

Diagenetic organic matter in Recent sediments and environments of deposition

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Organic geochemical studies of the reduced organic material in sedimentary rocks provide a valuable insight into the origin and history of the sediments. Information on the source of the organic matter (marine or non-marine), the depositional environment (oxic or anoxic), whether or not biodegradation has occurred, and the maturity of the organic matter can be obtained by studying the distribution of various organic compounds, known as biological markers, in extracts from these sediments. Selection of environments with a fairly narrow range of source material allows more direct correlations to be made between source material and specific biological markers.

Introduction

Studies of organic matter deposited in contemporary environments are of practical importance in obtaining a better understanding of the formation of coals, oil shales, crude oils, natural gas deposits, and, possibly, to a lesser extent, ore deposits. Correlations between specific organic compounds in Recent sediments and particular source organisms or plants permit information to be obtained on the type of organic matter deposited in ancient organic-rich sediments (Philp & others, 1976). Stereochemical changes occurring in molecules from Recent sediments can be extrapolated to provide information on the maturational history of ancient sediments (Mackenzie & others, 1980). Biodegradation of organic matter in any environment can produce specific compounds or induce specific stereochemical changes, which allow conclusions to be drawn with regard to the degree of biodegradation of the organic matter (Seifert & Moldowan, 1979). The fate of certain specific classes of compounds that serve as environmental indicators, namely isoprenoids, sterols, and triterpanes, are discussed in this paper.

Accumulation and preservation of organic matter in Recent sediments

Carbon is cycled through the biosphere by a combination of photosynthesis and oxidation. In simplest terms, plants can be thought of as incorporating carbon from atmospheric carbon dioxide into their cells (Fig. 1). The plants are subsequently consumed by animals, which partly or completely degrade the plant material and give off excess carbon dioxide. On death, decaying plants and organisms are largely oxidised, either microbially or chemically, to carbon dioxide, which is returned to the atmospheric pool of carbon dioxide. However, 99.9 percent of the carbon is recycled to the atmosphere as carbon dioxide, and only 0.1 percent deposited and incorporated into the sedimentary carbon sink. These preserved organic carbon compounds are, in many cases, extremely useful as indicators of the source of organic matter and the environmental conditions of deposition, and have been collectively referred to as biological markers or chemical fossils (Eglinton, 1973). Biological markers are generally defined as compounds whose carbon skeletons remain unaltered or are altered in a predictable manner over a long geolo-

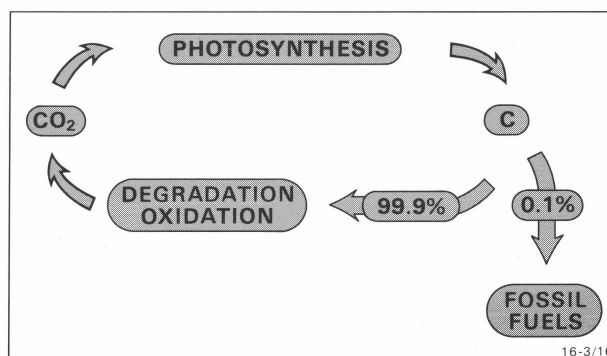


Figure 1. Highly simplified representation of the carbon cycle.

gical time, and can be correlated with a specific input of organic matter to the environment.

Following deposition and accumulation of the organic matter, a variety of maturational changes can occur during diagenesis (Fig. 2). In general, diagenetic effects are considered to occur at temperatures below 50°C at depths where no cracking of the molecules can occur from thermal effects.

The nature of the organic material exposed to these early-stage diagenetic reactions will, to a large extent, be determined by the depositional environment. The two extreme types of environment are non-marine and marine, and various intermediate environments exist: deltaic sediments, for example, contain a predominantly marine contribution that is diluted by terrigenous material from rivers and streams.

Figure 3 is a very simple diagram to show a few of the major factors that can affect the type of organic matter found in the sedimentary environment. In a marine environment, autochthonous material is generated from phytoplankton residing in the uppermost layers of the water column, which are illuminated by sunlight, i.e. the euphotic zone. As this organic matter percolates down through the water column it will be grazed by zooplankton, a proportion of which will in turn be consumed by large invertebrates and fish. A certain amount of phytoplankton and zooplankton debris may reach the sediment/water interface unaltered or may be attacked by bacteria in the water column. In addition, an allochthonous contribution of organic matter in a marine environment can be derived from continental run-off or by various other means such as aeolian transport or, in certain environments, ice-rafting.

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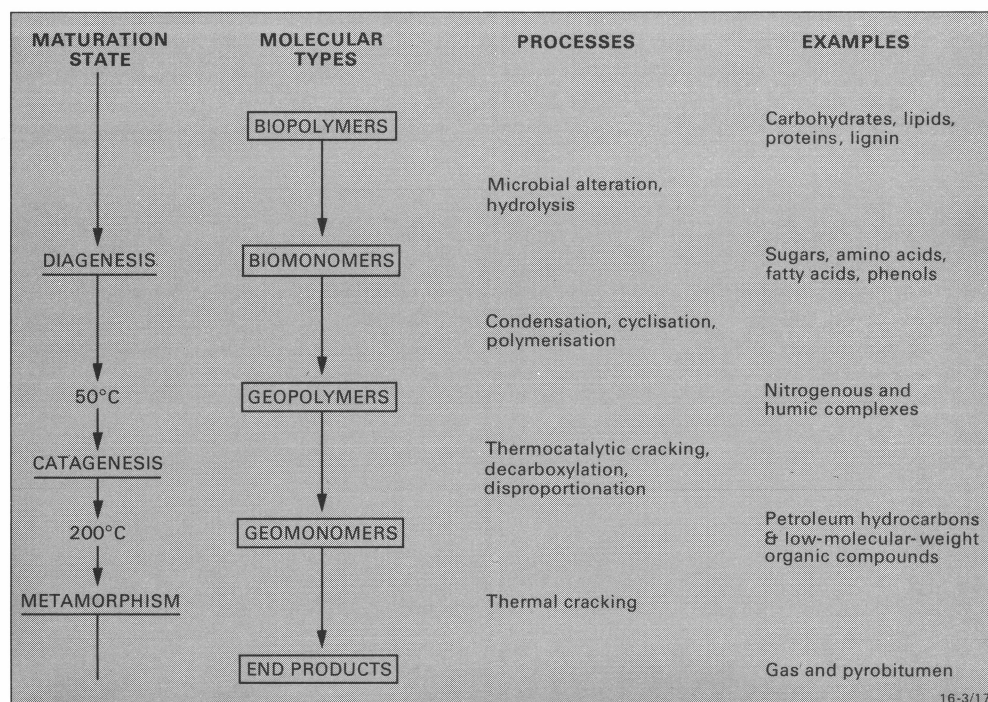


Figure 2. A summary of the major processes that can occur to the main types of organic matter in the geologic record.

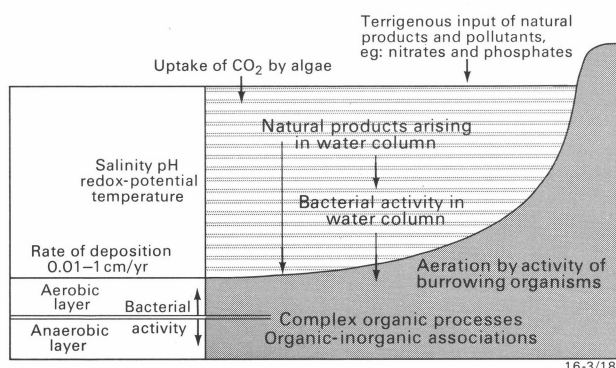


Figure 3. Schematic diagram of the various interdependent chemical and biological factors that affect the ultimate fate of biolipids in Recent sediments. (From Philp & others, 1976).

The organic matter from all sources may be further degraded by microbial attack in the water column, at the sediment/water interface, and in the upper few centimetres of the sediment itself, producing biological markers which cannot immediately be correlated with the source of the organic material.

The major factor controlling the rate of microbial degradation will be the amount of oxygen available either in the sediment or overlying water column. Ultimately, oxygen availability is reflected in the distribution of biological markers in the sedimentary record. For example, a benthic fauna will actively scavenge and rework organic material filtering down through an oxic water column. Below the sediment/water interface, little primary productivity occurs, and the main process is that of consumption of organic matter (Fig. 4). The bottom muds under oxygen-rich water columns are often anoxic, but can be extensively disrupted by invertebrates such as polychaetes, holo-

thurians, and bivalves. On the other hand, in an anoxic environment, oxygen depletion depresses and eventually eliminates benthic metazoan life (Fig. 5). At oxygen concentrations of 0.1 ml/l, and below, suspension feeders disappear, leaving anaerobic bacteria as the only effective reworkers of organic matter. Bacterial activity is slowed down by the lack of bioturbation, which limits the diffusion of oxidants into the sediment. The sediments formed under these conditions are generally laminated and very rich in organic matter.

The environments which appear to be best suited to the preservation, as distinct from accumulation, of organic matter can be divided into four categories.

Large anoxic lakes. Permanent stratification of such lakes promotes development of anoxic bottom waters. These lakes are formed under warm equable climatic conditions that favour lacustrine anoxia and, ultimately, deposition of source material that gives rise to non-marine oil; e.g. Lake Tanganyika.

Anoxic silled basins. These are landlocked silled basins with positive water balance, such as the Baltic and Black Seas.

Anoxic layers. These are caused by upwelling where there is high surface biological productivity and, hence, the oxygen supply in deep water cannot match demand; e.g. Benguela current and Peru coastal upwelling.

Open ocean anoxic layers. These are formed in oxygen minimum layers of the northeast Pacific and northern Indian oceans, far from the polar regions (Demaision & Moore, 1980).

Accordingly, it is clear that the distribution of biological markers in Recent sediments will be influenced both by the source material and the depositional environment. In the following section it is proposed to examine some of the changes that can occur to specific biological markers, the significance of these changes, and how they can be used as environmental indicators.

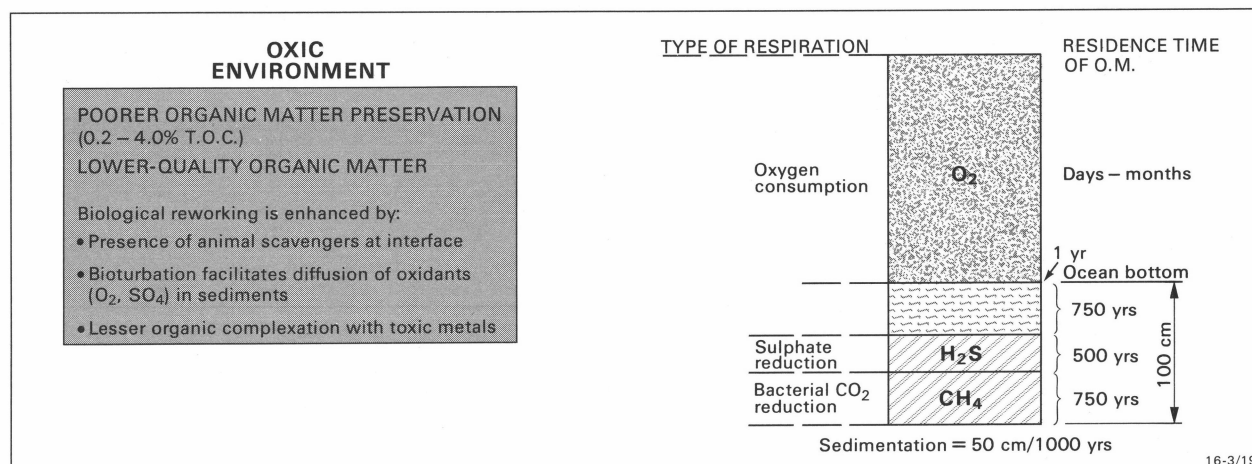


Figure 4. Degradation of organic matter in an oxic environment.
(Adapted from Demaison & Moore, 1980). Diagonally shaded area is anoxic.

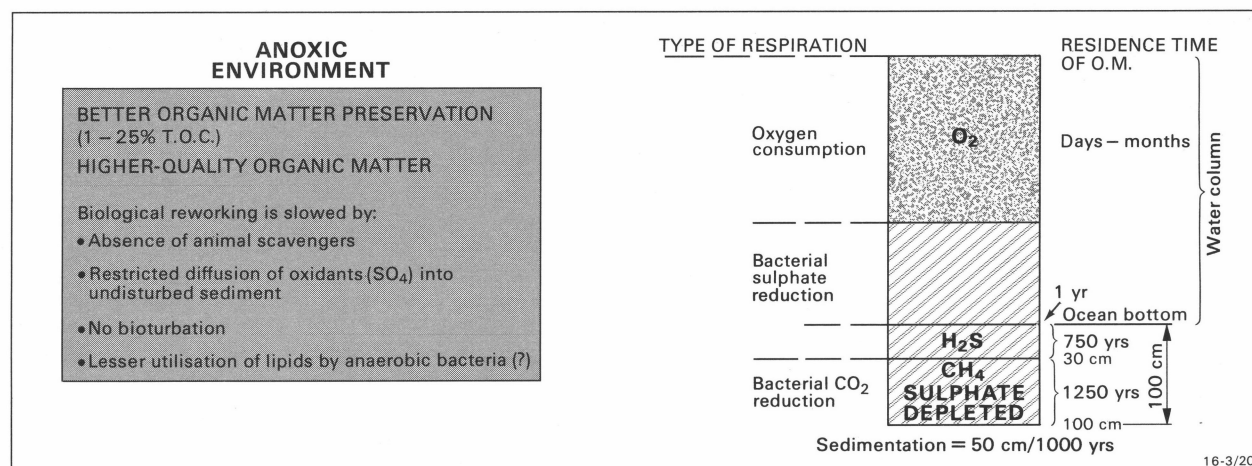


Figure 5. Degradation of organic matter in an anoxic environment.
(Adapted from Demaison & Moore, 1980). Diagonally shaded area is anoxic.

Diagenetic alteration of biological markers

Pristane and phytane

One of the most widely studied diagenetic reactions in Recent sediments is the fate of the phytol side-chain of chlorophyll. Brooks & others (1969) initially suggested that variations in pristane and phytane ratios reflect differences in oxidation conditions during the early stages of chlorophyll decomposition. Johns & others (1980) recently produced evidence of a two-step degradation process for chlorophyll. The first step is destruction of the chlorin ring system and the second, conversion of the phytol ester to soluble degradation products and non-solvent-extractable or bound phytol. The second step is definitely the more complex part of the degradation process. Didyk & others (1978) summarised various microbial and geochemical paths that have been demonstrated or postulated for the degradation of phytol under various environmental conditions.

The pristane/phytane ratio has been widely used to obtain information on palaeoenvironments of deposition (Powell & McKirdy, 1973). Preservation of the phytane skeleton is facilitated by a reducing environment, whereas the formation of pristane via decarboxylation

of phytanic acid occurs under oxidising conditions (Fig. 6). In Recent sediments, a low pristane/phytane ratio (< 1), together with high chlorine and sulphur contents, indicates an anoxic environment (i.e. path shown on left hand side of Fig. 6). Conversely, high pristane/phytane values (> 1) and low chlorine and sulphur contents may indicate an oxic environment.

Stereochemical studies of acyclic isoprenoid compounds can also provide information on their origin and paths of formation. Naturally-occurring phytol has been shown to have the relative stereochemical configuration of 7R, 11R. The stereochemistry of pristane in Recent sediments and naturally occurring marine zooplankton is compatible with an origin from phytol with retention of configuration, and is thus compatible with catabolism of phytoplankton phytol. Likewise, the major isoprenoid acids in the Green River oil shale have stereochemical configurations directly comparable with that of phytol. Pristane in the Green River shale comprises 80 percent of the 6R, 10S isomer, compatible with an origin from phytol and retention of configuration, and 20 percent of the 6R, 10R and/or 6S, 10S isomers. The presence of the latter isomers was interpreted as indicating derivation from either an acyclic isoprenoid other than phytol or phytol via reactions

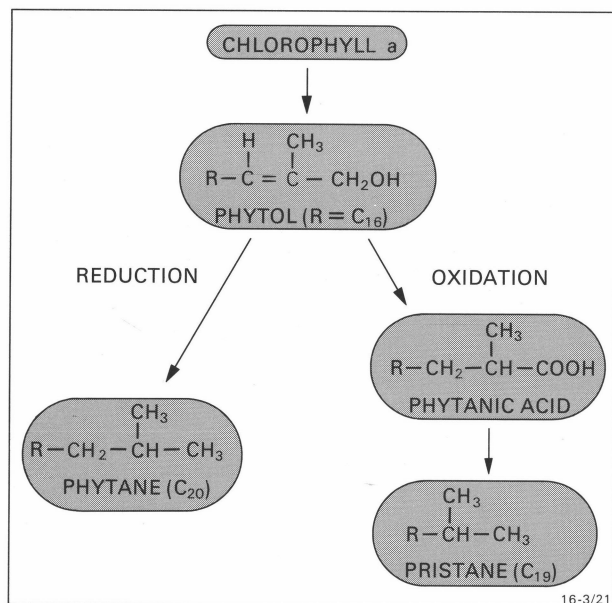


Figure 6. The major paths postulated for the formation of pristane and phytane in aquatic environments.

leading to epimerisation of the methyl branched positions (Patience & others, 1978).

Sterols

The steroid hydrocarbon structure is a relatively stable nucleus, which can incorporate functional groups such as alcohols, ketones, and olefinic linkages either in the nucleus or the C-17 side-chain (Fig. 7). Several species of plants and animals produce only specific sterols or have unique sterol fingerprints, which permit their use as tracers of supply from such sources. The sterols (1) (Fig. 7) can be subsequently converted into stenones (2), stanones (3), stanols (4), sterenes (5) and steranes (6) by a complex series of microbiological and chemical reactions.

Diagenetic alteration of steroids by geochemical and biochemical processes can lead to the accumulation of more stable transformation products in sea water and sediments. Several studies have been made of the structure and concentration of these products in marine and lacustrine environments to determine various paths and rates of steroid degradation.

In early studies, Gaskell & Eglinton (1975) showed that hydrogenation of unsaturated sterols occurs rapidly in contemporary aquatic sediments to give 5 α - and 5 β -stanols in a ratio dependent on the microbial population of the sediments. More recently, Gagosian & others (1981) examined the content of sterols and their transformation products in surface sediments and the overlying water column from three different marine environments. These included two anoxic sediments from the Black Sea and the South West African shelf, and a sample from a North Atlantic sediment, which was taken to represent a site of low productivity and oxic surface sediment.

Although the distribution of sterols in surface sediments is primarily controlled by the source of supply, their distribution in the sediments can be quite different from that in the overlying water column. Such differences are caused by the distribution of benthic macroorganisms, and the size, composition, and

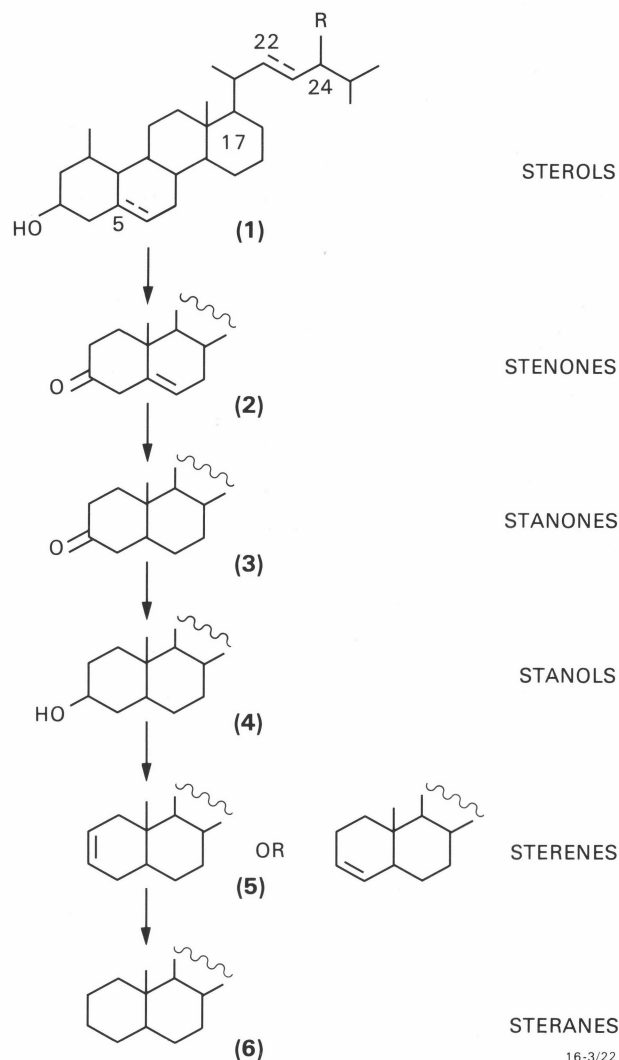
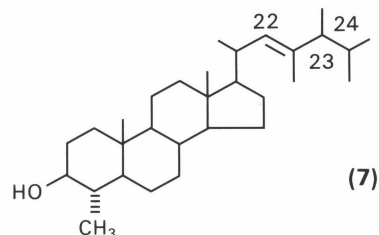


Figure 7. Structures and inter-relation of various sterols found in contemporary environments.

density of particulate material. The major sterol found by Gagosian & others (1981) in the Black Sea and Walvis Bay sediments was a 4-methyl dinosterol (7)



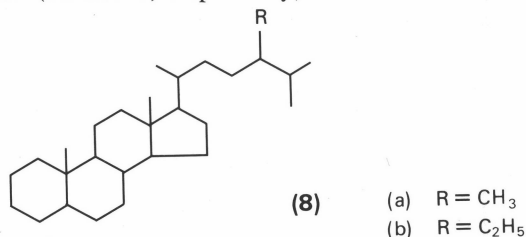
which had previously been identified in the Black Sea sapropel by Boon & others (1979). The same sterol has been encountered as a major sterol in some dinoflagellates and is thus a good example of the possibility of a direct correlation between a source organism and a specific biological marker compound.

Stanols in surface sediments can either be derived from organisms and incorporated unaltered into the sediments or produced by microbial reduction of sterols at the sediment/water interface or in the anoxic water column. Gagosian & others (1981) found that the

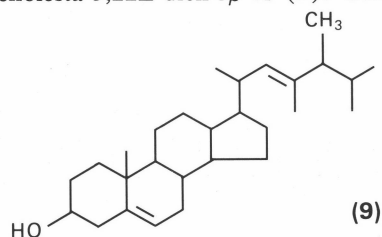
lowest stanol/sterol ratios were in oxic sediments (North Atlantic) and the highest in anoxic sediments (Black Sea and Walvis Bay). Microbial hydrogenation of sterols has been postulated as a major source of stanols in anoxic lacustrine sediments (Gaskell & Eglinton, 1975). Dehydration of stenols and stanols leads to the formation of steranes and rearranged steranes, or diasteranes, via intermediate sterenes. Gagosian & others (1981) found that, in surface sediments from Walvis Bay, concentrations of individual steradienes corresponded to the concentrations of related sterols, and the levels of the monosterene concentrations corresponded to the levels of their respective stanols. In oxic sediments from the North Atlantic, sterenes were virtually absent. This was postulated to be due either to the low levels of sterol precursors or alternative faster paths for sterol degradation in oxic sediments. Stanones in sediments are derived from planktic or benthic organisms and from microbial or chemical oxidation of sterols and stanols.

In summary, Gagosian & others (1981) found that in areas where there is low productivity in the surface waters and oxic sediments, sterol and stanol concentrations in the sediments are low, sterene concentrations are extremely low, and stanones are absent. In areas of high productivity and anoxic sediments, there are high sterol and stanol concentrations, and the distributions of 4-desmethyl steroids and steradienes correlate with stanols and monosterenes with stanols.

In addition to the relative distribution of sterols in the sediments, the stereochemical assignment of the alkyl group at the C_{24} position has important biosynthetic, taxonomic, and geochemical implications. Routine separation of the C_{24} sterane isomers in sediment extracts has the potential to provide information on the nature of contributing organisms and also the isomerisation reactions thought to occur in steranes with increasing depth of burial and associated temperature rise. Maxwell & others (1980) recently reported a method for the complete separation of the 24R and 24S isomers of the 24-methyl and 24-ethyl-5 α -cholestanane (8a and b, respectively). This method was used



to study the C_{24} configuration in steranes from a sedimentary rock and a crude oil, and those obtained from the reduction of sterols in a marine coccolithophorid. Maxwell & others (1980) found that the major free sterol from the marine alga *Emiliania huxleyi* was 24-methylcholesta-5,22E-dien-3 β -ol (9). Conversion to

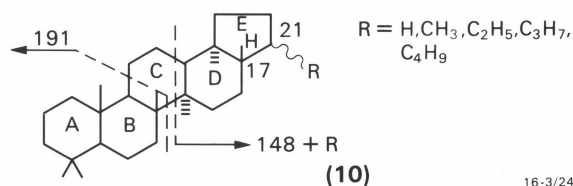


the corresponding sterane and analysis by high-resolution gas chromatography showed that the 24R and 24S

isomers were present in the ratio 4.3:1. It could, therefore, be concluded that the major free sterol of *E. huxleyi* is (24S)-24-methylcholesta-5,22-dien-3 β -ol. The same configuration is produced by the diatoms *Phaeodactylum tricornutum* and *Nitzschia closterium*. However, the phytoflagellate *Ochromonas* spp. (Chryso-phyceae) produced sterols with the opposite C-24 configuration to *E. huxleyi*. Such specific stereochemical differences may be useful in the classification of many such microscopic algae (which can be difficult by other techniques) and in determining the contribution of specific organisms to a sediment.

Triterpanes

Hopane-type triterpanes (10) have been shown to be ubiquitous biological markers in sedimentary organic matter (Ourisson & others, 1979). The mass spectrum



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of hopane derivatives is extremely useful, since it produces two major fragments that facilitate monitoring of these compounds in complex mixtures by gas chromatography-mass spectrometry (GC-MS).

In addition, the relative intensities of the fragments due to rings A and B (m/z 191) and rings D and E (m/z 148 + R) can be directly correlated with the *cis*- or *trans*- nature of the D/E ring junction. The stereochemistry of naturally occurring hopanes is 17 β H,21 β H. However, in more mature samples, the isomer that is thermally more stable is formed, i.e. 17 α H,21 β H. In addition, C_{31} -hopanes and above have an asymmetric carbon atom at the C_{22} position and, hence, it is also possible for R and S isomers to be formed at this position as the sample matures. In Recent sediments the profile of the hopanes consists only of 17 β H,21 β H isomers, but as the sediment is subjected to increasing

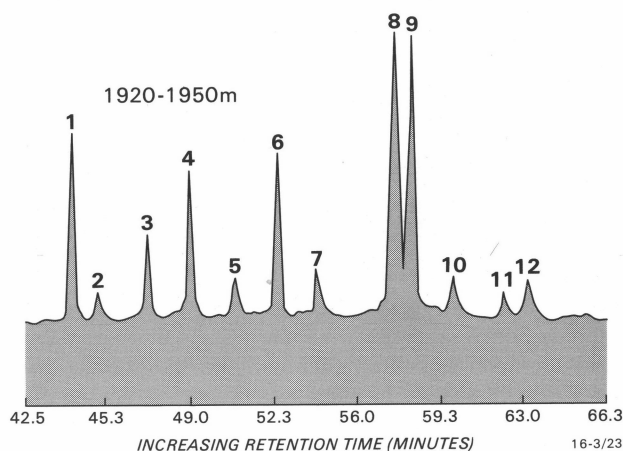


Figure 8. Single ion chromatogram of m/z 191 used to illustrate typical hopane distribution in sediment extract.

Peaks numbered 2, 5, 7, and 10 correspond to the C_{27} , C_{29} , C_{30} , C_{31} , 17 β H, 21 β H-hopanes. Peaks 1, 4, 6, 8, 9, 11, and 12 correspond to the 17 α H, 21 β H isomers with 8 and 9, and 11 and 12 being diastereomeric pairs. Peak 3 is a C_{28} -triterpane.

thermal stress, the 17 α H,21 β H isomers appear along with the 22R and S diastereomers. Figure 8 shows an example of the hopane distribution in a sample that has undergone limited diagenesis. The presence of both isomers at each carbon number is clearly indicated in this chromatogram, which has been obtained by GC-MS using the technique of single ion monitoring. Thus, although hopanes can be used as source indicators, these compounds also have the potential to be extremely useful as a maturation parameter.

Conclusions

The main aim of this paper has been to summarise some of the major factors affecting the preservation of organic matter in sediments. In addition it has illustrated the use of pristane/phytane ratios as indicators of the oxic/anoxic nature of the environments of deposition, and shown that sterols can be used as source indicators of organic matter in sediments, and that hopane-type triterpanes can be used as a maturation parameter.

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