., Oro, J., 1970. Hydrocarbons of geochemical significance in microscopic algae. *Phytochemistry* 9, 603–612.
- Giger, W., Schaffner, C., Wakeham, S.G., 1980. Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. *Geochim. Cosmochim. Acta* 44, 119–129.
- Goerck, R., Montoya, J.P., Fry, B., 1994. Physiology of isotopic fractionation in algae and cyanobacteria. In: Lajtha, K., Michener, R.H. (Eds.), *Stable Isotopes in Ecology and Environmental Science*. Blackwell, Oxford, pp. 187–221.
- Hayes, J.M., 1993. Factors controlling  $^{13}\text{C}$  contents of sedimentary organic compounds: principles and evidence. *Mar. Geol.* 113, 111–125.
- Hinga, K.R., Arthur, M.A., Pilson, M.E.Q., Whitaker, D., 1994. Carbon isotope fractionation by marine phytoplankton in culture: the effects of  $\text{CO}_2$  concentration, pH, temperature, and species. *Global Biogeochem. Cycles* 8, 91–102.
- Ho, E.S., Meyers, P.A., 1994. Variability of early diagenesis in lake sediments: evidence from the sedimentary geolipid record in an isolated tarn. *Chem. Geol.* 112, 309–324.
- Hollander, D.J., McKenzie, J.A., 1991.  $\text{CO}_2$  control on carbon isotope fractionation during aqueous photosynthesis: a paleo- $\text{pCO}_2$  barometer. *Geology* 19, 929–932.
- Hollander, D.J., Sinningh-Demasté, J.S., Hayes, J.M., DeLeeuw, J.W., Huc, A.Y., 1993. Molecular and bulk isotopic analyses of organic matter in marls of the Mulhouse basin (Tertiary, Alsace, France). *Org. Geochem.* 20, 1252–1263.
- Ishiwatari, R., Ogura, K., Horie, S., 1980. Organic geochemistry of a lacustrine sediment (Lake Haruna, Japan). *Chem. Geol.* 29, 261–280.
- Ishiwatari, R., Uzaki, M., Yamada, K., 1994. Carbon isotope composition of individual *n*-alkanes in recent sediments. *Org. Geochem.* 21, 801–808.
- Jasper, J.P., Hayes, J.M., 1990. A carbon-isotopic record of  $\text{CO}_2$  levels during the Late Quaternary. *Nature* 347, 462–464.
- Kawamura, K., Ishiwatari, R., Ogura, K., 1987. Early diagenesis of organic matter in the water column and sediments: microbial degradation and resynthesis of lipids in Lake Haruna. *Org. Geochem.* 11, 251–264.
- Kennicutt, M.C., Brooks, J.M., 1990. Unusual normal alkane distributions in offshore New Zealand sediments. *Org. Geochem.* 15, 193–197.
- Kvenvolden, K.A., Rapp, J.B., Golan-Bac, M., Hostettler, F.D., 1987. Multiple sources of alkanes in Quaternary oceanic sediment of Antarctica. *Org. Geochem.* 11, 291–302.
- Laws, E.A., Popp, B.N., Bidigare, R.R., Kennicutt, M.C., Macko, S.A., 1995. Dependence of phytoplankton isotopic composition on growth rate and  $[\text{CO}_2]_{\text{atm}}$ : theoretical considerations and experimental results. *Geochim. Cosmochim. Acta* 59, 1131–1138.
- Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., Tardieux, P., 1981. Experimental determination

of nitrogen kinetic isotope fractionation: some principles: illustration for the denitrification and nitrification processes. *Plant and Soil* 62, 413–430.

- Matsuda, H., Koyama, T., 1977a. Early diagenesis of fatty acids in lacustrine sediments: I. Identification and distribution of fatty acids in recent sediment from a freshwater lake. *Geochim. Cosmochim. Acta* 41, 777–783.
- Matsuda, H., Koyama, T., 1977b. Early diagenesis of fatty acids in lacustrine sediments: II. A statistical approach to changes in fatty acid composition from recent sediments and source materials. *Geochim. Cosmochim. Acta* 41, 1825–1834.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 144, 289–302.
- Meyers, P.A., Eadie, B.J., 1993. Sources, degradation, and recycling of organic matter associated with sinking particles in Lake Michigan. *Org. Geochem.* 20, 47–56.
- Meyers, P.A., Horie, S., 1993. An organic carbon isotopic record of glacial–postglacial change in atmospheric  $p\text{CO}_2$  in the sediments of Lake Biwa, Japan. *Paleogeogr. Paleoclimatol. Paleoecol.* 105, 171–178.
- Meyers, P.A., Ishiwatari, R., 1993a. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. *Org. Geochem.* 20, 867–900.
- Meyers, P.A., Ishiwatari, R., 1993b. The early diagenesis of organic matter in lacustrine sediments. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry*. Plenum, New York, pp. 185–209.
- Monson, K.D., Hayes, J.M., 1980. Biosynthetic control of the natural abundance of carbon 13 at specific positions within fatty acids in *Escherichia coli*. *J. Biol. Chem.* 55, 11435–11441.
- Monson, K.D., Hayes, J.M., 1982. Carbon isotopic fractionation in biosynthesis of bacterial fatty acids. Ozonolysis of unsaturated fatty acids as a means of determining the intra-molecular distribution of carbon isotopes. *Geochim. Cosmochim. Acta* 46, 139–149.
- Mortimer, C.H., 1987. Fifty years of physical investigations and related limnological studies on Lake Erie, 1928–1977. *J. Great Lakes Res.* 13, 407–435.
- O'Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553–567.
- Peters, K.E., Moldowan, J.M., 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice-Hall, Englewood Cliffs, NJ, 363 pp.
- Rau, G.H., Takahashi, Des Marais, D.J., 1989. Latitudinal variations in plankton  $\delta^{13}\text{C}$ : implications for  $\text{CO}_2$  and productivity in past oceans. *Nature* 341, 516–518.
- Rea, O.K., Owen, R.M., Meyers, P.A., 1981. Sedimentary processes in the Great Lakes. *Rev. Geophys. Space Phys.* 19, 635–648.
- Riele, G., Collier, R.J., Jones, D.M., Eglinton, G., Eakin, P.A., Fallick, A.E., 1991. Sources of sedimentary lipids deduced from stable carbon-isotope analysis of individual compounds. *Nature* 352, 425–427.
- Robbins, J.A., Edgington, D.N., 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. *Geochim. Cosmochim. Acta* 39, 285–304.
- Robbins, J.A., Keilty, T., White, D.S., Edgington, D.N., 1989. Relationships among Tubificid abundances, sediment composition, and accumulation rates in Lake Erie. *Can. J. Aquat. Sci.* 46, 223–231.
- Roeske, C.A., O'Leary, M.H., 1984. Carbon isotope effects on the enzyme-catalyzed carboxylation of ribulose bisphosphate. *Biochemistry* 23, 6275–6284.
- Rosa, F., 1987. Lake Erie central basin: total phosphorus trend analysis from 1968 to 1982. *J. Great Lakes Res.* 13, 667–673.
- Rosa, F., Burns, N.M., 1987. Lake Erie central basin oxygen depletion changes from 1929 to 1980. *J. Great Lakes Res.* 13, 684–696.
- Schelske, C.L., Hodell, D.A., 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* 36, 961–975.
- Schelske, C.L., Hodell, D.A., 1995. Using carbon isotopes of bulk sedimentary organic-matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. *Limnol. Oceanogr.* 40, 918–929.
- Schoell, M., Simoneit, B.R.T., Wang, T.-G., 1994. Organic geochemistry and coal petrology of Tertiary brown coal in the Zhoujing mine, Baise Basin, South China: IV. Biomarker sources inferred from stable carbon isotope compositions of individual compounds. *Org. Geochem.* 21, 713–720.
- Spooner, N., Riele, G., Collister, J.W., Lander, M., Cranwell, P.A., Maxwell, J.R., 1994. Stable carbon isotopic correlation of individual biolipids in aquatic organisms and a lake bottom sediment. *Org. Geochem.* 21, 823–827.
- Stevens, R.J.J., Neilson, M.A., 1987. Response of Lake Ontario to reductions in phosphorus load, 1967–1982. *Can. J. Fish. Aquat. Sci.* 44, 2059–2068.
- Takahashi, K., Yoshioka, T., Wada, E., Sakamoto, M., 1990. Temporal variations in carbon isotope ratio of phytoplankton in an eutrophic lake. *J. Plankton Res.* 12, 799–808.
- Taylor, J.R., 1982. *An Introduction to Error Analysis*. Oxford Univ. Press, Mill Valley, CA, 342 pp.
- Wong, W.W., Clarke, L.L., Johnson, G.A., Laurador, M., Klein, P.D., 1992. Comparison of two elemental-analyzer gas-isotope ratio mass spectrometer systems in the simultaneous measurement of  $^{13}\text{C}/^{12}\text{C}$  ratios and carbon content in organic samples. *Anal. Chem.* 64, 354–358.