

# **Organic Marine Geochemistry**



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# Organic Marine Geochemistry

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# FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

# PREFACE

**B**OTH ORGANIC AND INORGANIC AREAS of water-column and sediment geochemistry have recently served as the focus of much research. This book deals with major advances in organic marine and estuarine geochemistry, as well as the effects of organic substances on the speciation and distribution of inorganic and organometallic substances. The organization of this book is such that it should prove useful not only as a collection of related research articles, but also as a reference and a text suitable for graduate and advanced undergraduate courses in organic marine geochemistry.

The authors of the chapters include internationally acclaimed experts in their respective areas of specialization. Basic geochemical topics such as structures are included as well as diagenesis of organic natural products. Also discussed are anthropogenic pollutant substances in the marine environment and the effect of diagenesis and cycling on the distribution and fate of both toxic and nontoxic substances. I hope the combination of review and application chapters has produced a book that will be useful to many people in diverse fields.

Without the enthusiasm and cooperation of the exceptional authors and the encouragement of the former chairmen of the Geochemistry Division (F. Miknis, T. Weismann, and G. Helz), this book never would have materialized. In addition, I would like to thank my husband, Rolf, for assisting in the drafting of tables and figures and for helping with the organization of the book. I am also indebted to the Geochemistry Division for its support in sponsoring the symposium from which this book was developed and to The Petroleum Research Fund, administered by the American Chemical Society, for partial support of the symposium.

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# Organic Marine Geochemistry

## An Overview

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The use of modern hyphenated methods such as GC-MS have proven invaluable to the task of assigning specific sources to specific organic compounds isolated from marine sediments, suspended particulate matter, interstitial water and seawater. Early chapters of this volume discuss the correlation of various classes of compounds isolated largely from marine and brackish sediments with sources consisting of terrigenous plants, bacteria, phytoplankton, zooplankton and nonbiological components such as anthropogenic input, petroleum seepage, and the weathering of "mineral" deposits.

### Biomarkers

A biological marker (or "biomarker") may be defined as "a compound the structure of which can be interpreted in terms of a previous biological origin." Since the isolation and identification of metalloporphyrins in bitumens by Treibs (2) in the 1930's and their correlation with tetrapyrroles of chlorophylls, implying a biological origin for petroleum, an enormous amount of progress has been accomplished in this area of research.

In order to be a useful biomarker, a compound must retain enough of its original structure to be identified as a modified version of the original biological parent compound. The retention of the carbon backbone of biologically generated alcohols, in alkanes isolated from sediments and petroleum fractions, includes the classic cases of pristane and phytane as diagenetic products of phytol (the alcohol which esterifies the carboxylic acid group in chlorophyll-a) and 5 $\alpha$ -cholestane from cholesterol. Other examples of the usefulness of alkanes as biomarkers include correlations of various n-alkanes to bacterial populations (3), and the association of C<sub>30</sub>-steranes with marine versus nonmarine input (originally as C<sub>30</sub>-sterols) (4).

Another factor commonly used as a source indicator with respect to alkanes is the carbon number distribution. Briefly, n-alkane distributions with carbon number maxima in the 17-21 range (C<sub>17</sub>-C<sub>21</sub>) originate largely from aquatic algal sources, while maxima characterized by higher carbon numbers are

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indicative of higher plant input (leaf waxes of terrestrial plants) (1, 5). In addition,  $C_{23}$ - $C_{33}$  n-alkanes with a predominance of an odd number of carbons to an even number of carbons (OEP) is also indicative of terrestrial higher plant input (1, 6-9) although loss of odd numbered carbon predominance can occur with maturity (5). Thus, although petroleum is believed to be of biological origin, petroleum input is characterized by a lack of odd to even predominance (O.E.P. = 1.0). The isotopic composition of alkanes and of other classes of compounds can also be used as a general source input indicator. Isotopic fractionation resulting from the metabolic pathways involved in the synthesis of biologically produced compounds, when preserved in a diagenetic product, is frequently used to differentiate between terrestrial and aquatic sources. Hydrogen and carbon isotopic compositions of biogenic methanes from shallow aquatic environments is discussed in a later chapter of this volume (R. A. Burke and W. M. Sackett). The applicability of carbon isotopic data to tracing the source of deep-sea Mesozoic sediments is discussed by R.M. Joyce and E. S. Van Vleet.

Many other classes of lipids besides alkanes have proven to be valuable biomarkers, including fatty acids, sterols, amino acids, polysaccharides, glycerols, wax esters, porphyrins and many isoprenoids. The greater the extent of alteration of a compound by diagenetic processes, the harder it is to correlate the product to the biological precursor. However, the successive changes undergone by the precursor molecule can sometimes be deduced from the structure of the product. In these cases the "biomarker" is also a geochemical marker and may be referred to as a biogeochemical indicator. For example, stenol to stanol ratios can be used as an indicator of sediment oxicity. High stenol/stanol ratios are indicative of oxidizing rather than reducing environments (1, 20). Perylene provides an interesting example of a PAH of disputed origin, which may prove to be a reliable indicator of syn- and post-depositional anoxia when present in greater than trace amounts (11). Indicators of the biogeochemistry of chlorophyll and the temperature dependence of chlorophyll diagenesis is reviewed in the chapter by J.W. Louda and E. W. Baker. Other chapters in this volume concerned with source input markers and geochemical indicators include those by S.C. Brassell and G. Eglinton, J.W. de Leeuw, J. Whelan *et al.*, J.J. Boon *et al.*, R.M. Joyce and E. S. Van Vleet.

#### Humic Substances

Compared to the well defined structures and interrelationships of the discrete molecular biomarkers and geochemical indicators discussed above, relatively little is known about marine humic substances. Whether the major source of input to dissolved and sedimentary marine humic substances is of terrigenous or marine origin is still occasionally debated in the literature, although most interpretations point towards marine planktonic sources, (12-14), based most convincingly on isotopic ratios, GC-MS,  $^1H$  and  $^{13}C$  NMR and infrared spectra (15-17). Stuermer *et al* (12) propose a combination of  $^{13}C$  and H/C ratios as a

source input indicator of terrestrial versus marine derived humic substances.

One of the most useful tools for determining input sources, functional group content and diagenetic relationships between humic fractions has proven to be  $^{13}\text{C}$  NMR. The early applications of  $^{13}\text{C}$  NMR to humic substances were done by solution NMR and were thus limited to base soluble humic and fulvic acids (16, 18, 19). The subsequent application of solid-state  $^{13}\text{C}$  NMR to humic samples has allowed for direct comparisons between soluble and insoluble fractions as well as between humic substances from diverse environments.  $^{13}\text{C}$  NMR analysis of solid samples is made possible by the use of cross polarization and magic angle spinning (CP/MAS). Cross polarization is a sensitivity enhancing technique in which the application of  $^1\text{H}$  and  $^{13}\text{C}$  establishes contact between the two populations allowing for cross polarization (i.e. transfer of magnetization) from a large  $^1\text{H}$  population to a minute  $^{13}\text{C}$  population. Magic angle spinning (spinning the sample at several kHz at an angle of  $54.7^\circ$  relative to the externally applied magnetic field) minimizes line broadening due to chemical shift anisotropy (20-21). The combination of these techniques with high power decoupling and fourier transform analysis has yielded high resolution spectra which can provide reliable estimates of various carbon types, (21-24).

The important question of the reliability of quantification of solid state  $^{13}\text{C}$  NMR results can be answered in part by relaxation studies and the measurement of relaxation constants (25-27) and is discussed in greater detail by M.A. Wilson and A.H. Gillam in a later chapter of this volume. Quantification of the aromatic content ( $f_a$ ) of marine humic and fulvic acids by CP/MAS  $^{13}\text{C}$  NMR has demonstrated that these substances have low aromaticities relative to terrestrial counterparts (16, 28). The low aromatic (high aliphatic) content of marine humic substances is a result of their *in situ* production. Higher plants associated with terrestrial environments contribute lignin to soil humic substances. The lack of lignin in marine plants results in a low aromaticity of marine humic substances although coastal sediments may contain high levels of vascular plant residues (29). Lignin is an aromatic based natural polymer characterized by methoxyl group substitutions on the benzene ring structure. These lignin-associated methoxyl groups typically produce a distinctive  $^{13}\text{C}$  NMR peak which is normally interpreted as a source marker for terrestrial input. However, as discussed in the chapter by M.A. Wilson and A.H. Gillam, contributions from other carbon types (possibly amino acid carbon) may contribute to this signal. The relatively new technique of dipolar dephasing is capable of distinguishing between terrestrial lignin methoxyl signals and other protonated carbons which may resonate in the methoxyl region of the spectrum. Dipolar dephasing takes advantage of different relaxation rates of various types of carbon and utilizes this phenomenon to distinguish between protonated and nonprotonated carbon (26). The utilization of dipolar dephasing in studying the diagenetic changes undergone by organic matter in marine sediments is discussed in a chapter by W.T. Cooper *et al.*

Recent advances in the structural interrelationships among humic substances of marine and estuarine sedimentary origin is discussed in the chapter by P.G. Hatcher and W.H. Orem.

#### Organic Pollutants in the Marine Environment

The biogeochemistry of organic pollutants in marine systems is of enormous economic and environmental impact. The environmental behavior of polychlorinated biphenyls (PCB's) has been studied rather extensively because of their detrimental effects on human health and on living marine resources (30-32). As discussed in the chapters by J.W. Farrington *et al.*, due to recent advances in gas capillary chromatographic methods, it is now possible to study the biogeochemistry of individual PCB's rather than that of combined industrial mixtures of PCB's (33-36). In order to realistically assess the risks to animal health, it is important to be able to work with individual PCB levels rather than with unresolved mixtures because individual PCB's can vary greatly in terms of toxicity (37).

The contamination of coastal marine environments by anthropogenic hydrocarbon input is also a matter of urgent concern with respect to human health and preservation of natural resources. Hydrocarbon contamination by oil spills can often be traced to sources by fingerprinting techniques. An excellent review of current developments in this field is presented by E.S. Van Vleet (38) including discussions on computer interfaced total fluorescence, transmission infrared spectroscopy, GC and GC-MS, trace metal analysis etc.. The correlation of hydrocarbons with petroleum sources is frequently hindered by differential weathering. For a detailed discussion on the weathering of petroleum in the marine environment, the reader is referred to a current literature review (39). In this volume, the fingerprinting of hydrocarbon contamination from specific land use activities, supported by GC-MS analysis of polynuclear aromatic compounds (PNA) are discussed by R.H. Pierce *et al.* and by E.B. Overton *et al.*, while fingerprinting of hydrocarbon contamination from carbonized coal products (creosote and coal tar) is described by T.L. Wade *et al.*.

#### Volatile Organic Substances

The decomposition of complex organic substances by microbial marine populations results in the *in situ* production of biogenic methane, which is found in trace amounts in all fresh and salt waters. The relative importance of acetate assimilation and CO<sub>2</sub> reduction as primary methanogenic pathways is discussed in the chapter by R.A. Burke and W.M. Sackett. In the past, these pathways were studied by the use of <sup>14</sup>C labelled substrates. However, the authors demonstrate the advantages of using stable hydrogen and carbon isotopic compositions of biogenic methanes to evaluate the relative contributions from these two pathways. Seasonal distributions of methane are discussed in the chapter by J.D. Cline *et al.*.

Volatile halogenated methanes are also produced *in situ* in the marine environment and have been found to be associated with marine macroalgae (40). The release of these halogenated methanes

into coastal seawater has also been demonstrated (41-43) and is of environmental concern. A seasonal study of the release of polybromomethanes is described in the chapter by P.M. Gschwend and J.K. MacFarlane.

### Organic - Inorganic Interactions

The major influence of organic marine substances on the partitioning and speciation of inorganic and organometallic substances is discussed in the closing chapters of this volume. Complexation, adsorption and/or reduction of ions and compounds by organic matter in marine and brackish systems greatly affect the cycling and bioavailability of many potential nutrients and toxic substances.

The complexation of metal ions by humic substances is a well documented phenomenon (44-51). Due to the ubiquitous nature of these naturally occurring ligands, humic substances play an important role in determining the partitioning of metal ions and other substances in both terrestrial and aquatic environments (52-56). In order to predict or model the partitioning of a particular metal ion in a given environment, it is essential to be able to evaluate the magnitude of the interaction between the pertinent components of the environment (the substrates) and the metal ion. When dealing with the various solid phases which may be present, adsorption of the ion onto each phase (clay, sand, silt, hydrous metal oxides, humus) can be studied via the evaluation of adsorption isotherms (56). In the solution phase, complexation is an important process which competes with ion-pair formation and subsequent precipitation. The strength of the complexation reaction can be measured by evaluation of a conditional formation constant. (57-59, 46).

Adsorption of dissolved substances onto suspended matter is a primary process in the removal of dissolved substance from the water column and subsequent concentration in sediments. The major role played by adsorbed organic coatings on particulate matter is well known (60, 61). The processes of complexation and adsorption in marine systems and their effects on the speciation of various ions and compounds are discussed in the closing chapters.

### Literature Cited

1. Eglinton, G. In "Advances in Organic Geochemistry 1968"; Schenck, P.A.; Havenaar, I., Eds.; Pergamon Press: Oxford, 1968 pp. 1-24.
2. Treibs, A. Angew. Chemie 1936, 49, 682-686.
3. Volkman, J.K.; Farrington, J.W.; Gagosian, R.B.; Wakeham, S.G. In "Advances in Organic Geochemistry 1981"; Bjoroy, M., Ed.; John Wiley & Sons Limited: 1982, pp. 228-240.
4. Moldowan, J.M. Geochim. Cosmochim. Acta 1984, 48, 2767-2768.
5. Baker, E.W.; Louda, J.W. In "Advances in Organic Geochemistry 1981"; Bjoroy, M., Ed.; John Wiley & Sons Limited: 1982 pp 295-319.

6. Eglinton, G.; Hamilton, R.J. Science 1967, 156, 1322-1335.
7. Leenheer, M.J.; Flessland, K.D.; Meyers, P.A. Org. Geochem. 1984, 7, 141-150.
8. Brassell, S.C.; Comet, P.A.; Eglinton, G.; Isaacson, P.J.; McEvoy, J.; Maxwell, J.R.; Thomson, I.D.; Tibbetts, P.J.C.; Volkman, J.K. In "Advances in Organic Geochemistry 1981; Bjoroy, M., Ed.; John Wiley & Sons Limited: pp. 375-391.
9. Simoneit, B.R.T. In "Chemical Oceanography" Riley, J.P.; Chester, P., Eds.; Academic Press: New York, 1978; Vol. 7, pp. 233-311.
10. Gagosian, R. B.; Smith, S.O.; Lee, C.; Farrington, J.W.; Frew, N.M. In "Advances in Organic Geochemistry 1979" Douglas, A.G.; Maxwell, J.R., Eds.; Pergamon Press:, 1980; pp.407-419.
11. Louda, J.W.; Baker, E.W. Geochim. Cosmochim Acta 1984, 48, 1043-1058.
12. Stuermer, D.H.; Peters, K.E.; Kaplan, I.R. Geochim. Cosmochim. Acta 1978, 42, 989-997.
13. Nissenbaum, A.; Kaplan, I.R. Limol. Oceanogr. 1972, 17, 570-582.
14. Stuermer, D.H.; Harvey, G.R. Nature, 1974, 250, 480-481.
15. Stuermer, D.H.; Payne, J.R. Geochim. Cosmochim Acta 1976, 40, 1109-1114.
16. Hatcher, P.G.; Rowan, R.; Mattingly, M.A. Org. Geochem 1980, 2, 77-85.
17. Gillam, A.H.; Wilson, M.A. Org. Geochem. 1985, 8, 15-25.
18. Vila, F.J.G.; Lentz, H.; Ludemann, H.D. Biochem. Biophys. Res. Commun. 1976, 672, 1063-1069.
19. Wilson, M.A.; Goh, K.M., J. Soil Sci 1977, 28, 645-652.
20. Andrew, E.R. In "Progress in NMR Spectroscopy", Emsley, J.W.; Feeney, J.; Sutcliffe, L.H., Eds.; Pergamon, 1972; Vol. 8, pp. 1-39.
21. Bartuska, V.J.; Maciel, G.E.; Schaefer, J.; Stejskal, E.O. Fuel 1977, 56, 354-358.
22. Hatcher, P.G.; VanderHart, D.L.; Earl, W.L. Org. Geochem 1980, 2, 87-92.
23. Miknis, F.P.; Netzel, D.A.; Smith, J.W.; Mast, M.A.; Maciel, G.E. Geochim. Cosmochim. Acta 1982, 46, 977-984.
24. Resing, H.A.; Garroway, A.N.; Hazlett, R.N. Fuel, 1978, 57, 450-454.
25. Yoshida, T.; Maekawa, Y.; Fujito, T. Anal. Chem. 1983, 55, 388-390.
26. Wilson, M.A.; Pugmire, R.J.; Grant, D.M. Org. Geochem. 1983, 5, 121-129.
27. Wilson, M.A.; Vassallo, A.M. Org. Geochem. 1985, 8, 299-312.
28. Hatcher, P.G.; Breger, I.A.; Mattingly, M.A. Nature 1980, 285, 560-562.
29. Ertel, J.R.; Hedges, J.I. Geochim. Cosmochim. Acta 1984, 48, 2065-2074.
30. Miller, S. Environ. Sci. Technol 1982, 16, 98A-99A.
31. Bopp, R.F.; Simpson, H.J.; Olsen, C.R.; Kostyk, N. Environ. Sci. Technol. 1981, 15, 210-216.

32. Pierce, R.H.; Olney, C.E.; Felbeck, G.T. Geochim. Cosmochim. Acta 1974, 38, 1061-1073.
33. Ballschmiter, K.; Zell, M. Frezenius Z. Anal. Chem. 1980, 302, 20-31.
34. Duinker, J.C.; Hillebrand, M.T.J. Environ. Sci. Technol. 1983, 17, 449-456
35. Mullin, M.D.; Pochini, C.M.; McCrindle, S.; Romkes, M.; Safe, S.H.; Safe, L.M. Environ. Sci. Technol. 1984, 18, 468-476.
36. Duinker, J.C.; Hillebrand, M.T.J.; Boon, J.P. Netherlands J. Sea. Res. 1983, 17, 19-38.
37. Kimbrough, R.D. "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Elsevier/North Holland Biomedical Press: New York, 1980, 406 pp.
38. Van Vleet, E.S. Mar. Techn. Soc. J. 1984, 18, 11-23.
39. Payne, J.R.; McNabb, G.D., Jr. Mar. Techn. Soc. J. 1984, 18, 11-23.
40. Hewson, W.D.; Hager, L.P. J. Phycol 1980, 16, 340.
41. Gschwend, P.M.; MacFarlane, J.K.; Newman, K.A. Science 1985, 227, 1033.
42. Dryssen, D.; Fogelquist, E. Oceanol. Acta 1981, 4, 313.
43. Lovelock, J.E.; Maggs, R.J.; Wade, R.J. Nature 1973, 256, 193.
44. Adhikari, M.; Hazra, G.C. J. Indian Chem. Soc. 1972, 49, 947-951.
45. Ardakani, M.; Stevenson, F.J. Soil Sci. Soc. Am. Proc. 1972, 36, 884-890.
46. Gamble, D.S.; Schnitzer, M.; Hoffman, I. Can. Journ. Chem. 1970, 48, 3197-3204.
47. Gamble, D.S. Anal. Chem. 1980, 52, 1901-1908.
48. Mantoura, R.F.C.; Riley, J.P. Analyt. Chim. Acta 1975, 78, 193-200.
49. Mantoura, R.F.C.; Dickson, A.; Riley, J.P. Est. Coast. Mar. Sci. 1978, 6, 387-408.
50. Mills, G.L.; Hanosn, A.K. Jr.; Quinn, J.G.; Lammela, W.R.; Chasteen, N.D. Mar. Chem. 1982, 11, 355-377.
51. Piotrowicz, S.R.; Harvey, G.R.; Boran, D.A.; Weisel, C.P.; Springer-Young, M. Mar. Chem. 1984, 14, 333-346.
52. Nissenbaum, A.; Swaine, D.J. Geochim. Cosmochim. Acta. 1976, 40, 809.
53. Rashid, M.A.; Leonard, J.D. Chem. Geol. 1973, 11, 89-97.
54. Theis, T.L.; Singer, P.C. In "Trace Metals and Metal-Organic Interactions in Natural Waters"; Singer, P.C., Ed.; Ann Arbor Science Publishers, 1973.
55. Wallace, G.T. Mar. Chem. 1982, 11, 379-394.
56. Davies-Colley, R.J.; Nelson, P.O.; Williamson, K.J. Environ. Sci. Technol. 1984, 18, 491-499.
57. Gamble, D.S.; Schnitzer, M.; Kerndorff, H. Geochim. Cosmochim. Acta 1983, 47, 1311-1323.
58. Clark, J.S.; Turner, R.C. Soil Sci. 1969, 107, 8-11.
59. Elgala, A., El-Damaty, A.; Abel-Latif, I. Z. Pflanz. Rodenk. 1976, 3, 293-300.

60. Davis, J.A.; Leckie, J.O. Environ. Sci. Technol. 1978, 12, 1309-1315.
61. Balistrieri, L.S.; Brewer, P.G.; Murray, J.W. Deep-Sea Res. 1981, 28A, 101-121.

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## Molecular Geochemical Indicators in Sediments

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Sediments from contemporary aquatic environments contain a diversity of compounds that provide an assessment of the sources of their organic matter. These components include lipids with structural features that are indicative of their biological origins. Thus, specific diterpenoids and triterpenoids are markers for sediment contributions from terrigenous vegetation. Similarly, among the numerous sterols recognised in sediments many are diagnostic of their algal origins, notably 4 $\alpha$ -methylsterols derived from dinoflagellates. Several lipid types characterise contributions from bacteria; for example, acyclic isoprenoid alkanes arising from methanogens. Illustrative examples of such diagnostic lipid distributions show the possibilities for differentiating between sediments receiving allochthonous terrigenous organic matter and those dominated by autochthonous algal and bacterial contributions. Within the hydrocarbon distributions, by contrast, several features can denote non-biological sources of organic components, such as the weathering of ancient sediments, oil seepage and oil spillage. A further development in environmental assessment using molecular indicators stems from the recent recognition that the unsaturation of specific lipids contributed to sediments by coccolithophorid algae provide a measure of water temperatures.

This paper concentrates on three aspects of the application of molecular organic geochemistry to the interpretation of the biological origins of sedimentary organic matter and the use of such information in the evaluation of depositional environments. First, the basis

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for the assignment of specific compounds as diagnostic markers for the contributions of particular biota to sediments is considered and illustrative examples of such molecular indicators are given. Second, the sedimentary distributions of such components are discussed and the possibilities for their use in the qualitative assessment of contributions from different biological sources to sediments is addressed. Third, one group of lipids which occur widely in marine sediments, namely long-chain ( $C_{37}$  to  $C_{39}$ ) alkenones, are considered in terms of their potential to provide an assessment of oceanic water temperatures in the shallow subsurface from the sedimentary molecular record.

The standard methodology used in investigations of the organic constituents of sediments typically involves their extraction, then fractionation according to polarity or compound class and finally their evaluation and identification by gas chromatography (gc) and computerised gas chromatography-mass spectrometry (gc-ms). Details of such procedures are not given here, but can be found in the references cited.

### Molecular Indicators in Sediments

The development of molecular markers as indicators of biological contributions to sedimentary organic matter relies on the information from the lipid composition of appropriate organisms. Such information is often scant. Therefore, existing data is used to propose working hypotheses that can be modified or amended when additional information becomes available. The underlying rationale for this approach is the tacit assumption that the biochemical pathways of lipid biosynthesis in different organisms are not necessarily uniform at the present time, nor have they been over geological history. Rather, it seems that the lipid compositions of biota have been tailored throughout evolution to meet their environmental needs. Hence, the discrepancies and similarities between the lipids of different organisms can be used to assess their generic relationships leading to chemotaxonomy. Such chemotaxonomic description of organisms using lipid components relies on the information obtained from the analysis of both laboratory cultures and natural populations of individual species. The assignment of a given compound recognised in sediments to a specific biological source is based on such classifications aided by information from environmental analyses, such as the investigation of sediments thought to receive dominant inputs from a particular species or class of organism.

Indeed, the verification of the biological source and significance of individual lipid components of geochemical interest is often best served by studies designed to evaluate their origins in a chosen environment.

For some years it has been held that dinoflagellates are the biological source of the 4 $\alpha$ -methylsterols that occur, frequently as abundant components, in marine sediments (1-3). Such assignments were initially based on the widespread literature concerning 4 $\alpha$ -methylsterols in cultured dinoflagellates (4) and the abundance of these compounds in sediments known to receive major contributions from this class of algae. The distributions of 4 $\alpha$ -methylsterols, and also 4 $\alpha$ -methylstanones, observed in the bottom sediments of Priest Pot, a small lake in the English Lake District, were almost identical to those recognised in a bloom of the dinoflagellate Peridinium lomnickii collected from the overlying waters (5). This study demonstrated that P. lomnickii is the source of the 4-methylsteroids in Priest Pot sediments and, in more general terms, provided convincing evidence in support of the link between sedimentary 4 $\alpha$ -methylsteroids and their presumed biological source, dinoflagellate algae.

Overall, there are clear indications that particular organic components may be specific to single or multiple biological sources or, alternatively, may be non-diagnostic of their biological origins. In simple terms an individual component, or the distribution of a specific compound class, may be representative of contributions to sedimentary lipids from either algal, terrigenous higher plant or bacterial sources. Not all components, however, can be placed into one of these three classes; for example, some occur in all three, some may only occur in animals, whereas the origins of others are unknown. In addition to considerations of their ultimate biological origins individual compounds in sediments can be either unaltered biosynthetic products or, alternatively, derivatives formed by diagenetic / catagenetic processes, which retain structural elements that attest to their original biological source. Most biological marker compounds occurring in sediments can be considered as markers of one of the following five groups:

- (i) non-diagnostic components
- (ii) algae
- (iii) terrigenous higher plants
- (iv) bacteria
- (v) 'unknown'

Examples of individual components held to be representative of these five categories are shown in Figures 1-5. The majority are known lipid constituents of organisms, whereas others are either diagenetic products or of an as yet undefined origin. The compounds chosen provide an illustrative, rather than a comprehensive, indication of the range of structural types in each category. Most of them have been discussed elsewhere in a fuller review paper (6), together with other structurally similar examples. Also, the individual compounds and compound distributions biosynthesised by, and held to be diagnostic for, algal, terrigenous higher plant and

bacterial inputs to recent sediments are published elsewhere (3). Within categories (ii), (iii) and (iv) individual marker compounds can be uniquely representative of a particular species, genus or class of organism. Alternatively, they can be non-specific components which occur widely in different, but perhaps distantly related, families. Clearly, similarities in the lipid compositions of related species or genera may reflect their ancestral links, whereas differences may stem from the divergence of their biosynthetic pathways.

Non-diagnostic biological markers. The components considered to be non-diagnostic indicators (Figure 1) are likely to be those that play a fundamental role in biosynthetic processes. For example, essential constituents of cell structures (e.g. membranes) or similar physiological units might be expected to be common to many different types of organism and therefore occur ubiquitously. Hexadecanoic acid, for example, is a typical constituent of the membranes of numerous land and aquatic plants, animals and bacteria. It may be present in the form of wax esters or triacylglycerols but is generally of little value in differentiating between contributions to sediments from its various sources. Similarly squalene is the biosynthetic precursor of many triterpenoids and, thus, occurs widely in organisms. Cholesterol, like hexadecanoic acid, is a constituent of the cell membranes of many different families of organisms, with the notable exception of bacteria. It acts as a 'rigidifier' in cell membranes. It is a prominent sterol of many algae and land plants, and is often the only sterol component of copepods. Tocopherols are held to play an important role in photosynthetic processes. Hence, they are abundant in many photosynthetic organisms, including higher plants, algae and cyanobacteria (7), making them non-diagnostic markers of the sources of sedimentary organic matter.

Algal indicators. Individual marker compounds indicative of sediment contributions from algae (Figure 2) may occur in both marine and lacustrine environments, although their source species will differ. Indeed, botryococcene is the only component shown which has yet to be recognised in both environmental regimes. Carotenoids are perhaps the most source specific lipid constituents of organisms. For example, diatoxanthin occurs only in diatoms and can therefore be regarded as a highly specific marker for their contributions to sediments. Its absence in a sediment, however, cannot be taken as evidence for the lack of diatom contributions to organic matter, due to its lability. Indeed, this lability makes carotenoids of limited use as markers of the sources of organic matter in most sedimentary environments, with the notable exception of relatively shallow water systems, such as post-glacial lakes (8). Recent work (2,5) has provided convincing

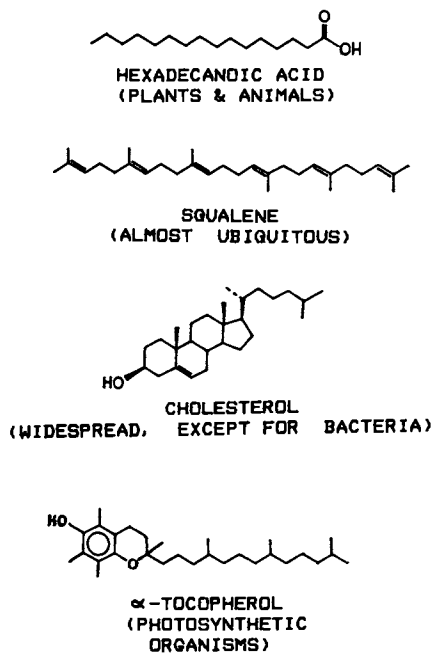


Figure 1. Compound structures, names and biological origins of examples of non-diagnostic indicators of the sources of sedimentary organic matter.