4 Organic Matter: The Driving Force for Early Diagenesis

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4.1 The Organic Carbon Cycle

The organic carbon cycle on Earth is divided into two parts (Fig. 4.1; Tissot and Welte 1984). The biological cycle starts with photosynthesis of organic matter from atmospheric carbon dioxide or carbon dioxide/bicarbonate in the surface waters of oceans or lakes. It continues through the different trophic levels of the biosphere and ends with the metabolic or chemical oxidation of decayed biomass to carbon dioxide. The half-life is usually days to tens of years depending on the age of the organisms. The geological organic carbon cycle has a carbon reservoir several orders of magnitude larger than that of the biological organic carbon cycle ($6.4 \cdot 10^{15}$ t C compared with $3 \cdot 10^{12}$ t C in the biological cycle) and a turn-over time of millions of years. It begins with the incorporation of biogenic organic matter into sediments or soils. It then leads to the formation of natural gas, petroleum and coal or metamorphic forms of carbon (e.g. graphite), which may be reoxidized to carbon dioxide after erosion of sedimentary rocks or by combustion of fossil fuels.

The tiny leak from the biological to the geological organic carbon cycle, particularly if seen from the point of view of a petroleum geochemist in the context of the formation of petroleum source rocks (see Littke et al. 1997a for an overview), is represented by the deposition and burial of organic matter into sediments. If looked at in detail, the transition from the biosphere to the geosphere is less well defined. The transformation of biogenic organic matter to fossil material starts immediately after the decay of living organisms. It may involve processes during transport, e.g. sinking through a water column, and alteration at the sediment surface or in the upper sediment layers where epi- and endobenthic organisms thrive. Furthermore, it may extend deeply into the sedimentary column where bacteria during the last decade or so were found to be still active at several hundreds of meters depth in layers deposited millions of years ago (Parkes et al. 1994; Wellsbury et al. 2002).

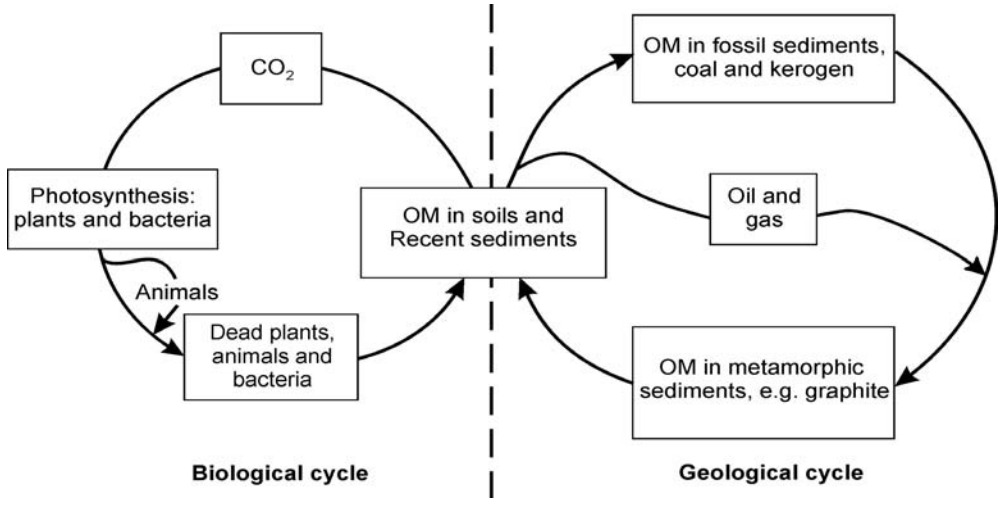

Fig. 4.1 The two major parts of the organic carbon cycle on Earth (after Tissot and Welte 1984). OM = Organic matter.

4.2 Organic Matter Accumulation in Sediments

In the fossil record, dark-colored organic-matter-rich layers (black shales, sapropels, petroleum source rocks in general) witness periods of time when conditions for organic matter accumulation in sediments apparently were particularly favorable. As the other extreme, massive sequences of white- or red-colored sedimentary rocks are devoid of organic matter. Although these rocks may contain abundant calcareous or siliceous plankton fossils, the organic matter of the organisms apparently was destroyed before it could be buried in the sediments.

Biogenic organic matter is considered labile (or metastable) under most sedimentary conditions due to its sensitivity to oxidative degradation, either chemically or biologically mediated. This is particularly true in well-oxygenated oceanic waters as they presently occur in the oceans almost worldwide. Thus, abundant accumulation of organic matter today is the exception rather than the rule. It is mainly restricted to the upwelling areas on the western continental margins and a few rather small oceanic deeps with anoxic bottom waters (such as the Cariaco Trench off Venezuela). In the geological past, more sluggish circulation in the deep ocean or in shallow epicontinental seas, accompanied by water column stratification, was probably one of the main causes leading to the deposition of massive organic-matter-

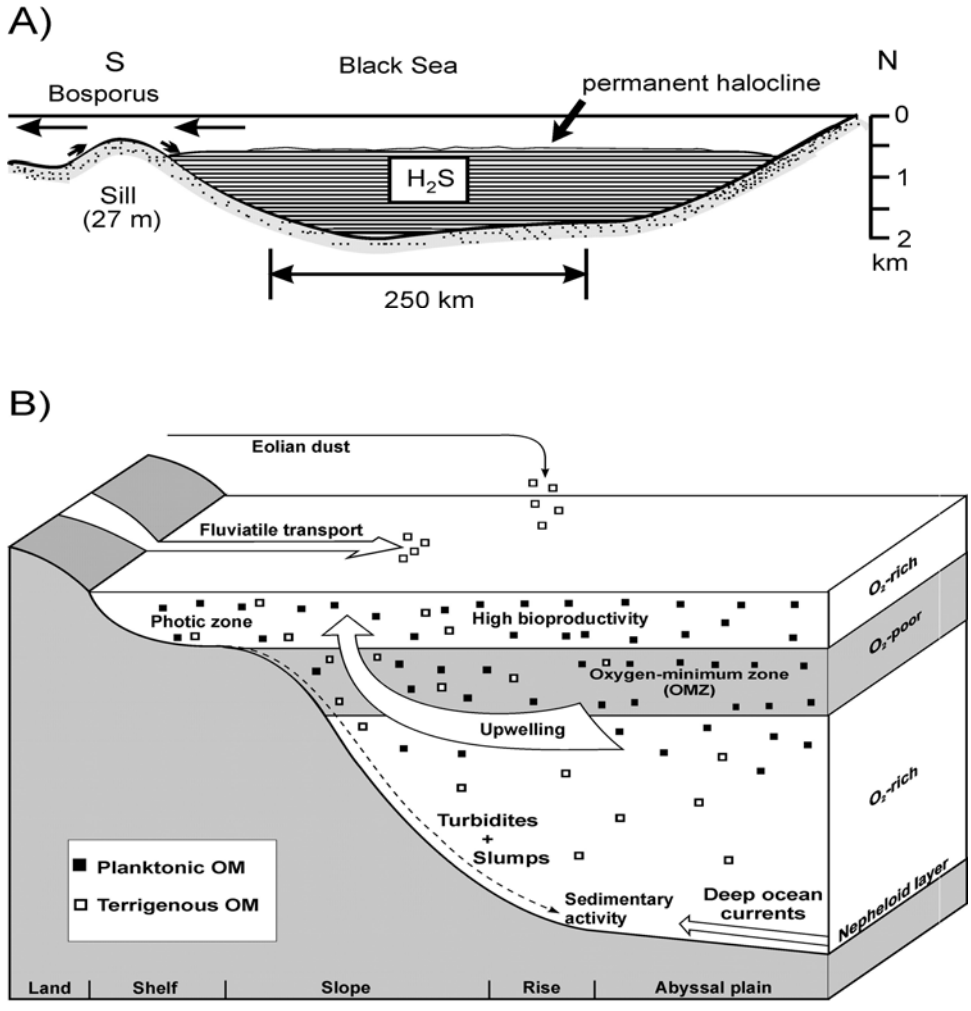

Fig. 4.2 Schematic models for organic matter accumulation in sediments. A) Stagnant basin or Black Sea model (after Demaison and Moore 1980 and Stein 1991); B) Productivity model (after Rullkötter et al. 1983). OM = Organic matter.

Table 4.1 Terminology for regimes of low oxygen concentrations and the resulting biofacies according to Tyson and Pearson (1991)

Oxygen (ml/l)	Environments	Biofacies	Physiological regime
8.0-2.0	Oxic	Aerobic	Normoxic
2.0-0.2	Dysoxic	Dysaerobic	Hypoxic
2.0-1.0	Moderate		
1.0-0.5	Severe		
0.5-0.2	Extreme		
0.2-0.0	Suboxic	Quasi-anaerobic	
0.0 (H_2S)	Anoxic	Anaerobic	Anoxic

rich rocks. A few examples are the Jurassic Posidonia Shales or Kimmeridge Clays in northwestern Europe, the Cretaceous black shales of the Atlantic Ocean and other oceanic areas of the world, and the Pliocene to Holocene sapropels of the Mediterranean Sea.

Stagnant oceanic bottom waters with a low concentration or absence of oxygen (anoxia) for a long time were considered the main prerequisite for the accumulation of high amounts of organic matter in sediments (Demaison and Moore 1980). More recently, a controversy developed about two contrasting models to explain the deposition of organic-matter-rich sediments in the marine realm, either (1) by preservation under anoxic conditions in a static situation or (2) by high primary productivity in a dynamic system (Fig. 4.2; Pedersen and Calvert 1990, 1991; Demaison 1991). The relative importance of these two dominant controlling parameters is still being heavily debated, although Stein (1986a) already conceived that either one of these parameters could play a decisive role in different oceanographic situations. Another parameter brought into discussion more recently is the protective role of organic matter adsorption on mineral surfaces and its influence on organic matter accumulation in marine sediments (Keil et al. 1994a, b; Mayer 1994, 1999; 2005; Ransom et al. 1998).

4.2.1 Productivity *Versus* Preservation

Recognition of the sensitivity of organic matter toward oxidative destruction led to the idea that the concentration of free oxygen in the water column and particularly at the sediment/water interface is the most important factor determining the amount of organic matter that is incorporated into sediments (e.g. Demaison and Moore 1980). The stagnant basin or Black Sea model (Fig. 4.2A), developed from this idea, is based on the observation that lack of replenishment of oxygen by restricted circulation in the bottom part of larger water bodies can lead to longer-term oxygen-depleted (anoxic, suboxic; see Table 4.1 for definition) conditions in the water column and at the sediment/water interface. In the Black Sea (exceeding 2000 m water depth in the center), this is caused by the development of a very stable halocline (preventing vertical mixing) at about 100 m to 150 m water depth. The surface layer is fed by relatively light riverine freshwater from the continent, and denser saline deep water is flowing in at a low rate from the Mediterranean Sea over the shallow Bosporus sill. Over time, oxidation of sinking remnants of decayed organisms consumed all of the free oxygen in the deeper water, which was not effectively replenished by Mediterranean water. Instead, the deep water in the Black Sea (like in Lake Tanganyika, an analogous contempora-neous example of a large stratified lake; Huc 1988) contains hydrogen sulfide restricting life to anaerobic microorganisms that are commonly thought to degrade organic matter less rapidly than aerobic bacteria, although there are also opposing views (see, e.g., discussion by Kristensen et al. 1995; Hulthe et al. 1998). Lack of intense organic matter degradation under anoxic conditions would then not necessarily require high surface water bioproductivity for high organic carbon concentrations to occur in the sediment.

The proponents of primary productivity as the decisive factor controlling organic matter accumulation (e.g. Calvert 1987; Pedersen and Calvert 1990; Bailey 1991) suggested that changes in primary productivity with time in different areas of the world, induced by climatic and related oceanographic changes, explain the distribution of Cretaceous black shales and more recent (Quaternary) organic-matter-rich sediments better than the occurrence of anoxic conditions in oceanic bottom waters. Reduced oxygen concentrations in the water column, according to these authors, are a consequence of large amounts of decaying biomass

settling toward the ocean bottom and consuming the dissolved oxygen.

The productivity model (Fig. 4.2B) is based on high primary bioproductivity in the photic zone of the ocean as it presently occurs in areas of coastal upwelling primarily on the western continental margins, along the equator and as a monsoon-driven phenomenon in the Arabian Sea and along the Oman and Somali coasts. Upwelling brings high amounts of nutrients to the surface, which stimulate phytoplanktonic growth (e.g. Suess and Thiede 1983; Thiede and Suess 1983; Summerhayes et al. 1992). On continental margins, the formation of oxygen-depleted water masses (oxygen minimum zones) usually implies that they impinge on the ocean bottom where they create depositional conditions similar to those in a stagnant basin. To which extent the reduction in oxygen concentration at the sediment/water interface enhances, or is required for, the preservation of organic matter in the sediments, is the main subject of debate between the proponents of the productivity and the preservation models (e.g. Pedersen and Calvert 1990, 1991; Demaison 1991). For the geological past, e.g. the Cretaceous, it is also conceivable that the equable climate on our planet led to a more sluggish circulation of ocean water worldwide. The lack of turnover in the water column may have caused the development of anoxic bottom water conditions in some parts of the ocean that may explain the formation of Cretaceous black shales almost synchronously in different areas (Sinninghe Damsté and Köster 1998 and references therein). Also, transgression as a consequence of eustatic sealevel rise may have enhanced accumulation of organic matter in shelf areas (Wenger and Baker 1986) whereas times of regression may have promoted organic matter accumulation in prograding delta fans in deeper water. A detailed discussion of organic matter accumulation in different oceanic settings, including deep marine silled basins, progradational submarine fans, upwelling areas, anoxic continental shelves and fluviodeltaic systems was provided by Littke et al. (1997a).

4.2 Primary Production of Organic Matter and Export to the Ocean Bottom

The total annual primary production by photosynthetic planktonic organisms in the modern world oceans has been estimated to be in the order of $30\text{-}50 \cdot 10^9$ tons of carbon (Berger et al. 1989; Hedges and Keil 1995). Oceanic carbon fixation is not evenly distributed, but displays zones of higher activity on continental margins (several hundred g $C_{org} m^{-2} yr^{-1}$), whereas the central ocean gyres are mostly characterized by low primary production (about 25 g $C_{org} m^{-2} yr^{-1}$; e.g. Romankevitch 1984; Berger 1989). Due to plate tectonics and the variable distribution of land masses together with climatic developments, the global amount and distribution of organic matter production in the ocean is likely to have undergone significant changes with geological time.

Of the total biomass newly formed in the photic zone of the ocean, only a very small portion reaches the underlying seafloor and is ultimately buried in the sediment (for reviews of water column processes see Emerson and Hedges 1988; Wakeham and Lee 1989). Most of the organic matter enters the biological food web in the surface waters and is respired or used for new heterotrophic biomass production. Because of this intense recycling, it is difficult to determine the organic matter flux at different levels of the photic zone. Oceanographers and biogeochemists usually consider only the flux of organic matter through the lower boundary of the photic zone and term it 'new' production (Fig. 4.3). It equals 100 % of export production (see below) and is not to be confused with net photosynthesis which is gross photosynthesis minus algal respiration. Below this boundary, the content of organic matter in the water column decreases due to consumption in the food web and to microbiological and chemical degradation as observed from the analysis of material in sediment traps deployed at different water depths.

The water depth-dependent flux is termed export production (Fig. 4.3). Export production decreases rapidly just below the photic zone. Then, there is mostly a quasi-linear, slower decline at greater water depths until the organic matter reaches the benthic boundary (nepheloid) layer close to the sediment/water interface where the activity of epibenthic organisms enhances organic matter consumption again. This enhanced consumption continues in the upper sediment layer where burrowing organisms depend on the supply from the water column. Organic matter degradation eventually extends deeply into the sediment pile as became evident from the detection of a so-called deep biosphere at several hundred meters below the seafloor (e.g. Parkes et al. 1994). However, the rate of organic matter degradation apparently decreases significantly with increasing depth of burial. Overall, it is estimated that only 1 to 0.01 % of the primary production is buried deeply in marine sediments (cf. Fig. 12.1). The fraction strongly depends on a number of parameters including level of primary productivity, water depth, (probably) oxygen content in the water column and surface

sediments (the latter affects benthic activity), particle size, adsorption to mineral surfaces and sediment porosity.

Although the fraction of organic matter burried in sediments is small relative to the amount produced by photosynthesis in oceanic surface waters, empirical relationships were derived from the analysis of sedimentary organic matter to estimate oceanic paleoproductivity (PaP [g C $m^{-2}yr^{-1}$]) in the geological past:

$$PaP = C \cdot \rho(100-\phi/100)/0.003 \cdot S^{0.3} \quad (4.1)$$

In this equation of Müller and Suess (1979), the Pleistocene paleoproductivity of the (oxic) ocean is related to the organic carbon content of a sediment in percent dry weight (C), the density of the dry sediment (ρ; g cm^{-3}), its porosity (ϕ; %) and the linear bulk sedimentation rate (S; cm of total sediment per 1000 yr). The exponential factor was obtained from calibration with data from the present ocean. Because it was shown later that the organic carbon accumulation rate is a function of the carbon flux near the seafloor, which is related to both productivity and water depth, Stein (1986a, 1991) derived a more complex empirical relationship using flux data of Betzer et al. (1984):

$$PaP = 5.31[C(\rho_{WB} - 1.026\phi/100)]^{0.71} \cdot S^{0.07} \cdot D^{0.45} \quad (4.2)$$

with ρ_{WB} being the wet bulk density of the sediment and D the water depth. Values from this equation are proportional, although numerically not identical, to the results obtained from a third empirical relationship developed by Sarnthein et al. (1987, 1988):

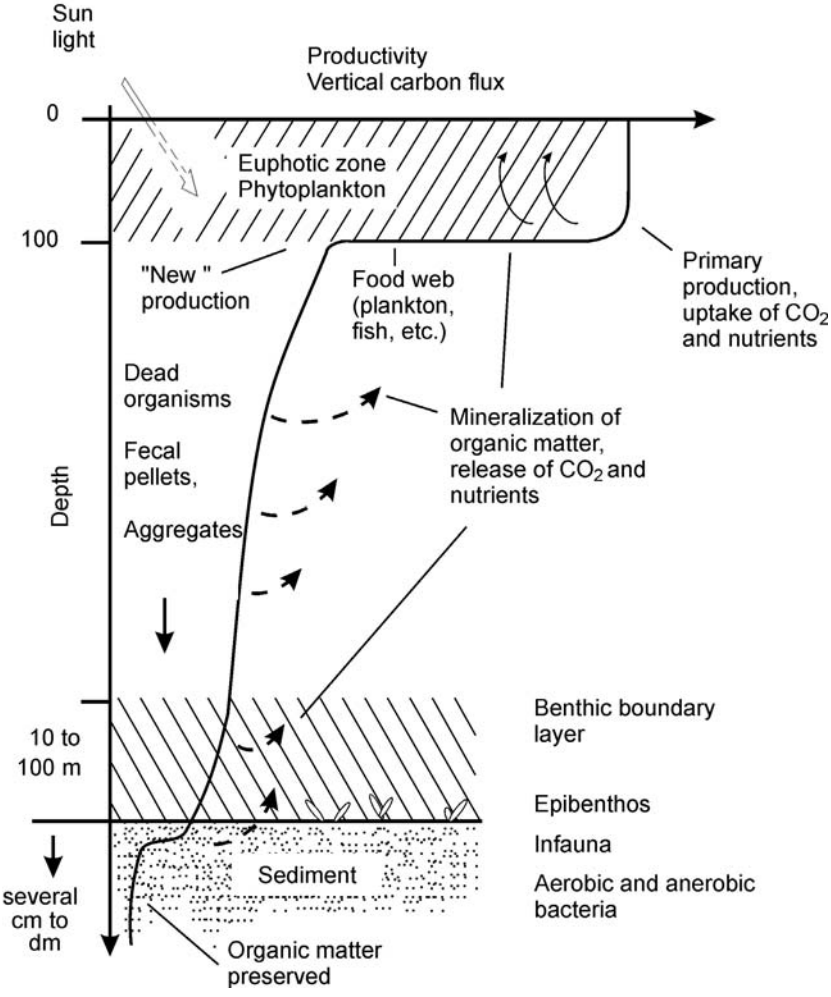

Fig.4.3 Schematic representation of organic matter flux to the ocean bottom.

$$PaP = [15.9C \cdot S \cdot \rho(1-\phi)]^{0.66} \cdot S_{B\text{-}C}^{-0.71} \cdot D^{0.32} \quad (4.3)^1$$

where $S_{B\text{-}C}$ is the organic-carbon-free linear bulk sedimentation rate. Given the complexity of the sedimentation and burial processes of organic matter, the wide range of chemical and physical properties of organic matter from different organisms and the effects of organic matter alteration during diagenesis after incorporation in the sediment, the equations can only be considered rough estimates. It can be expected that the investigation of more oceanic sediment profiles in the future will result in further modification of the equations (cf. also Sarnthein et al. 1992; Stein and Macdonald 2005 and references therein). In particular, the extent of mixing of autochthonous marine organic matter with allochthonous organic matter from the continents (see 4.2.5) is difficult to estimate. Stein (1986a) used data from Rock-Eval pyrolysis, calibrated by organic petrographic data from microscopic analysis, to derive the marine organic matter fraction of a sediment from bulk pyrolysis measurements, but the correlation displays substantial scatter and can only be regarded a crude approximation.

Müller and Suess (1979) applied their paleoproductivity relationship (Eq. 4.1) to sediments from the deep ocean off Northwest Africa. They found that the Pleistocene interglacial periods had about the same productivity as that measured in the present-day ocean. It was three times higher during glacial periods, probably due to a higher nutrient supply by more intense mixing of water masses or stronger coastal upwelling. The more sophisticated Equation 4.3 of Sarnthein et al. (1987, 1988) yielded essentially the same results for the last 500,000 years as those from Equation 4.1. Typical Pleistocene productivities in the upwelling area off Northwest Africa ranged between 150 and 300 g $C_{org}m^{-2}yr^{-1}$, whereas the values were 20 to 50 g $C_{org}m^{-2}yr^{-1}$ in the central Atlantic Ocean (Stein et al., 1989).

The paleoproductivity equations above describe the relationship between surface-water productivity and organic carbon accumulation, specifically under conditions of an oxic water column. A different relationship for anoxic depositional settings, suggested by Bralower and Thierstein (1987), implies that at least 2 % of the organic carbon in the gross photosynthetic production is preserved in the sediments:

$$PaP = 5C \cdot S(\rho_{WB} - 1.026\phi/100) \quad (4.4)$$

Stein (1986a) used this equation to calculate paleoproductivity in the Mesozoic Atlantic Ocean. Interpretation was considered preliminary due to the difficulty of obtaining precise age information, and thus sedimentation rate data, for the older and more compacted Mesozoic sediments lean in microfossils. The estimated productivity appeared to have been low off Northwest Africa in the Jurassic, to have increased during the Early Cretaceous and to have reached maximum values similar to those today during Aptian-Albian times (about 110 million years ago). Interestingly, low paleoproductivity was calculated for the time of deposition of black shales at the Cenomanian-Turonian boundary (90 million years ago) indicating that preservation may have played a more important role for organic matter accumulation than productivity.

The empirical relationships for paleoproductivity assessment illustrate how organic matter accumulation is related to primary productivity through factors such as organic carbon flux through the water column and bulk sedimentation rate. In addition, there is evidence that reduced oxygen concentrations in the water column enhance organic matter preservation. Thus, organic-carbon-rich sediments and sedimentary rocks are likely to be formed by the mutually enhancing effects of oxygen depletion (static or dynamic; anoxia), and productivity. In view of this, it appears to be too restrictive to assign a single controlling factor (Pederson and Calvert 1990). For example, an anoxic water column in the Holocene Black Sea is in itself apparently not sufficient to lead to black shale formation, whereas the enhanced primary productivity in equatorial upwelling areas is not reflected in a high organic carbon content of the underlying sediments due to oxidation of the sinking organic matter in the deep oxic waters below the oxygen-minimum zone.

4.2.3 Transport of Organic Matter Through the Water Column

The extent of degradation of particulate organic matter as it sinks through the water column is influenced by the residence time of organic matter particles in the water column. A measure of vertical transport is the sinking velocity (vs; m s^{-1}), which for a spherical particle follows Stokes' law:

$$vs = [(\rho_2 - \rho_1) \cdot g \cdot D^2]/18\eta \quad (4.5)$$

ρ_2 and ρ_1 are the densities (g cm^{-3}) of the particle and the water, respectively, g is the acceleration due to

[1] Numerical values in this equation were rounded because the author of this chapter believes that the number of decimals in the original publication suggests more accuracy than is both justified by, and required for, this empirical estimative approach.

gravity (m s^{-2}), D is the particle diameter (cm) and η is the dynamic viscosity (g $cm^{-1}s^{-1}$). Representative travel times of different idealized organic particles through a water column of 1000 m cover a wide range (Table 4.2). They reflect the effects of different densities and diameters. Smaller, less dense particles clearly settle very slowly.

The vastly different travel times of the particle types range from hours to years. They would be only slightly higher in saline ocean water. The density values in the table imply some association of the organic matter with mineral matter, either biogenic calcareous or siliceous (plankton) frustules or detrital mineral matter like clay. Pure organic matter would have a lower density than water and not sink to the ocean bottom at all. Densities, e.g., of coal macerals usually vary between 1.1 and 1.7 g cm^{-3} (van Krevelen 1961), and zooplankton fecal pellets often contain more mineral than organic matter. Degens and Ittekott (1987) strongly favored the transfer of organic matter by fecal pellets "which are jetted to the seafloor at velocities of about 500 m day^{-1}." Mineral-poor algal particles may have a very long residence time in the water column and a high chance of being metabolized before reaching the ocean floor. In deep oxic ocean water, the "fecal pellet express" may be an important mechanism of transporting marine organic matter to the seafloor. Microscopic analysis often revealed that all of the labile marine organic matter in such sediments occurred as 'amorphous' degraded material in rounded bodies which were ascribed to fecal pellets (e.g. Rullkötter et al. 1987). On the other hand, Plough et al. (1997) measured rapid rates of mineralization of fecal pellets (relative to their sinking time toward the seafloor). This is consistent, however, with the observation that only intact fecal pellets occur in deep-sea sediments (PK Mukhopadhyay, personal communication 1987). Obviously, lysis of fecal pellet walls leads to rapid mineralization of the entire organic content, and only those fecal pellets reach the seafloor and are embedded in the sediment which escape this degradative process in the water column.

Other than noted in Table 4.2, real sinking velocities strongly depend on particle shape. For example, von Engelhardt (1973) showed that the sinking velocity of quartz grains of 10-100 µm diameter is greater by a factor of about one hundred than that of muscovite plates of equal diameter. Most organic matter particles, apart from fecal pellets, are not spherical or well rounded and thus have a lower sinking velocity than indicated in Table 4.2. The typical shape of terrigenous organic particles in young open-marine sediments is irregularly cylindrical with the longest axis being about twice the length of the shortest axis (Littke et al. 1991a).

4.2.4 The Influence of Sedimentation Rate on Organic Matter Burial

Müller and Suess (1979) demonstrated the influence of sedimentation rate on organic carbon accumulation under oxic open-ocean conditions. They found that the organic carbon content of marine sediments increases by a factor of about two for every tenfold increase in sedimentation rate. The underlying mechanism was believed to be the more rapid removal and protection of organic matter from oxic respiration and benthic digestion at the sediment/water interface by increasingly rapid burial (cf. Sect. 12.3.3). Also

Table 4.2 Sinking velocity and travel time for spherical particles in nonturbulent freshwater (after von Engelhardt 1973, Littke et al. 1997a)

Particle type	Sinking velocity ($m \cdot s^{-1}$)	Travel time (1000 m water)
Large terrigenous organic matter particle $\varnothing$ = 100 µm, ρ = 1.3 $g \cdot cm^{-3}$	$1.6 \cdot 10^{-3}$	7.1 days
Small terrigenous organic matter particle $\varnothing$ = 10 µm, ρ = 1.3 $g \cdot cm^{-3}$	$1.6 \cdot 10^{-5}$	1.9 years
Fecal pellet $\varnothing$ = 1 mm, ρ = 1.3 $g \cdot cm^{-3}$	$1.6 \cdot 10^{-1}$	2 hours[a]
Quartz grain $\varnothing$ = 10 µm, ρ = 2.6 $g \cdot cm^{-3}$	$8.7 \cdot 10^{-5}$	133 days

[a]Measured travel times for real fecal pellets: 4-20 days/1000 m (JK Volkman, pers. com. 1998)

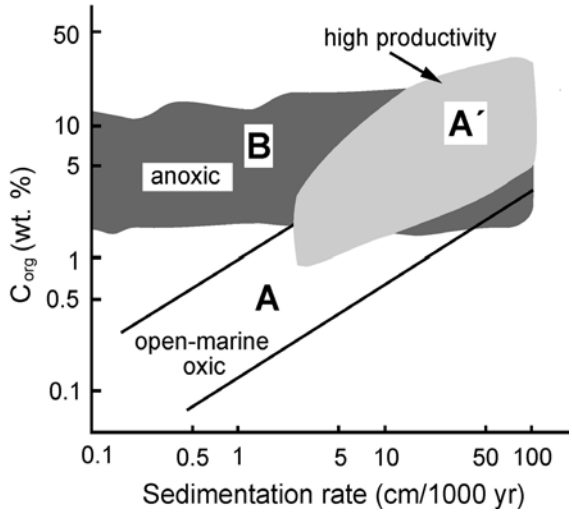

Fig. 4.4 Correlation between marine organic carbon content and sedimentation rate (after Stein 1986b, 1990). The distinction between fields A, A' and B is based on data derived from Recent to Miocene sediments deposited in normal open-ocean environments (field A), upwelling high-productivity areas (field A') and anoxic environments (field B).

conceivable, however, is that the relationship between sedimentation rate and organic carbon content is based on the protective effect of organic matter adsorption on mineral (particularly clay) surfaces, so that organic matter preservation increases with the increase of mineral surface available for adsorption (Keil et al. 1994a, b; Mayer 1994,1999, 2005; Collins et al. 1995; Ransom et al. 1998).

There is general agreement on the positive relationship between sedimentation rate and organic carbon content (e.g. Heath et al. 1977; Ibach 1982; Stein 1986a, b; Bralower and Thierstein 1987; Littke et al. 1991b). However, in cases where biostratigraphy provides accurate time control, it has been noted by Tyson (1987) that deposition of marine sediments with very high organic matter contents (petroleum source rocks) often appears to be associated with low rather than high sedimentation rates. Very high sedimentation rates at some point may lead to low organic matter concentrations in sediments due to dilution even if much of the sinking organic matter is preserved (Note difference between linear sedimentation rate [cm kyr^{-1}] and sediment accumulation rate [g $cm^{-2}yr^{-1}$], i.e. in a highly diluted sediment with a moderate to low organic carbon content deposited at a high linear bulk sedimentation rate, organic matter accumulation (or preservation) with time may still be high).

According to Stein (1986b, 1990), the effects of oxic and anoxic conditions on marine organic matter preservation in oceanic sediments can be illustrated by a simple diagram of sedimentation rate versus organic carbon content (Fig. 4.4). Field A inside the diagonal lines represents the sedimentation rate-controlled accumulation of organic matter under open-marine oxic conditions. The hatched area B indicates anoxic or strongly oxygen-depleted conditions over a wide range of sedimentation rates with low rates being typical for stagnant basins like the Black Sea. The shaded area A', where areas A and B overlap at high sedimentation rates and high organic carbon contents, is typical of upwelling areas with high primary productivity on continental margins where the oxygen-minimum zone impinges on the shelf and upper slope. Strong dilution with mineral matter would place a sediment to the right of area A. Interestingly, the highly organic-matter-rich Atlantic Ocean black shales from a so-called 'world-wide anoxic event' at the Cenomanian-Turonian boundary (about 90 million years ago; see Herbin et al. 1986) all fall in the left part of area B, i.e. they appear to have been deposited at low sedimentation rates under anoxic conditions (Stein 1986b).

4.2.5 Allochthonous Organic Matter in Marine Sediments

As schematically indicated in Fig. 4.2B, marine sediments do not only accumulate organic matter from the (mainly planktonic) productivity in the overlying water column (autochthonous organic matter). Allochthonous organic matter originates from two other sources. One of them involves redeposition of marine sediments after erosion, often from a nearby location. Typical examples are contour currents along continental margins or downslope transport events on (steep) continental margins. In these cases, sediment initially deposited at shallow(er) water depth is eroded by currents, mechanical instability (oversteepening), earthquakes or other tectonic movements. The eroded sediment is transported down the continental slope and redeposited at a deeper location. This may occur as a turbidity current by which sediment is suspended in the near-bottom water column and then settles again. This process often involves particle size fractionation, i.e. at the new site the larger particles are deposited first and become overlain by a sequence of progressively finer particles (Bouma series). Alternatively, a massive package of sediment material (slump) of variable size, from very small to cubic kilometers, may be redeposited as a whole, usually in a deep slope or continental rise setting. The effect on the organic

matter is different in these two cases. Turbidity currents may expose the (fossil) organic matter to an oxygen-rich water mass causing further degradation during resettling. Compact slump masses may transport significant amounts of labile organic matter from an initial depositional setting, favorable for organic matter preservation (e.g. in an oxygen-minimum zone), to an oxygen-rich deep-water environment. There is no enhanced mineralization in this case due to the undisturbed embedding of organic matter in the sediment matrix (cf., e.g., Cornford et al. 1979; Rullkötter et al. 1982).

Redeposition may occur almost synsedimentarily, i.e. the redeposited allochthonous sediment will differ only very little in age from the underlying autochthonous sediment. The organic matter content of both may reflect more or less contemporaneous primary productivity with the only exception that the remains of shallow(er)-water species are relocated to a deep-water environment. This may be more evident in the mineral fossils than in the organic matter assemblage, however. Alternatively, redeposition may occur a long time after initial sedimentation took place. Deep-sea drilling on the Northwest African continental margin, for example, has recovered extended Miocene sediment series which evidently contained slumps a few centimeters to several meters thick and of various age, from Tertiary to Middle Cretaceous (von Rad et al. 1979; Hinz et al. 1984). Investigation of the organic matter on a molecular level clearly demonstrated the correspondence between slump clasts embedded in the Lower Miocene sequence and underlying autochthonous Cenomanian series, whereas paleontological analysis showed a difference between outer shelf/upper slope species in the slumps and pelagic species in the autochthonous Cenomanian sediment (Rullkötter et al. 1984).

The second main source of allochthonous organic matter in marine sediments are the continents. Wind, rivers and glaciers transport large amounts of land-derived organic matter into the ocean (e.g. Romankevitch 1984; Hedges and Keil 1995; Hedges et al. 1997). Again, two principal types of organic matter have to be distinguished: (1) fresh or (in geological terms) recently biosynthesized land plant material and (2) organic matter contained in older sediments that were weathered and eroded on the continent in areas ranging from mountains to coastal swamps. Organic matter in older sedimentary rocks that are being eroded may have had an extended history of geothermal heating at great burial depth into the stages of oil or bituminous coal formation and beyond. This organic matter carries a distinct signal of geochemical maturation that can easily be detected by bulk (e.g. atomic composition, pyrolysis yields, vitrinite reflectance; see Tissot and Welte 1984) and molecular geochemical parameters (e.g. compound ratios of specific geochemical fossils or biomarkers; see Peters et al. 2005). Due to its advanced level of diagenetic alteration, even peat can be distinguished from fresh organic matter in marine sediments. Only when sediments have been buried to a depth corresponding to the temperature which the eroded organic matter earlier experienced do both fresh and prematured organic matter continue diagenesis or maturation at the same rate. Geochemical reactions are virtually stopped (i.e. reaction rates become very low) as soon as sediments (and their organic matter contents) in the course of tectonic uplift are cooled to a temperature of about 15° C lower than their previous maximum temperature. During transport to the ocean, oxidation of organic matter eroded on land – and of terrestrial organic matter in general – has an effect similar to maturation. The product is a highly refractory, inert material , which in organic petrography is termed inertinite and which is easily recognizable under the microscope by its high reflectance (see Taylor et al. 1998 for details). Nevertheless, a substantial fraction of the terrigenous organic matter is reactive and metabolizable in the ocean (Hedges et al. 1997).

Wind-driven dust and aerosols carry terrigenous organic matter over long distances into the oceans and are estimated to contribute a total annual amount of $3.2 \cdot 10^8$ t carbon each year (Romankevitch 1984). Entire organoclasts, like pollen and spores, are blown offshore as are lipids from the waxy coatings of plant cuticles adsorbed to mineral grains (e.g. Rommerskirchen et al. 2003 and references therein). This wind-blown terrestrial material may comprise the bulk of the organic matter in open-ocean sediments where very little of the primary marine organic matter reaches the deep ocean floor. The higher resistance of terrestrial organic matter toward oxidation has been invoked to explain this selective enrichment. Summerhayes (1981) estimated that most organic-matter-rich sediments in the Atlantic Ocean, including the Cretaceous and Jurassic black shales, contain a 'background level' of 1 % terrestrial organic matter in total dry sediment.

Not all of this terrigenous material is brought into the ocean by winds. The most important contributors are the rivers draining into the ocean. Each year rivers transport approximately $0.4 \cdot 10^9$ t of dissolved and particulate organic carbon from continents to oceans (Schlesinger and Melack 1981). About 60 % of the river run-off derives from forested catchments, and the ratio of the contribution of tropical to temperate and boreal forests is about two to one (Schlesinger and Melack 1981). Much

of the organic matter discharged by rivers appears to be soil-derived (Meybeck 1982; Hedges et al. 1986a, b) and highly degraded (Ittekott 1988; Hedges et al. 1994).

4.3 Early Diagenesis

4.3.1 The Organic Carbon Content of Marine Sediments

The content of organic carbon in marine surface sediments from different environments of the present-day oceans varies over several orders of magnitude depending on the extent of supply of organic matter, preservation conditions and dilution by mineral matter. The results of organic carbon measurements are usually expressed as TOC (total organic carbon) or C_{org} values in percent of dry sediment. Romankevich (1984) compiled data from a great number of analyses of ocean bottom sediments by various authors and from all over the world. The TOC values range from 0.01 % to more than 10 % C_{org} in a few cases. A statistical evaluation of data from the early phase of deep-sea drilling (Deep Sea Drilling Project Legs 1-31) showed deep-sea sediments to have a mean organic carbon content of 0.3 %, with a median value of 0.1 % (McIver 1975). However, the range of samples was certainly not representative, and the organic carbon contents are probably biased toward higher values. For example, in the vast abyssal plains and other deep-water regions far away from the continents, an organic carbon content as high as 0.05 % is the exception rather than the rule.

In contrast to this, nearshore sediments on continental shelves and slopes usually have considerably higher organic carbon contents. Typical hemipelagic sediments on outer shelves and continental slopes range between 0.3 and 1 % C_{org}. Sediments within the oxygen-minimum zone of upwelling areas contain several percent of organic carbon with exceptional values exceeding 10 % C_{org} where upwelling is very intense, e.g. off Peru and southwest Africa, and where the oxygen-minimum zone extends into the shallow waters of the shelf. Still, generalizations are difficult to make because sedimentation conditions are highly variable in space.

Generalizations are also difficult to make with respect to variation of organic carbon content with time. For long periods of the geological record the present-day conditions of organic carbon burial can be projected to the past. There were times, however, mostly relatively

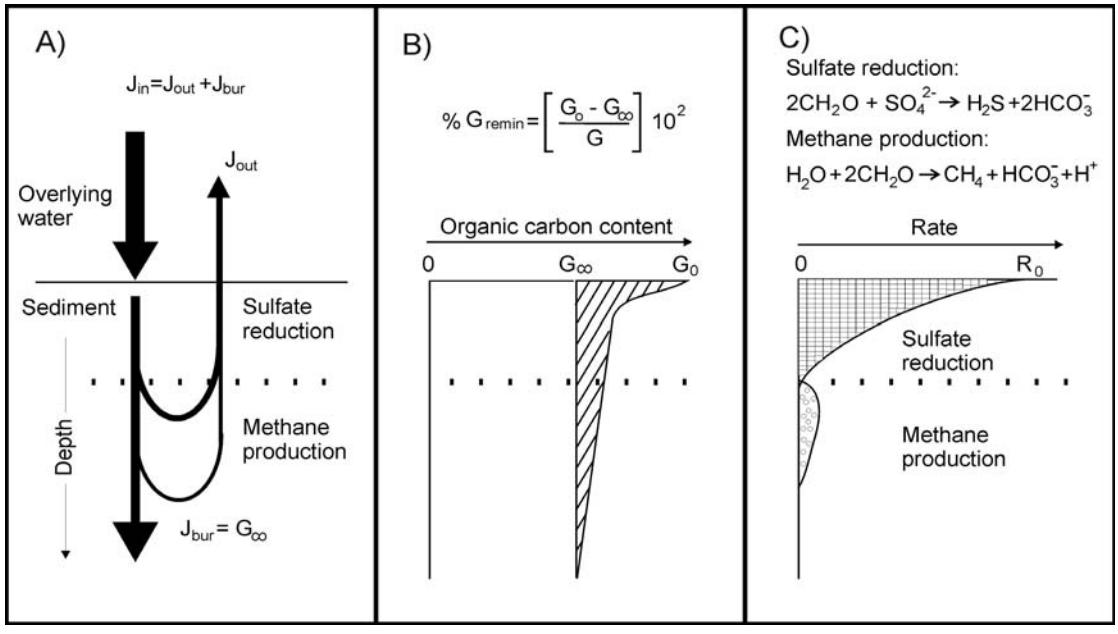

Fig. 4.5 Three independent approaches used to quantify organic matter degradation in anoxic coastal sediments: (A) carbon budget based on measurement of recycled (J_{out}; CO_2 and methane) and calculation of buried (J_{bur}) carbon fluxes; (B) kinetic modeling of the concentration/depth distribution of organic carbon (G; G_0 and G_∞ are organic carbon contents at the top and the bottom of the studied depth interval, respectively); (C) calculated organic carbon remineralization based on modeled or measured rates of sulfate reduction and methanogenesis (CH_2O stands for organic matter) (after Martens and Klump 1984).

short and often termed an event, when high amounts of organic matter were preserved, not only in shallow epicontinental seas, but also in deep-sea sediments. Examples are the Jurassic and particularly Cretaceous black shales of the Atlantic and Pacific Oceans with extreme organic carbon contents of 20-30 % and more (e.g. Herbin et al. 1986; Dumitrescu and Brassell 2005). Specific oceanographic conditions prevailed during the younger geological past in semi-enclosed basins like the Mediterranean Sea. Plio-Pleistocene sapropels in the eastern Mediterranean Sea were deposited at regular time intervals due to climatic changes induced by orbital forces, in this case the 23,000 year cycle of precession of the Earth's axis. Some of the Mediterranean sapropels, recovered during Leg 160 of the international Ocean Drilling Program, yielded more than 30 % C_{org} (Emeis et al. 1996).

The range of organic carbon contents in sediments and the associated variation in conditions for organic matter preservation imply that the amount of biogenic information incorporated in sediments as organic matter may vary drastically. In the same way, the extent to which the preserved organic matter is representative of the ecosystem in the water column above, may be vastly different. It is not surprising then that organic geochemists have preferentially investigated sediments with high organic carbon contents particularly when emphasis was on the formation of fossils fuels (petroleum or natural gas) or on molecular organic geochemical analysis which – at least in its early days – required relatively large amounts of material. It has to be kept in mind that this bias has certainly also influenced the choice of examples given throughout this chapter, although attempts are made to contrast case studies representing different environmental conditions in the oceanic realm.

Within a sediment, the organic carbon content decreases with increasing depth due to mostly microbiological remineralization, but possibly also due to abiological oxidation, during early (and later) diagenesis. The entire process takes place in a complex redox system where organic matter is the electron donor and a variety of substrates are electron acceptors. In other words, whenever organic matter is destroyed or altered by oxidation, a reaction partner has to be reduced. In an extended investigation of the biogeochemical cycling in an organic-matter-rich coastal marine basin, Martens and Klump (1984) schematically illustrated three independent approaches to quantify organic matter degradation in sediments with anoxic surface layers (Fig. 4.5). These involve (a) a mass balance of incoming, recycled and buried carbon fluxes, (b) kinetic modeling of the concentration/depth distribution of organic carbon and (c) measurement of degradation rates in the sediment column. The redox zones in the example given in Fig. 4.5 are restricted to a depositional environment with anoxic surface sediment and comprise only sulfate reduction and methanogenesis. In the case of oxic conditions in the upper sediment layer, there would be additional oxygen, nitrate, Mn(IV) and Fe(III) reduction zones (Froelich et al. 1979; cf. also Fig. 4.6, where these zones are indicated, and Chap. 5).

Martens et al. (1992) applied the approaches in Fig. 4.5 to study the composition and fate of organic matter in coastal sediments of Cape Lookout Bight[2]. In separate studies it had previously been established that organic matter was mostly supplied from back-barrier island lagoons and marshes landward of the bight at a steady rate. Furthermore, the organic matter was extensively physically and biologically recycled in the lagoon before it ultimately accumulated in the sediments. Thus, systematic downcore decreases in amount of labile organic matter had to result from early diagenesis rather than variations of supply. The authors tried to answer the question of what fraction of the incoming particulate organic carbon (POC) is remineralized during early diagenesis under the conditions described by solving the simple mass balance equation.

$$\text{POC input} = \text{POC remineralized} + \text{POC buried} \qquad (4.6)$$

In their experience it has proven easiest to measure fluxes resulting from POC remineralization and burial and then to calculate POC input by adding these fluxes together. Numerical values of the fluxes are given in Figure 4.6. In this model, the incoming POC is either remineralized to CO_2, CH_4 and DOC (dissolved organic carbon) or buried. The CO_2, CH_4 and DOC produced during remineralization are either lost to the water column via sediment-water chemical exchange or buried as carbonate and dissolved components of sediment pore waters. Using ^{210}Pb-based sedimentation rates, the POC burial rate was found to be 117±19 mol C $m^{-2}yr^{-1}$. Sediment-water chemical exchange accounts for losses of 40.6±6.6 mol C $m^{-2}yr^{-1}$ as CO_2, CH_4 and DOC, whereas 7.0±1.1 mol C $m^{-2}yr^{-1}$ of these species, including

[2] Cape Lookout Bight (North Carolina, U.S.A.) is an "end member" environment with respect to sedimentation rate (10 cm per year!), organic matter composition, domination of anoxic degradation processes and direct ebullition of methane gas, i.e. not typical for present-day open-ocean marine sediments.

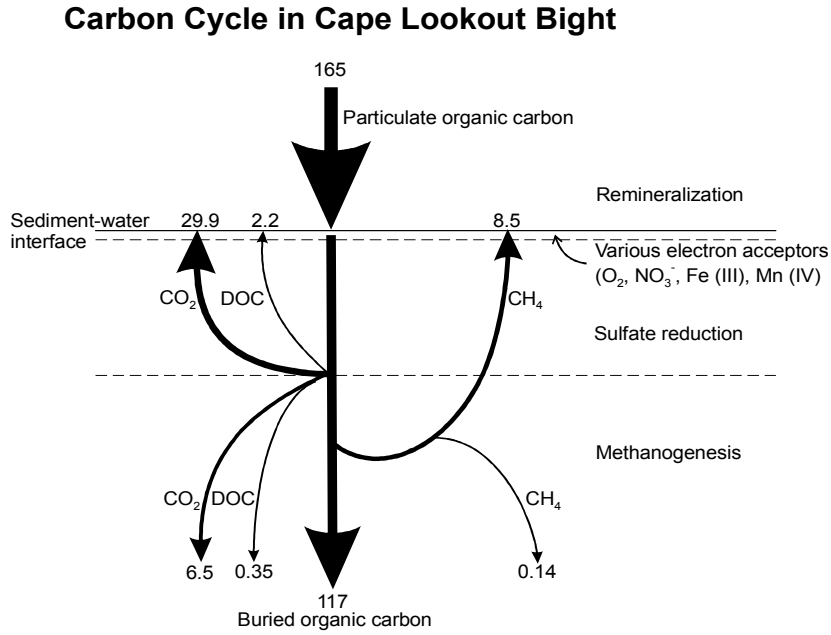

Fig. 4.6 Fluxes of carbon associated with organic matter supply, degradation and burial in Cape Lookout Bight sediments. The unit of all numerical flux values is moles C $m^{-2}yr^{-1}$ (after Martens et al. 1992).

carbonate formed from CO_2, are buried (Fig. 4.6). The dissolved sediment-water exchange and burial fluxes sum to a total POC remineralization rate of 47.6±5.7 mol C $m^{-2}yr^{-1}$. When this value is added to the POC burial rate, a total POC input of 165±20 mol C $m^{-2}yr^{-1}$ can be calculated from equation 4.6. From this result it follows that 29±5 % of the incoming POC is remineralized as an average over the first about ten years after sedimentation in Cape Lookout Bight.

Using a similar approach, Alperin et al. (1992) determined the POC remineralization rate for sediments of Skan Bay, Alaska, a pristine embayment with oxygen-depleted bottom water (<0.4 ml O_2/l water) and sulfidic surface sediments and with a shallow sill limiting advection of oxygen-rich water from the Bering Sea. Total sediment remineralization rate was calculated by three independent approaches: (1) the difference between POC deposition and preservation; (2) the quantity of carbon recycled to the water column and buried at depth; (3) depth-integrated rates of bacterial metabolism. The budget indicates that 84±3 % of the organic carbon deposited is remineralized in the upper meter of the sediment column representing approximately 100 years. A steady state is nearly reached, however, at a depth of about 70 cm, i.e. remineralization is already very slow after approximately 70 years of burial in Skan Bay. The initial content of more than 9 % organic carbon at the sediment surface dropped to less than 2 % of dry sediment at 0.7 to 1 m depth and most of that would survive deeper burial.

A third case study of organic carbon recycling and preservation in coastal environments, including a comprehensive budget of inorganic reactants and products, is from the Aarhus Bay (Denmark), a shallow embayment in the Kattegat that connects the North Sea with the Baltic Sea (Fig. 4.7; Jørgensen 1996). The bulk annual sedimentation rate in Aarhus Bay is about 2 mm yr^{-1}. Photosynthesis is in the upper mesotrophic range and annually produces organic matter corresponding to 21.8 mol C $m^{-2}yr^{-1}$. Planktonic oxygen respiration corresponds to mineralization of 68 % of the primary productivity and 32% sedimentation, whereas direct sediment trap measurements accounted for 45% deposition. Of these 9.9 mol C $m^{-2}yr^{-1}$, about 2.2 mol C $m^{-2}yr^{-1}$ are buried below the bioturbated zone. Metabolization in the sediment mainly occurs by oxygen and sulfate as electron acceptors, whereas nitrate, Mn(IV) and Fe(III) play a subordinate role. Methanogenesis was not included in the study of the carbon budget because only the water column and the shallow surface sediment were studied.

The three case studies show that organic matter preservation and, thus, organic carbon contents strongly depend on the specific local environmental conditions. The extent of remineralization in these three

cases ranges from about 30 to 85 % in the upper sediment layers comprising, however, different time ranges. They correspond to the range quoted for continental shelf and estuarine sediments (20 to 90 %) by Henrichs and Reeburgh (1987). Apparently, organic carbon flux, bulk sedimentation rate, water depth, oxygen concentration in the bottom water and related extent of bioturbation of surface sediments all have an influence on the intensity of organic matter remineralization during early diagenesis and on how much organic matter is buried to a sediment depth where further remineralization only proceeds very slowly. Only that organic matter fraction can be considered to become fossilized in a strict sense and to enter the geological organic carbon cycle.

Methanogenesis

As indicated in Figure 4.6, the last step in the sedimentary metabolic pathway is methanogenesis. The formation of methane at a depth level, where all sulfate has been consumed, involves a group of strictly anaerobic archaea, collectively called methanogens. They use a small number of different low-molecular-weight substances for the biosynthesis of methane which, together with elemental hydrogen, in turn are formed by bacterial fermentation from more complex organic substances during early diagenesis. The terminal electron acceptor in methanogenesis is carbon. The most prominent pathways are the reduction of carbon dioxide with molecular hydrogen and the transformation of acetic acid into methane and carbon dioxide (Eq. 4.7), although formic acid or methanol may be used as substrates as well.

$$\begin{aligned} CO_2 + 4\,H_2 &\rightarrow CH_4 + 2\,H_2O \\ CH_3COOH &\rightarrow CH_4 + CO_2 \end{aligned} \qquad (4.7)$$

Methanogenesis is widespread in the marine environment, particularly on continental margins or in stagnant basins, where sufficient organic matter is deposited so that anoxic conditions occur at shallow depth below the seafloor (e.g. D'Hondt et al. 2002). The amounts of methane formed can be enormous in certain areas. Under suitable conditions of low temperature and high pressure this biogenic methane and pore water may form a solid, ice-like substance called methane clathrate or, more generally, gas hydrate (see Chap. 14). Another important process which is related to methanogenesis and of which many microbiological and biogeochemical details have only been revealed in recent years and still are being investigated,

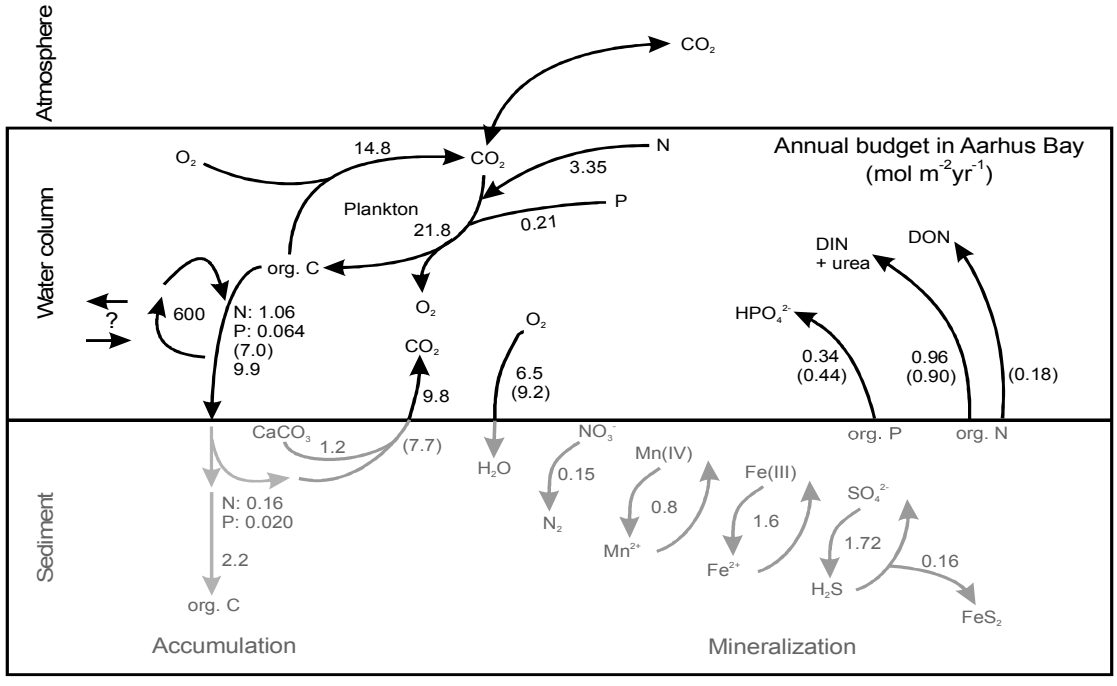

Fig. 4.7 Summary of fluxes and process rates measured in Aarhus Bay between May 1990 and May 1991. Numbers in parentheses were derived by difference while the others are based on independent rate measurements and calculations. Unit are given in mol $m^{-2}yr^{-1}$ for each component. DIN = dissolved inorganic nitrogen; DON = dissolved organic nitrogen (after Jørgensen 1996).

is the anaerobic methane oxidation by consortia of archaea and sulfate-reducing bacteria, formally the reverse of methanogenesis (AOM; see Chap. 8).

4.3.2 Chemical Composition of Biomass

Apart from considering the fate of bulk organic matter (or organic carbon) during diagenesis, organic geochemistry has developed a more sophisticated understanding of diagenetic organic matter transformation down to the molecular level. Fundamental to this understanding is a comparison of the organic constituents of geological samples with the inventory of extant organisms. This was, and still partly is, hampered by the limited knowledge of the natural product chemistry particularly of unicellular marine algae, protozoans and bacteria.

The simplest way of describing the chemical nature of biomass is by its elemental composition. For marine phytoplankton as primary producers a relationship was found to the nutrients available in seawater which led to the definition of the Redfield ratio as C:N:P = 106:16:1 (Redfield et al. 1963). Derived from this is an average molecular formula of phytoplankton organic matter related to the general process of phytosynthesis (of which the reverse signifies remineralization):

$$106\ CO_2 + 106\ H_2O + 16\ NH_3 + H_3PO_4 \rightarrow (CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106\ O_2 \qquad (4.8)$$

The formula of the organic matter product is often reduced to the summary version of $C_{106}H_{263}N_{16}O_{110}P$. It has no real chemical meaning in terms of molecular structure because it contains more hydrogen than the bonds of all the other atoms can account for. The reason is that the generalized average formula (i.e. the product in Eq. 4.8) is just the sum of separate neutral molecules which are involved in biosynthesis of organic matter. The formation of a molecular structure requires the formal loss of a number of molecules of water for condensation. Whereas the formula does not represent the correct elemental organic matter composition of marine phytoplankton, at least not for hydrogen and oxygen, it has to be kept in mind that it is a crude generalisation in itself. It would certainly vary with nutrient conditions and planktonic species as has been observed, e.g., by Takahasi et al. (1985) in a study of plankton biomass from the Atlantic and Indian Oceans which resulted in a modified Redfield ratio of 122(±18) : 16 : 1. There are quite a number of more recent studies that confirm this kind of deviation from the Redfield ratio or extend the ratio by inclusion of trace metals (e.g. Leonardos and Geider 2004; Ho et al. 2003; cf. also Chap. 6).

Food chain and early diagenetic processes change the initial elemental composition drastically. Organic matter in sediments relative to the primary producers is enriched particularly in carbon and hydrogen, whereas it is depleted in oxygen (but the degree depends on the extent of oxidation of sedimentary organic matter), nitrogen and phosphorus. Depletion in phosphorus is due to the facile hydrolytic cleavage of bound phosphate groups. Loss of nitrogen occurs by preferential degradation of organic nitrogen compounds as discussed later (see Sect. 4.4 for a discussion of C/N ratios). Sulfur, not originally included in the general formula, would be equal to or less in content than phosphorus. The enrichment of sulfur in fossil organic matter is, however, not due to a relative enrichment in the course of preferential loss of other elements (as is the case for C and H). Sulfur enrichment rather is a consequence of diagenetic incorporation of reduced inorganic sulfur species (like HS^- or corresponding polysulfides) which are formed from seawater sulfate by sulfate-reducing microorganisms in shallow sediments under anoxic conditions (see Chap. 8).

On the next higher level, the chemical composition of living organisms in the biosphere, despite their diversity, can be confined to a limited number of principal compound classes. Their proportions vary in the different groups of organisms as is evident from the estimates of Romankevitch (1984) for a few types of marine organisms (Table 4.3). Also, within the groups the compound class composition is highly variable (Table 4.4). It may even depend on the growth stage for a single species. The compound classes in turn comprise a very large number of single compounds with different individual chemical structures, although enzymatic systems limit the potential chemical diversity (that is why there are chemical biomarkers of taxonomic significance). Many of the compound classes are also represented in fossil organic matter, although not in the same proportions as they occur in the biosphere because of their different stabilities toward degradation and modification of original structures during sedimentation and diagenesis.

Nucleic Acids and Proteins

Nucleic acids, as ribonucleic acids (RNA) or desoxyribonucleic acids (DNA), are biological macromolecules carrying genetic information. They consist of a regular sequence of phosphate, sugar (pentose) and a small variety of base units, i.e. nitrogen-bearing heterocyclic

compounds of the purine or pyrimidine type. During biosynthesis, the genetic information is transcribed into sequences of amino acids, which occur as peptides, proteins or enzymes in the living cell. These macromolecules vary widely in the number of amino acids and thus in molecular weight. They account for most of the nitrogen-bearing compounds in the cell and serve in such different functions as catalysis of biochemical reactions and formation of skeletal structures (e.g. shells, fibers, muscles).

During sedimentation of decayed organisms, nucleic acids and proteins are readily hydrolyzed chemically or enzymatically into smaller, water-soluble units. Refined analytical techniques, however, allow traces of DNA in sedimentary sequences, in combination with lipids, to be used to trace changes in phytoplanktonic populations with geological time (e.g. Coolen et al. 2004). Amino acids occur in rapidly decreasing concentrations in recent and subrecent sediments, but may also survive in small concentrations in older sediments, particularly if they are protected, e.g., by the calcareous frustules or shells of marine organisms. Nitrogen-bearing aromatic organic compounds in sediments and crude oils may relate to the purine and pyrimidine bases in nucleic acids, but this awaits unequivocal confirmation. A certain fraction of the nucleic acids and proteins reaching the sediment surface may be bound into the macromolecular organic matter network (humic substances, kerogen) of the sediments and there become protected against further rapid hydrolysis. Experiments in the laboratory have shown that kerogen-like material (melanoidins) can be obtained by heating amino acids with sugar.

Saccharides, Lignin, Cutin, Suberin

Sugars are polyhydroxylated hydrocarbons that together with their polymeric forms (oligosaccharides, polysaccharides) constitute an abundant proportion of the biological material, particularly in the plant kingdom. Polysaccharides occur as supporting units in skeletal tissues (cellulose, pectin, chitin) or serve as an energy depot, for example, in seeds (starch). Although polysaccharides are largely insoluble in water, they are easily converted to soluble C_5 (pentoses) and C_6 sugars (hexoses) by hydrolysis and, thus, in the sedimentary environment will have a short-term fate similar to that of the proteins.

Lignin is a structural component of plant tissues where it occurs as a three-dimensional network together with cellulose. Lignin is a macromolecular condensation product of three different propenyl (C_3-substituted) phenols (one type of few biogenic aromatic compounds). It is preserved, even during transport from land to ocean and during sedimentation to the seafloor where it occurs predominantly in humic organic matter of deltaic environments.

Cutin and suberin are lipid biopolymers of variable composition which are part of the protective outer coatings of all higher plants. Chemically, cutin and suberin are closely related polyesters composed of long-chain fatty and hydroxy fatty acid monomers. Both types of biopolymers represent labile, easily metabolizable terrigenous organic matter because they are sensitive to hydrolysis. After sedimentation, they have only a moderate preservation potential.

Table 4.3 Biochemical composition of marine organisms (after Romankevitch 1984).

Organism	Proteins (%)	Carbohydrates (%)	Lipids (%)	Ash (%)
Phytoplankton	30	20	5	45
Phytobenthos	15	60	0.5	25
Zooplankton	60	15	15	10
Zoobenthos	27	8	3	62

Table 4.4 The main chemical constituents of marine plankton in percent of dry weight (after Krey 1970).

Organism	Proteins (%)	Carbohydrates (%)	Lipids (%)	Ash (%)
Diatoms	24-48	0-31	2-10	30-59
Dinoflagellates	41-48	6-36	2-6	12-77
Copepods	71-77	0-4	5-19	4-6

Insoluble, Nonhydrolyzable Highly Aliphatic Biopolymers

Insoluble, nonhydrolyzable aliphatic biopolymers were discovered in algae and higher plant cell walls as well as in their fossil remnants in sediments (see de Leeuw and Largeau 1993; van Bergen et al. 2004 for overviews). These substances are called algaenan, cutan or suberan according to their origin or co-occurrence with cutin and suberin in extant organisms. They consist of aliphatic polyester chains cross-linked with ether bridges (Blokker et al. 1998, 2000) which render them very stable toward degradation. Pyrolysis and other rigorous methods are needed to decompose these highly aliphatic biopolymers. This explains why they are preferentially preserved in sediments.

Monomeric lipids

Biologically produced compounds that are insoluble in water but soluble in organic solvents such as chloroform, ether or acetone are called lipids. In a wider sense, these also include membrane components and certain pigments. They are common in naturally occurring fats, waxes, resins and essential oils. The low water solubility of the lipids derives from their hydrocarbon-like structures which are responsible for their higher survival rates during sedimentation compared to other biogenic compound classes like amino acids or sugars.

Various saturated and unsaturated fatty acids are the lipid components bound to glycerol in the triglyceride esters of fats (see Fig. 4.8 for examples of chemical structures of lipid molecules). Cell membranes consist to a large extent of fatty acid diglycerides with the third hydroxyl group of glycerol bound to phosphate or another hydrophilic group. In waxes, fatty acids are esterified with long-chain alcohols instead of glycerol. Plant waxes contain unbranched, long-chain saturated hydrocarbons (*n*-alkanes) with a predominance of odd carbon numbers (e.g. C_{27}, C_{29}, C_{31}) in contrast to the acids and alcohols which show an even-carbon-number predominance.

Isoprene (2-methylbuta-1,3-diene), a branched diunsaturated C_5 hydrocarbon, is the building block of a large family of open-chain and cyclic isoprenoids and terpenoids (Fig. 4.8). Essential oils of higher plants are enriched in monoterpenes (C_{10}) with two isoprene units. Farnesol, an unsaturated C_{15} alcohol, is an example of a sesquiterpene with three isoprene units. The acyclic diterpene phytol is probably the most abundant isoprenoid on Earth. It occurs esterified to chlorophyll *a* and some bacteriochlorophylls and is, thus, widely distributed in the green pigments of aquatic and subaerial plants. Sesterterpenes (C_{25}) are of relatively minor importance except in some methanogenic bacteria (cf. Volkman and Maxwell 1986).

Cyclization of squalene (or its epoxide) is the biochemical pathway to the formation of a variety of pentacyclic triterpenes (C_{30}) consisting of six isoprene units. Triterpenoids of the oleanane, ursane, lupane and other less common types are restricted to higher plants, and in exceptional cases may dominate the extractable organic constituents of deep-sea sediments like in Baffin Bay (ten Haven et al. 1992). The geochemically most important and widespread triterpenes are from the hopane series, like diploptene which occurs in ferns, cyanobacteria and other eubacteria. The predominant source of hopanoids are bacterial cell membranes, however, which contain bacteriohopanetetrol (and closely related molecular species) as rigidifiers. This C_{35} compound has a sugar moiety attached to the triterpane skeleton via a carbon-carbon bond (Fig. 4.8). The widespread distribution of bacteria on Earth through time makes the hopanoids ubiquitous constituents of all organic-matter assemblages (Rohmer et al. 1992).

Steroids are tetracyclic compounds that are also biochemically derived from squalene epoxide cyclization, but have lost, in most cases, up to three methyl groups. Cholesterol (C_{27}) is the most important sterol of animals and occurs in some plants as well. Higher plants frequently contain C_{29} sterols (e.g. sitosterol) as the most abundant compound of this group. Steroids together with terpenoids are typical examples of biological markers (chemical fossils) because they contain a high degree of structural information that is retained in the carbon skeleton after sedimentation (e.g. Poynter and Eglinton 1991; Peters et al. 2005) and often provides a chemotaxonomic link between the sedimentary organic matter and the precursor organisms in the biosphere.

Carotenoids, red and yellow pigments of algae and land plants, are the most important representatives of the tetraterpenes (C_{40}). Due to their extended chain of conjugated double bonds (e.g. β-carotene; Fig. 4.8) they are labile in most depositional environments and are found widespread but in low concentrations in marine surface sediments. Aromatization probably is one of the dominating diagenetic pathways in the alteration of the original structure of carotenoids in the sediment. Diagenetic intermolecular cross-linking by sulfur bridges may preserve the carotenoid carbon skeletons to a certain extent.

A second pigment type of geochemical significance are the chlorophylls and their derivatives that during

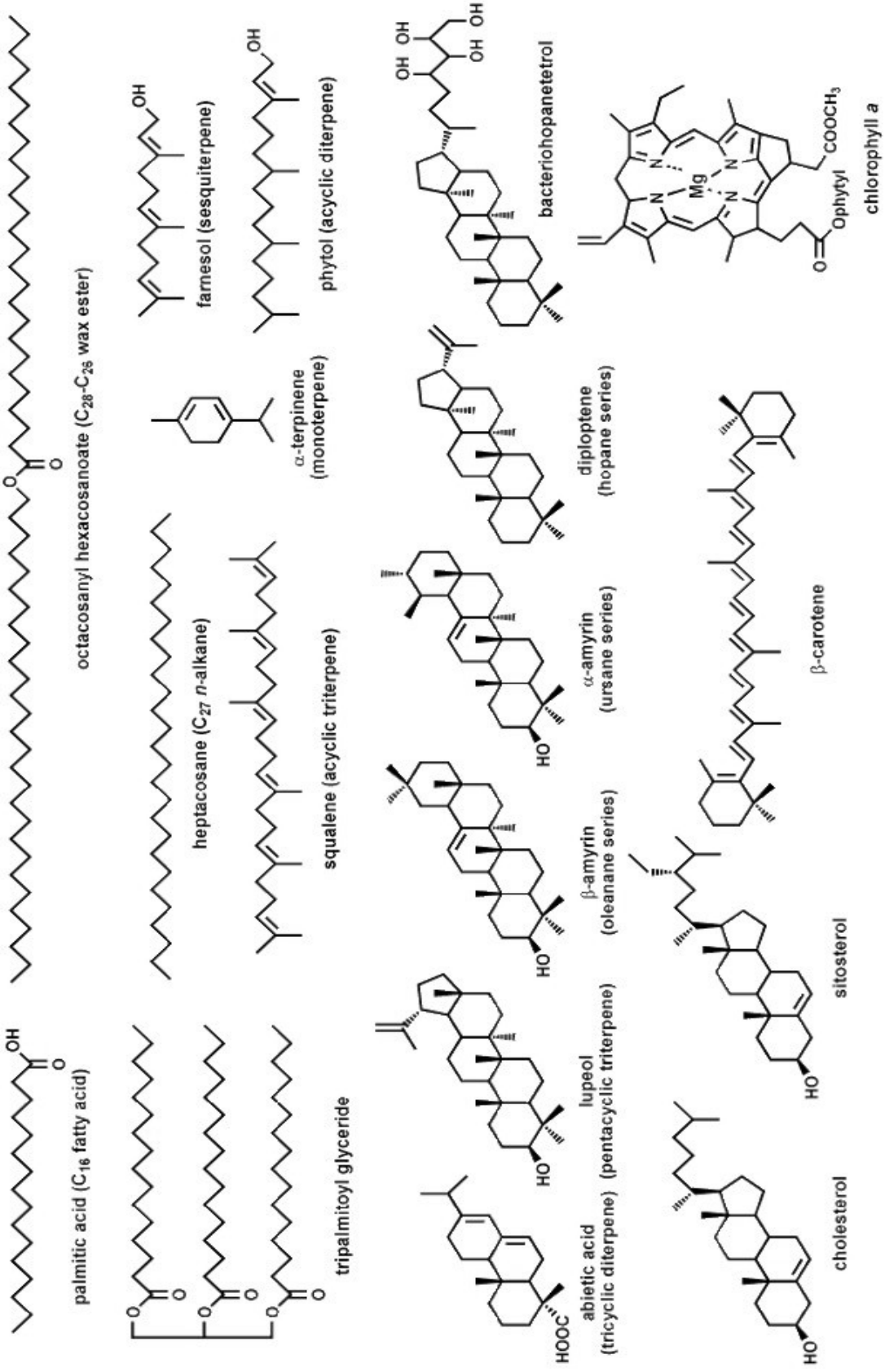

Fig. 4.8 Structural formulae of representative low-molecular-weight lipids in living organisms and surface sediments (after Rullkötter 2001).

diagenesis are converted into the fully aromatized porphyrins. Most porphyrins in sediments and crude oils are derived from the green plant pigment chlorophyll *a* and from bacteriochlorophylls.

4.3.3 The Principle of Selective Preservation

Organic compounds and compound classes differ in their potential to be preserved in sediments and to survive early diagenesis. As a general rule, water-soluble organic compounds, or organic macromolecules, which are easily hydrolyzed to water-soluble monomers, have a low preservation potential. In contrast to this, compounds with a low solubility in water such as lipids and hydrolysis-resistant macromolecules are selectively enriched in the sedimentary organic matter. Table 4.5 is a compilation of the source and preservation potential of some common organic compound types. It is based on anticipated chemical stabilities related to structures, reported biodegradability and reported presence in the geosphere, but not on mechanisms of preservation such as mechanical protection or bacteriostatic activities of certain chemicals in the (paleo)environment (de Leeuw and Largeau 1993).

The near-surface sediment layers represent the transition zone where biological organic matter is transformed into fossil organic matter. There are two slightly differing views about the nature of this process. The classical view (Fig. 4.9; Tissot and Welte 1984) implies that biopolymers are (mainly) enzymatically degraded into the corresponding biomonomers. The monomers then are either used by sediment bacteria and archaea to synthesize their own biomass or as a source of energy. Alternatively, they may randomly recombine by condensation or polymerization to geomacromolecules (see Sect. 4.3.4). The discovery of nonhydrolyzable, highly aliphatic biopolymers in extant organisms and geological samples has led to a reappraisal of the processes involved in the formation

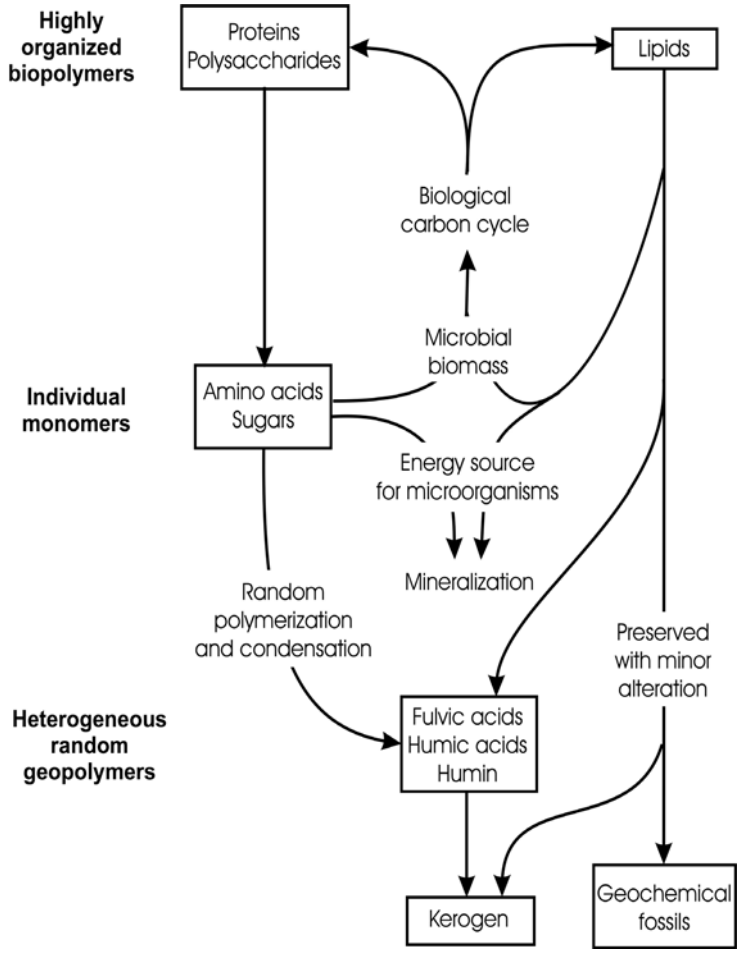

Fig. 4.9 From biomass to geomacromolecules - a summary of the classical view of processes involved in the transformation of biogenic organic matter into kerogen and geochemical fossils (after Tissot and Welte 1984).

of geomacromolecules (Tegelaar et al. 1989; de Leeuw and Largeau 1993). In a scheme modified from that of Tissot and Welte (1984), more emphasis is placed on the selective preservation of biopolymers (Fig. 4.10). This means that the role of consecutive and random polymerisation and polycondensation reactions of biomonomers formed by hydrolysis or other degradative pathways may be less important than previously thought. Support to this view is given by the detection of the close morphological relationship between some fossil 'ultralaminae' and the thin resistant outer cell walls of green microalgae (Largeau et al. 1990).

To complete the modified view of geomacromolecule formation, the process of 'natural vulcanisation' (Fig. 4.10) has been proposed to play a major role under suitable conditions (e.g. Sinninghe Damsté et al. 1989a, 1990; de Leeuw and Sinninghe Damsté 1990). Many marine sediments contain high-molecular-weight organic sulfur substances that are thought to be derived from intermolecular incorporation of inorganic sulfur species (HS^-, polysulfides) into functionalized lipids during early diagenesis. This requires the reduction of seawater sulfate by sulfate-reducing microorganisms under anoxic conditions (see Chap. 8). Sulfur incorporation into organic matter is further enhanced in depositional systems that are iron-limited, i.e. organosulfur compounds are particularly abundant in areas that receive little continental detritus with clays enriched in iron and where instead biogenic carbonate or opal is the dominant mineral component of the sediment.

As a consequence of the discussion of organo-mineral interaction for the preservation of organic matter in sediments (see Sect. 4.2), Collins et al. (1995) raised the question if sorption of organic matter on mineral surfaces did not lead to a rebirth of the classical

Table 4.5 Inventory of selected biomacromolecules, their occurrence in extant organisms, and their potential for survival during sedimentation and diagenesis (after Tegelaar et al. 1989 and de Leeuw and Largeau 1993; see there for chemical structures). The 'preservation potential' ranges from - (extensive degradation under all depositional conditions) to ++++ (little degradation under any depositional conditions).

Biomacromolecules	Occurrence	'Preservation potential'
Starch	Vascular plants; some algae; bacteria	-
Glycogen	Animals	-
Poly-β-hydroxyalkanoates	Eubacteria	-
Cellulose	Vascular plants; some fungi	-/+
Xylans	Vascular plants; some algae	-/+
Galactans	Vascular plants; algae	-/+
Gums	Vascular plants	+
Alginic acids	Brown algae	-/+
Dextrans	Eubacteria; fungi	+
Xanthans	Eubacteria	+
Chitin	Arthropods; copepods; crustacea; fungi; algae	+
Proteins	All organisms	-/+
Mureins	Eubacteria	+
Teichoic acids	Eubacteria	+
Bacterial lipopolysaccharides	Gram-positive eubacteria	++
DNA, RNA	All organisms	-
Glycolipids	Plants; algae; eubacteria	+/++
Polyisoprenoids (rubber, gutta)	Vascular plants	+
Polyprenols and dolichols	Vascular plants; bacteria; animals	+
Resinous polyterpenoids	Vascular plants	+/++
Cutins, suberins	Vascular plants	+/++
Lignins	Vascular plants	++++
Sporopollenins	Vascular plants	+++
Algaenans	Algae	++++
Cutans	Vascular plants	++++
Suberans	Vascular plants	++++

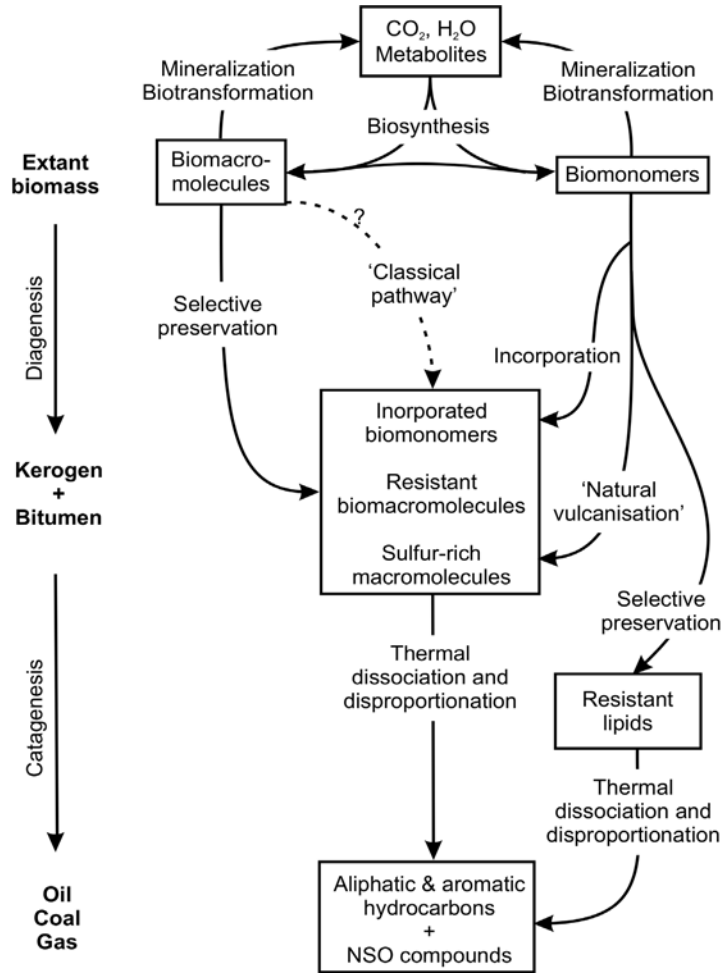

Fig. 4.10 The selective preservation pathway model of kerogen formation (after de Leeuw and Largeau 1993 and Tegelaar et al. 1989).

condensation pathway for geomacromolecule formation. Neither adsorption nor condensation alone may be a satisfactory process for preservation of labile organic substances. Adsorption of monomers can merely retard their biodegradation, and condensation is not favored in (pore water) solution. However, if the processes operate in concert – adsorption promoting condensation and condensation enhancing adsorption of further reactants – a plausible mechanism for the preservation of organic matter arises. Condensation reactions between adsorbed compounds would lead to the formation of very strongly bound macromolecules resulting in a marked divergence in the diagenetic history of the adsorbed monolayer and nonmineral-bound organic matter. More direct evidence is, however, still required to establish the quantitative importance of this process relative to other processes, such as selective preservation.

4.3.4 The Formation of Fossil Organic Matter and its Bulk Composition

The geomacromolecular organic matter surviving microbial degradation in the early phase of diagenesis consists of three fractions, termed fulvic acids, humic acids and humin. They are ill-defined in their chemical structures, but are operationally distinguished by their solubilities in bases (humic and fulvic acids) and acids (fulvic acids only). All three are considered to be potential precursors of kerogen, which designates the type of geomacromolecules formed at a later stage of diagenesis. Kerogen is also only operationally defined as being insoluble in non-oxidizing acids, bases and organic solvents (Durand 1980; Tissot and Welte 1984). Besides this high-molecular-weight organic material, sediments contain low-molecular-weight organic substances that are collectively called bitumen and are

extractable with organic solvents. Bitumen consists of nonpolar hydrocarbons and a variety of polar lipids with a great number of different functional groups, such as ketones, ethers, esters, alcohols, fatty acids and corresponding sulfur-bearing compounds.

Fulvic acids and subsequently humic acids decrease in their concentrations over time as a result of progressive combination reactions with increasing diagenesis. This process of kerogen formation concurrently involves the elimination of small molecules like water, carbon dioxide, ammonia or hydrogen sulfide (Huc and Durand 1977). As a consequence, the degree of condensation of the macromolecular kerogen increases. In terms of elemental composition it becomes enriched in carbon and hydrogen and depleted in oxygen, nitrogen and sulfur. This carbon- and hydrogen-rich kerogen ultimately is the source material for the formation of petroleum and natural gas which starts when burial is deep and temperatures are so high that the carbon-carbon bonds in the kerogen are thermally cracked. The main phase of oil formation typically occurs between 90 °C and 120 °C, but the range largely depends on the heating rate (slow or rapid burial) and on the chemical structure of the kerogen. For example, kerogens rich in sulfur start oil formation earlier because carbon-sulfur bonds are broken more easily than carbon-carbon bonds. The product, however, is a heavy oil (high density, high viscosity) rich in sulfur

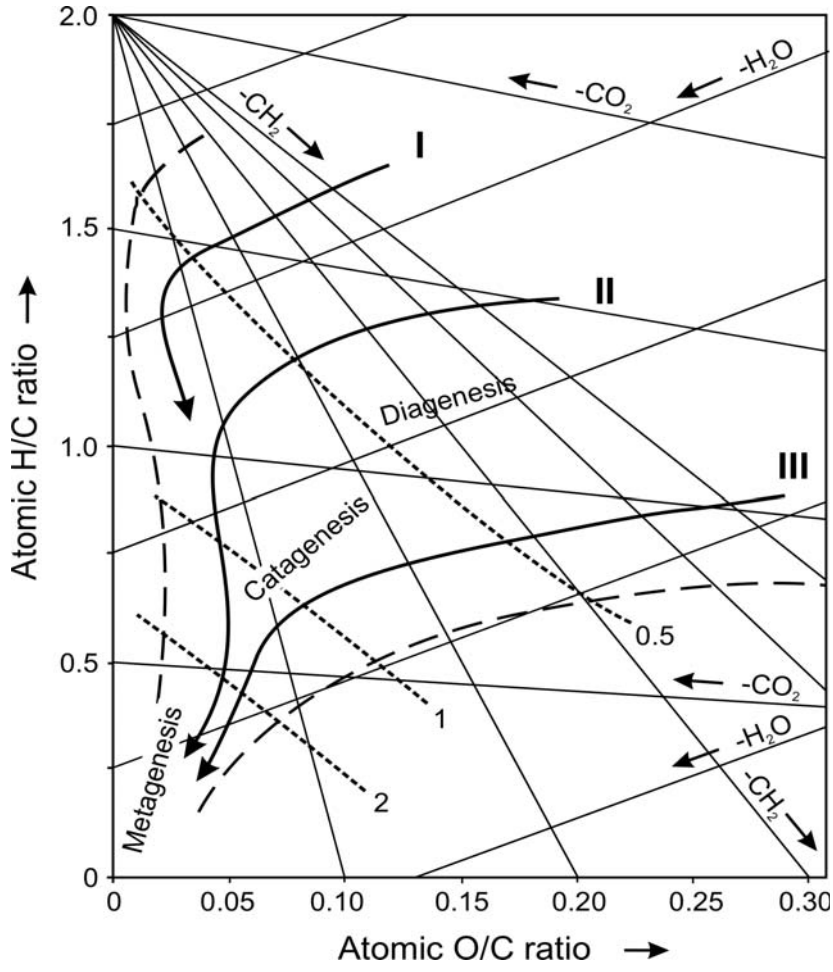

Fig. 4.11 Kerogen types and their geochemical evolution with increasing burial (temperature increase) in a van Krevelen diagram of atomic H/C versus O/C ratios from elemental analysis (after Tissot and Welte 1984). Roman numbers indicate kerogen types, bold trend lines are idealized average values from a large number of data points. In organic geochemistry, diagenesis is the early (low-temperature) range of this evolution, catagenesis signifies the phase of petroleum and wet gas formation by thermal cracking, and metagenesis is the high-temperature range where still some dry gas (methane, ethane) is formed. Numbers associated with broken lines in the diagram (0.5, 1, 2) indicate approximate vitrinite reflectance (R_o) values commonly measured to indicate thermal maturity. Vitrinites are fossil woody organic particles of characteristic shape which increase their reflectivity as a function of geothermal history; the amount of reflected light can be quantitatively measured with a light microscope under defined conditions (see Sect. 4.5.3 and Taylor et al. 1998 for more details).

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and economically less valuable than light and sulfur-lean crude oil. The difference between an oil shale and a rock actively generating petroleum is only the thermal history. An oil shale simply has not completed the phase of diagenetic release of small molecules described above. For more details on petroleum formation consult the textbooks of Tissot and Welte (1984), Hunt (1996) and Welte et al. (1997).

Molecular structural information about kerogen can be inferred from elemental analysis, spectroscopic methods and the results of pyrolysis and selected chemical degradation experiments (see Rullkötter and Michaelis 1990 for an overview). Yet, with the understanding that kerogen is a complex heterogeneous macromolecular substance with contributions from a variety of organisms and a wide range of chemical alterations that occurred during diagenesis, it becomes clear that there will be no single molecular structure of kerogen, and only certain characteristic units can be described at the molecular level.

Kerogens have been classified into types derived from H/C and O/C atomic ratios in a van Krevelen diagram (Fig. 4.11). The types indicated are related to the hydrogen and oxygen richness, relative to carbon, of the biogenic precursor material. Roughly, kerogen Type I is related to hydrogen-rich organic matter as occurring, e.g., in waxes and algal mats, kerogen Type II represents typical oceanic plankton material, and kerogen Type III is typical of land-derived organic matter which has been transformed into lignite or coal. A kerogen type IV not indicated in the diagram has occasionally been defined to have very low H/C ratios and to represent highly oxidized, largely inert organic matter. The bold solid trend lines indicated in Figure 4.11 then represent the changes in elemental composition initially occuring during diagenesis (evolution grossly parallel to the x-axis due to loss of oxygen functionalities) and later during oil and gas formation (catagenesis; evolution grossly parallel to y-axis due to loss of hydrogen-rich petroleum hydrocarbons), until a carbon-rich residue is the ultimate product (near origin in xy diagram). For more details see Tissot and Welte (1984).

4.3.5 Early Diagenesis at the Molecular Level

A small portion of sedimentary organic matter is soluble in organic solvents and contains lipid compounds that are either directly inherited from the biological precursor organisms or cleaved by hydrolysis from larger cellular units like cell walls or membranes (cf. Figs. 4.9 and 4.10). The compounds include individual substances as well as homologous series of structurally related compounds. Most of them are functionalized polar lipids that undergo decarboxylation (organic acids) and dehydration reactions (alcohols) during early diagenesis to produce saturated and olefinic hydrocarbons, of which the latter are progressively hydrogenated into their saturated analogs during later diagenesis. Alternatively, aromatic hydrocarbons are formed by the loss of hydrogen. If these hydrocarbons essentially have the same carbon skeletons and steric configurations as their functionalized biogenic precursors, they are called biological markers or molecular fossils (see Sections 4.3.2 and 4.3.5). Parallel to retention of the biogenic carbon skeleton, structural rearrangements, catalyzed by clay minerals, partial cleavage of substituents or ring opening may occur as side reactions during diagenetic transformation of biogenic lipids. During the earlier phases of diagenesis, including processes occurring in the water column, such alterations appear to be mediated by microbial activity. With increasing burial they are more and more driven by thermodynamic constraints as temperature increases.

The following discussion of biological marker reactions of course only applies to that fraction of lipid compounds that have escaped the highly efficient degradation in the uppermost sediment layer. It has been established through quantitative assessment of transformation reactions that degradation in this zone may occur over timescales of days and that reaction rates have often been underestimated by an order of magnitude (Canuel and Martens 1996). It was furthermore demonstrated in this study that the degradation processes can be highly selective and depend on the origin of the compounds (marine, bacterial or terrestrial). Fatty acids apparently are particularly sensitive to degradation whereas sterols and hydrocarbons have a higher chance of entering the deeper sediment. As a consequence, quantitative assessment of the source and fate of organic matter based on biological markers will be strongly limited as long as diagenetic effects cannot be separated from variations in organic matter supply.

4.3.6 Biological Markers (Molecular Fossils)

Molecules with a high degree of structural complexity are particularly informative and thus suitable for studying geochemical reactions because they provide the possibility of relating a certain product to a specific precursor. For example, specific biomarkers have been assigned to some common groups of microalgae. These compounds include long-chain (C_{37}-C_{39}) *n*-alkenones,

highly-branched isoprenoid alkenes, long-chain *n*-alkandiols, 24-methylenecholesterol and dinosterol. They have been found to be unique for, or obviously be preferentially biosynthesized by, haptophytes, diatoms, eustigmatophytes, diatoms and dinoflagellates, respectively (see Volkman et al. 1998; Volkman 2005 for comprehensive overviews). Other long-chain *n*-alkyl lipids (e.g. Eglinton and Hamilton 1967), diterpenoids and 3-oxygenated triterpenoids (e.g. Simoneit 1986) are considered useful tracers for organic matter from vascular land plants.

Although certain biological markers may be chemotaxonomically very specific, care has to be taken when using relative biomarker concentrations in geological samples to derive quantitative figures of the biological species that have contributed to the total organic matter. First of all, different types of biological markers may have different reactivities and, thus, may be selectively preserved during diagenesis (Hedges and Prahl 1993). In this respect, sequestering of reactive biomarkers by the formation of high-molecular-weight organic sulfur compounds may play an important role (e.g. Sinninghe Damsté et al 1989b; see Fig. 4.10). Furthermore, there may be a fractionation between high- and low-molecular-weight compounds. An extreme example is the (lacustrine) Messel oil shale. In its organic matter fraction, the residues of dinoflagellates are represented by abundant 4-methyl steroids in the bitumen whereas the labile cell walls were not preserved. On the other hand, certain green algae are clearly identifiable under the electron microscope due to the highly aliphatic biopolymers in their cell walls, but no biomarkers specific for green algae were found in the extractable organic matter (Goth et al. 1988).

The scheme in Figure 4.12 is an example of extensive and variable biomarker reactions after sedimentation. It illustrates the fate of sterols particularly during diagenesis. Although the scheme looks complex, it shows only a few selected structures out of more than 300 biogenic steroids and geochemical conversion

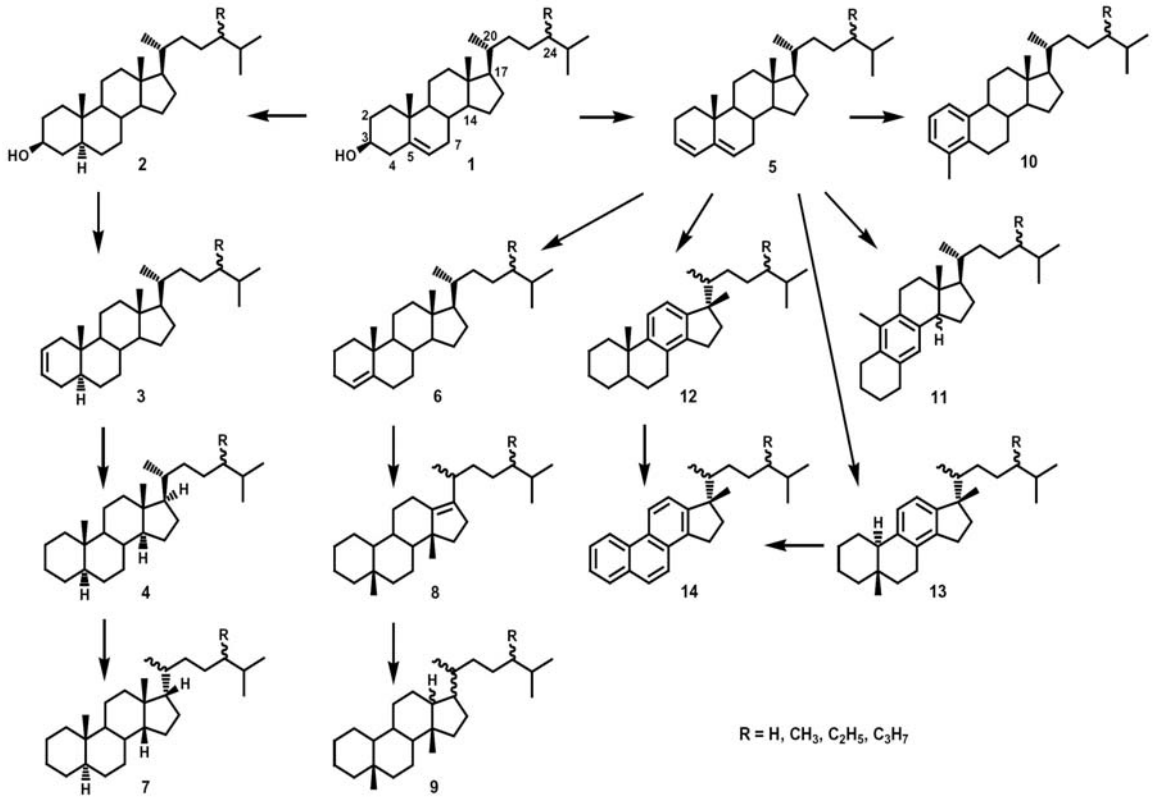

Fig. 4.12 Diagenetic and catagenetic transformation of steroids. The precursor sterols are gradually transformed during diagenesis into saturated hydrocarbons by dehydration (elimination of water) and hydrogenation of the double bonds. At higher temperatures, during catagenesis, the thermodynamically most stable stereoisomers are formed. Alternatively, dehydration leads to aromatic steroid hydrocarbons which are stable enough to occur in crude oils (after Rullkötter 2001). See text for detailed description of the reaction sequences.

products presently known to occur in sediments. The biogenic precursor chosen as an example in Figure 4.12 is cholesterol (structure 1, R=H), a widely distributed steroid in a variety of plants, but more typical of animals (e.g. zooplankton). Hydrogenation of the double bond leads to the formation of the saturated cholestanol (2). This reaction occurs in the uppermost sediment layers soon after deposition and is believed to involve microbial activity. Elimination of water gives rise to the unsaturated hydrocarbon 3. At the end of the diagenetic stage, the former unsaturated steroid alcohol 1 will have been transformed to the saturated steroid hydrocarbon 4 after a further hydrogenation step. An alternative route to the saturated sterane 4 is via dehydration of cholesterol (1, R=H), which yields the diunsaturated compound 5. Hydrogenation leads to a mixture of two isomeric sterenes (6; isomer with double bond in position 5 like in the starting material (1) not shown in Fig. 4.12). This compound cannot be formed from 3 as suggested for a long time, because such a double bond migration would require more energy than is available under the diagenetic conditions in sediments (de Leeuw et al. 1989). Further hydrogenation of 6 affords the saturated hydrocarbon 4. A change in steric configuration of this molecule, e.g. to form 7, occurs only during the catagenesis stage at elevated temperatures. A side reaction from sterene 6 is a skeletal rearrangement leading to diasterene 8 where the double bond has moved to the five-membered ring and two methyl groups (represented by the bold bonds) are now bound

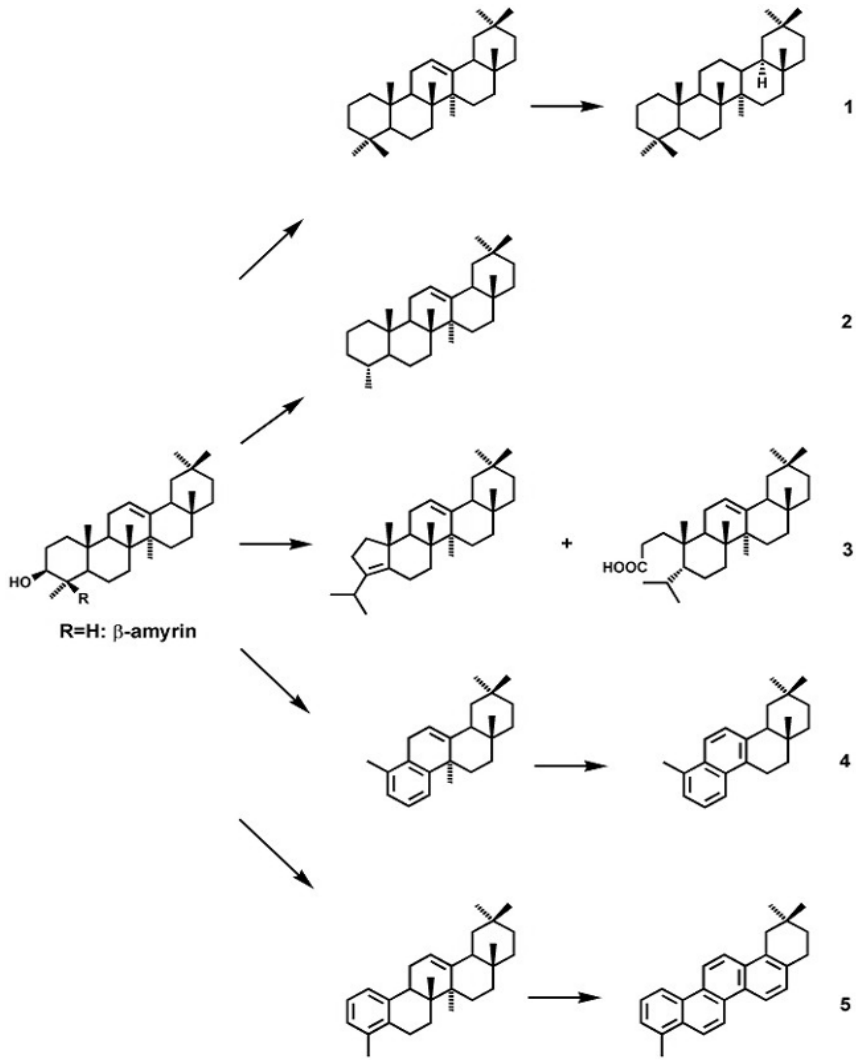

Fig. 4.13 Schematic representation of five different (mostly oxidative) diagenetic reactions of triterpenoids from higher plants. R in the starting material should be an oxygen function, at least in the second pathway (after Rullkötter et al. 1994).

to the bottom part of the ring system. This reaction has been shown in the laboratory to be catalyzed by acidic clays. Thus, diasterenes (8) and the corresponding diasteranes (9), formed from diasterenes by hydrogenation during late diagenesis, are found in shales but not in those carbonates that lack acidic clays.

An additional alternative diagenetic transformation pathway of steroids leads to aromatic instead of saturated hydrocarbons. The diolefin 5 is a likely intermediate on the way to the aromatic steroid hydrocarbons 10-14. Compounds 10 and 11 are those detected first in the shallow sediment layers. They obviously are labile and do not survive diagenesis. During late diagenesis, the aromatic steroid hydrocarbon 12 with the aromatic ring next to the five-membered ring cooccurs with compounds 10 and 11 in the sediments, but is also stable enough to survive elevated temperatures and thus to be found in crude oils. There is also a corresponding rearranged monoaromatic steroid hydrocarbon (13). During catagenesis, monoaromatic steroid hydrocarbons are progressively transformed into triaromatic hydrocarbons (14) before the steroid record is completely lost by total destruction of the carbon skeleton at higher temperatures.

As a second example, Figure 4.13 shows five different diagenetic reaction pathways for pentacyclic triterpenoids of terrestrial origin that were found to be abundant, e.g., in Tertiary deep-sea sediments of Baffin Bay (ten Haven et al. 1992). Diagenetic alteration with full retention of the carbon skeleton (e.g. in the case of β-amyrin; R=H) leads to an olefinic hydrocarbon after elimination of the oxygen functionality in the A-ring and later to the fully saturated hydrocarbon. If the substituent group R is a hydroxyl or carboxylic acid group, oxidation would yield an unstable ketocarboxylic acid, which instantaneously eliminates CO_2 leading to a carbon skeleton with one carbon atom less than the starting molecule (second pathway; see Rullkötter et al. 1994). Direct chemical elimination of the hydroxyl group in ring A causes ring contraction, and eventually the ring is opened by oxidative cleavage of the double bond (third pathway). If the carbon atoms of the A-ring are completely lost during degradation, then subsequent aromatization may lead into the fourth pathway. Alternatively, aromatization may start with the intact carbon skeleton giving rise to a series of partly or fully aromatized pentacyclic hydrocarbons (fifth pathway). All these alterations are typical for terrigenous triterpenoids. They probably start soon after the decay of the organisms (or parts thereof, e.g. leaves) and continue during transport into the ocean. The compounds described and several others have been found in numerous marine sediments (see Corbet et al. 1980 and Rullkötter et al. 1994 for overviews).

4.4 Organic Geochemical Proxies

4.4.1 Total Organic Carbon and Sulfur

Organic carbon profiles in a sedimentary sequence, particularly if they are obtained with high stratigraphic resolution (e.g. Stein and Rack 1995), provide direct evidence for changes in depositional patterns. An in-depth interpretation, however, usually requires additional information on the quality of the organic matter, i.e. on its origin (marine versus terrigenous) and/or its degree of oxidation during deposition. The relationship between organic carbon and sedimentation rate may help to distinguish different depositional environments or to determine paleoproductivity as already discussed in Section 4.2.

Furthermore, the relationship between organic carbon and sulfur is also characteristic of the paleoenvironment. Leventhal (1983) and Berner and Raiswell (1983) observed an increase in pyrite sulfur content in marine sediments with increasing amount of total organic carbon (Fig. 4.14). The rationale behind this is that the amount of metabolizable organic matter available to support sulfate-reducing bacteria increases

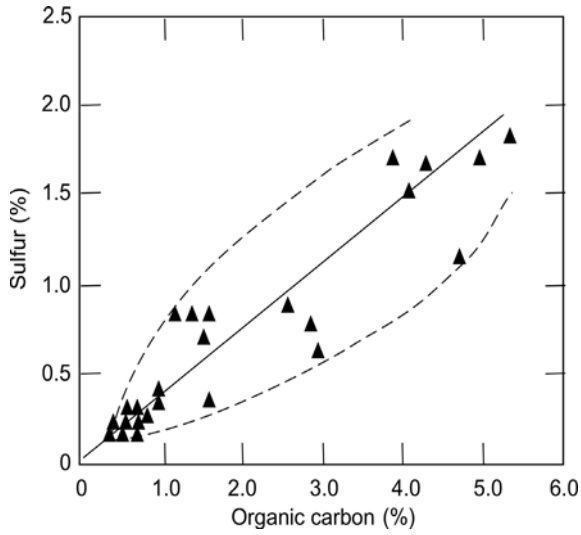

Fig. 4.14 Plot of weight percent organic carbon vs. weight percent pyrite sulfur for normal-marine modern sediments. Each plotted point represents the average value of samples in a given core, taken at a sediment depth where contents of organic carbon and pyrite have attained quasi-steady-state values, i.e. where early diagenesis of carbon and sulfur is (essentially) complete. The dashed lines enclose data from a variety of other studies (after Berner and Raiswell 1983). Sediments deposited under anoxic (euxinic) conditions would plot above the trend line, freshwater sediments significantly below.

with the total amount of organic matter arriving at the sediment-water interface. As a consequence, the sedimentary pyrite sulfide content is positively correlated with the non-metabolized (resistant or unused) organic matter content (TOC). The trendline in Figure 4.14 is considered representative of normal marine (oxic) environments. Data from the Black Sea plot above the trendline (higher S/C ratios) because consumption of organic matter by sulfate-reducing bacteria leads to excess hydrogen sulfide, available for pyrite formation, in the water column. In contrast to this, freshwater sediments have very low S/C (or high C/S) ratios because of the low sulfate concentrations in most freshwater bodies. Although the trendline is based on pyrite sulfur, it is not important whether the reduced sulfur is present as metal sulfide (mostly pyrite) or bound to the organic matter. This is a question of iron limitation rather than sulfate reduction.

As outlined in Section 4.3.1 (and discussed more extensively in Chap. 8) there is a close connection between organic matter remineralization during early diagenesis and microbial sulfate reduction. If all of the sulfate reduction products were precipitated as pyrite or bound into (immobile) organic matter, measuring the amount of sulfur in these species would provide an easy way for determining the amount of organic matter that has been remineralized and was not preserved in the sediment. However, the main product of sulfate reduction, hydrogen sulfide, is volatile and can escape from the sediment, particularly when bioturbation of the surface sediment supports this transport.

Release of hydrogen sulfide from the sediment plays a less important role under strictly anoxic conditions where fine lamination indicates that the environment is hostile to burrowing organisms and bioturbation does not occur. It has been shown that in these cases the initial amount of organic matter deposited can be estimated by measuring concentrations of reduced sulfur in such sediments. Considering the amount of organic matter consumed by sulfate reduction, Lallier-Vergès (1993) defined a sulfate reduction index (SRI) as

$$\text{SRI} = \%\ \text{initial organic carbon} / \%\ \text{preserved organic carbon} \qquad (4.9)$$

The amount of initial organic carbon then is the sum of the preserved organic carbon (measured as TOC) and the metabolized organic carbon (determined from the sulfur content with stoichiometric correction for the sulfate reduction process). Furthermore, the diffusive loss has to be taken into account. With a correction factor of 0.75 and a term $1/(1\text{-}qH_2S)$ for the diffusive loss, Vetö et al. (1994) calculated the initial (or original) organic carbon content of a sediment before sulfate reduction as

$$TOC_{orig} = TOC + 0.75S \cdot 1/(1\text{-}qH_2S) \qquad (4.10)$$

where TOC and S are the measured values of total organic carbon and total sulfur. The authors estimate that the diffusive H_2S loss in non-bioturbated sediments usually is less than 45 % and that this value can only be reached in cases of very high organic matter supply, high reactivity of this organic matter and iron limitation. Littke et al. (1991b) and Lückge et al. (1996) calculated that sulfate reduction consumed between 20 and 50 % of the initially sedimented organic matter (or 1-3 % of primary productivity) both from ancient rocks (Posidonia Shale) and recent sediments (Oman Margin and Peru upwelling systems). In a study of the Pakistan continental margin in the northern Arabian Sea (Littke et al. 1997b), they clearly demonstrated that the carbon-sulfur relationship only holds in the laminated sections of the sediment profile whereas it fails (strongly underestimates sulfate reduction) in the intercalated homogeneous, i.e. bioturbated, sediments for the reason explained before.

4.4.2 Marine *Versus* Terrigenous Organic Matter

As pointed out in Section 4.2.5, even deep-sea sediments deposited in areas remote from continents may contain a mixture of marine and terrigenous organic matter. For any investigation of autochthonous marine organic matter preservation or marine paleoproductivity, these two sources of organic matter have to be distinguished. Furthermore, global or regional climate fluctuations have changed the pattern of continental run-off and ocean currents in the geological past (see Sect. 4.4.3). Being able to recognize variations in marine and terrigenous organic matter proportions may, thus, be of great significance in paleoclimatic and paleoceanographic studies.

A variety of parameters are used to assess organic matter sources. Bulk parameters have the advantage that they are representative of total organic matter, whereas molecular parameters address only part of the extractable organic matter, which in turn is only a small portion of total organic matter. Some successful applications of molecular parameters show that the small bitumen fraction may be representative of the total, but there are many other examples where this is not the case. On the other hand, oxidation of marine organic

matter has the same effect on some bulk parameters as an admixture of terrigenous organic matter, because the latter is commonly enriched in oxygen through biosynthesis. It is, therefore, advisable to rely on more than one parameter, and to obtain complementary information.

C/N Ratio

Carbon/nitrogen (C/N) ratios of phytoplankton and zooplankton are around 6, freshly deposited marine organic matter ranges around 10, whereas terrigenous organic matter has C/N ratios of 20 and above (e.g. Meyers 1994, 1997 and references therein). This difference can be ascribed to the absence of cellulose in algae and its abundance in vascular plants and to the fact that algae are instead rich in proteins. Both weight and atomic ratios are used by various authors, but due to the small difference in atomic mass of carbon and nitrogen, absolute numbers of ratios do not deviate greatly.

Selective degradation of organic matter components during early diagenesis has the tendency to modify (usually increase) C/N values already in the water column. Still, these ratios are sometimes sufficiently well preserved in shallow-marine sediments to allow a rough assessment of terrigenous organic matter contribution (e.g. Jasper and Gagosian 1990; Prahl et al. 1994). A different trend exists in deep oceanic sediments with low organic carbon contents. Inorganic nitrogen (ammonia) is released during organic matter decomposition and adsorbed to the mineral matrix (particularly clays) where it adds significantly to the total nitrogen. The C/N ratio is then changed to values below those of normal marine/terrigenous organic matter proportions (Müller 1977; Meyers 1994). This effect should be small in sediments containing more than 0.3 % organic carbon. On the other hand, many sapropels from the eastern Mediterranean Sea and organic-matter-rich sediments underlying upwelling areas have conspicuously high C/N ratios (>15), i.e. well in the range of land plants despite a dominance of marine organic matter, for reasons yet to be determined (see Bouloubassi et al. 1999 for an overview). Because such "atypical" C/N ratios were determined in quite a number of sediments more recently it is advised not to place too much emphasis on the significance of this bulk parameter.

Hydrogen and Oxygen Indices

Hydrogen Index (HI) values from Rock-Eval pyrolysis (see Sect. 4.5.2) below about 150 mg HC/g TOC are typical of terrigenous organic matter, whereas HI values of 300 to 800 mg HC/g TOC are typical of marine organic matter. Deep-sea sediments rich in organic matter usually show values of only 200-400 mg HC/g TOC, even if marine organic matter strongly dominates. Oxidation has lowered the hydrogen content of the organic matter in this case. It should also be mentioned that Rock-Eval pyrolysis was developed as a screening method for rapidly determining the hydrocarbon generation potential of petroleum source rocks (Espitalié et al. 1985) and that a range of complications may occur with sediments buried only to shallow depth. For example, unstable carbonates may decompose below the shut-off temperature of 390 °C (cf. Sect. 4.5.2) which increases the Oxygen Index and falsely indicates a high oxygen content of the organic matter. Furthermore, Rock-Eval pyrolysis cannot be used for sediments with TOC < 0.3 % because of the so-called mineral matrix effect. If sediments with low organic carbon contents are pyrolyzed, a significant amount of the products may be adsorbed to the sediment minerals and are not recorded by the flame ionization detector, thus lowering the Hydrogen Index (Espitalié et al. 1977).

Maceral Composition

If the morphological structure of organic matter is well preserved in sediments, organic petrographic investigation under the microscope is probably the most informative method to distinguish marine and terrestrial organic matter contributions to marine sediments by the relative amounts of macerals (organoclasts) derived from marine biomass and land plants (see Sect. 4.5.3). Many marine sediments, however, contain an abundance of non-structured organic matter (e.g. in upwelling areas; Lückge et al. 1996) which cannot easily be assigned to one source or the other. Furthermore, comprehensive microscopic studies are time-consuming. In his paleoproductivity assessments (see Sect. 4.2), Stein (1986a) calibrated Hydrogen Indices from Rock-Eval pyrolysis of marine sediments with microscopic data and suggested to use the more readily available pyrolysis data as a proxy for marine/terrigenous organic matter proportions.

Stable Carbon and Hydrogen Isotope Ratios

Carbon isotope ratios are principally useful to distinguish between marine and terrestrial organic matter sources in sediments and to identify organic matter from different types of land plants. The stable carbon isotopic composition of organic matter reflects the isotopic composition of the carbon source as well as the discrimination (fractionation) between ^{12}C and

^{13}C during photosynthesis (e.g. Hayes 1993). Most plants, including phytoplankton and almost all trees and most shrubs, incorporate carbon into their biomass using the Calvin (C_3) pathway which discriminates against ^{13}C to produce a shift in $\delta^{13}C$ values of about -20 ‰ from the isotope ratio of the inorganic carbon source. Some plants use the Hatch-Slack (C_4) pathway (many subtropical savannah grasses and sedges) which leads to an isotope shift of about -7 ‰. Other plants, mostly succulents, utilize the CAM (crassulacean acid metabolism) pathway, which more or less switches between the C_3 and C_4 pathways and causes the $\delta^{13}C$ values to depend on the growth dynamics.

Organic matter produced from atmospheric carbon dioxide ($\delta^{13}C \approx -7$ ‰) by land plants using the C_3 pathway has an average $\delta^{13}C$ value of approximately -27 ‰ and by those using the C_4 pathway approximately -14 ‰. Marine algae use dissolved bicarbonate, which has a $\delta^{13}C$ value of approximately 0 ‰. As a consequence, marine organic matter typically has $\delta^{13}C$ values varying between -20 ‰ and -22 ‰. Isotopic fractionation, among others, is also temperature dependent which, e.g., in cold polar waters may lead to carbon isotope values for marine organic matter of -26‰ or lower (e.g. Rau et al. 1991). The fact that a number of environmental and biological variables influence the stable carbon isotope composition of plants may cause variations from the generalized numbers given above (see Killops and Killops 2005 for an overview). The 'typical' difference of about 7 ‰ between organic matter of marine primary producers and land plants has nevertheless been successfully used to trace the sources and distributions of organic matter in coastal oceanic sediments (e.g. Westerhausen et al. 1993; Prahl et al. 1994; Rommerskirchen et al. 2003 and references therein). Figure 4.15 shows data for a continental margin setting with the Congo Fan as an example. The carbon isotope ratios are measured values compiled from various sources and show the pathway from the different biological systems to the mixed data in the sediments in a transect from the shallow continental margin to the deep ocean.

The availability of dissolved CO_2 in ocean water has an influence on the carbon isotopic composition of algal organic matter because isotopic discrimination toward ^{12}C increases when the partial pressure of carbon dioxide (pCO_2) is high and decreases when it is low (see Fogel and Cifuentes 1993 for an overview). Organic-matter $\delta^{13}C$ values, therefore, become indicators not only of origins of organic matter but also of changing paleoenvironmental conditions on both short- and long-term scales. For example, the $\delta^{13}C$ values

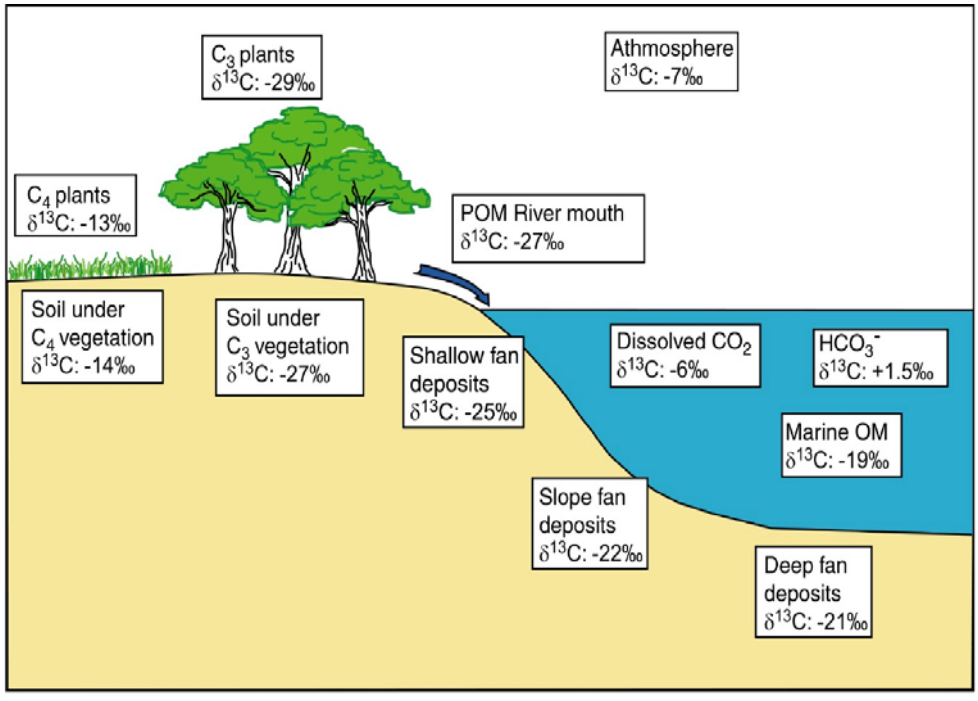

Fig. 4.15 Carbon stable isotope data in different compartments of a continental margin settings with the Congo Fan as an example. Data for $\delta^{13}C$ values of biota and sediments are from measurements in the Congo Fan and the Congo River catchment area (Mariotti et al. 1991, Müller et al. 1994, Muzuka 1999, Schwartz et al. 1986, Westerhausen et al. 1993).

of dissolved inorganic carbon (DIC; CO_2, bicarbonate, carbonate) available for photosynthesis in the cells varies over the year with the balance between photosynthetic uptake and respiratory production. During summer and spring, when rates of photosynthesis are high, the isotope ratio of remaining DIC is enriched in ^{13}C. In fall, when respiration is the dominant process, the $\delta^{13}C$ of DIC becomes more negative because organic matter is remineralized.

Fluctuations that have been measured in the $\delta^{13}C$ values of sedimentary organic matter over the Earth's history (e.g. Schidlowski 1988) can thus be interpreted in terms of the productivity in the water column and the availability of DIC in a particular geological time period. In a study of sediments from the central equatorial Pacific Ocean spanning the last 255,000 years it has been demonstrated that the carbon isotopic composition of fossil organic matter depends on the exchange between atmospheric and oceanic CO_2. Changes with time can then be used to estimate past atmospheric carbon dioxide concentrations (Jasper et al. 1994).

Other than stable carbon isotopes the stable hydrogen isotopes do not reflect the fixation processes in photosynthesis, but rather the hydrological cycle under which the respective plants have grown (Sessions et al. 1999; Sauer et al. 2001). This means that lake biota will differ in hydrogen isotope composition from marine organisms, and land plants thriving under humid or arid conditions will show a large spread in hydrogen isotope ratios. This is schematically illustrated in the $\delta^{13}C$ *vs.* $\delta^{2}H$ diagram in Figure 4.16 where C_4 and CAM plants are clearly separated from each other, which is often not the case when only carbon isotope ratios are determined. Due to the large atomic weight difference between hydrogen and deuterium (^{2}H), $\delta^{2}H$ values extend over a much larger range than $\delta^{13}C$ values, and the former may require specific mathematical algorithms to calculate hydrogen isotopic fractionations in biogeochemical systems (Sessions and Hayes 2005).

Carbon fixation during photosynthesis is not the only process causing isotope fractionation. Further fractionation occurs during the subsequent biosynthetic reactions leading to a deviation of the carbon isotopic signature of important groups of natural products from the bulk isotopic value of the organism. Lipids have the lightest $\delta^{13}C$ values, whereas proteins and carbohydrates are significantly heavier (more enriched in ^{13}C). Even within the lipids, e.g., compound groups may differ in their carbon isotope ratios as a consequence of their individual biosynthetic pathways. Still, the general difference in carbon isotope signatures between plants of different origins is largely maintained. In a diagram like that in Figure 4.16, $\delta^{13}C$ values of individual lipids would just be collectively shifted to lighter values on the x-axis compared to the total carbon values of their source organisms.

Compound-specific isotope analysis allows stable carbon (and hydrogen) isotope analysis of individual biomarkers for the assessment of organic matter sources and paleoenvironmental reconstruction (e.g. Hayes et al. 1987, 1990). Since the implementation of the new analytical technique in the last 15 years, numerous applications have been published. Examples are the analysis of plant wax lipids in Atlantic Ocean deep sea sediments to reconstruct organic matter flux from the African continent and the effect of climatic change on the vegetation in Africa (e.g., Huang et al. 2000; Rommerskirchen et al. 2003; Schefuß et al. 2004). Molecular carbon isotope analysis has recently become particularly important in the investigation of the methane cycle. Biogenic methane produced by archaea is isotopically particularly light ($\delta^{13}C$ = -60 to -100 ‰). Methanotrophic organisms using this biogenic methane as their carbon source biosynthesize, among others, membrane lipids which may isotopically be as light as -120 ‰. The combination of molecular and isotope analysis has, thus, helped a great deal in unraveling the complex processes particularly involved in anaero-

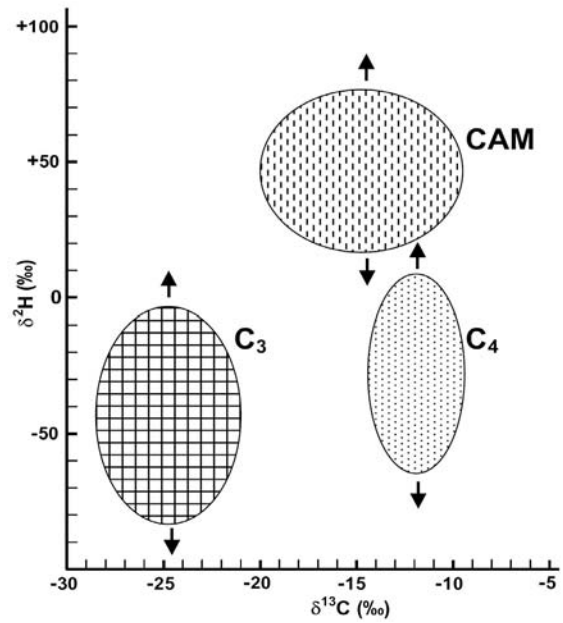

Fig. 4.16 Schematic representation of carbon and hydrogen stable isotope ratios of plants with different biosynthetic pathways. See text for more details. Arrows indicate that hydrogen isotope ratios may cover an even larger range than indicated by the encircled areas.

bic methane oxidation (e.g. Orphan et al. 2001, 2002; Elvert et al. 2003; Wakeham et al. 2003).

Marine sediments may not only be a mixture from autochthonous and allochthonous sources, the different biogenic components may also be of different age. Whereas mixing by redeposition of continental slope sediments by slumping or turbidite flow are well known and often recognizable on a bulk level, there may also be more intimate mixing of components of diverse age when, e.g., terrestrial organic matter is transported to the ocean through rivers taking a significant amount of time. Radiocarbon analysis of individual biomarkers has revealed that their ^{14}C ages can differ significantly within a given sediment sample, but some of these differences are not easy to explain (e.g. Eglinton et al. 1997; Pearson et al. 2001). Mollenhauer et al. (2003) compared the ^{14}C ages of carbonate frustrules of planktonic foraminifera with those of long-chain alkenones (cf. Sect. 4.4.3), both widely used for reconstructing the chronostratigraphy of near-surface marine sediments, in hemipelagic muds from the Namibia continental margin in the South Atlantic Ocean. They found the alkenones to be systematically and up to 2000 years older than the foraminifera. Among several possible alternative explanations for this discrepancy they favored long-range transport of the alkenones, possibly from the Argentine basin across the Atlantic Ocean, before they were ultimately deposited together with the autochthonous, younger foraminifera.

4.4.3 Molecular Paleo-Seawater Temperature and Climate Indicators

Past Sea-Surface Temperatures (SST) Based on Long-Chain Alkenones

Paleoceanographic studies have taken advantage of the fact that biosynthesis of a major family of organic compounds by certain microalgae depends on the water temperature during growth. The microalgae belong to the class of *Haptophyceae* (often also named *Prymnesiophyceae*) and notably comprise the marine coccolithophorids *Emiliania huxleyi* and *Gephyrocapsa oceanica*. The whole family of compounds, which are found in marine sediments of Recent to Lower Cretaceous age throughout the world ocean, is a complex assemblage of aliphatic straight-chain ketones and esters with 37 to 41 carbon atoms and two to four double bonds (see Brassell 1993 and Brassell et al. 2004 for more details). Principally only the C_{37} methylketones with 2 and 3 double bonds are used for past sea-surface temperature assessment (Fig. 4.17), although the relationship of the tetra-unsaturated C_{37} alkenone, which is commonly more abundant in lacustrine systems, to salinity and temperature was recently given special attention (Sikes and Sicre 2002).

It was found from the analysis of laboratory cultures and field samples that the extent of unsaturation (number of double bonds) in these long-chain ketones varies linearly with growth temperature of the algae over a wide temperature range (Brassell et al. 1986; Prahl and Wakeham 1987). To describe this, an unsaturation index was suggested, which in its simplified form is defined by the concentration ratio of the two C_{37} ketones:

$$U^{K'}_{37} = [C_{37:2}]/[C_{37:2} + C_{37:3}] \qquad (4.11)$$

Calibration was then made with the growth temperatures of laboratory cultures of different haptophyte species and with ocean water temperatures at which plankton samples had been collected. From these data sets, a number of different calibration curves evolved for different species and different parts of the world ocean so that some doubts arose as to the universal applicability of the unsaturation index. In a major analytical effort, Müller et al. (1998) resolved the complications and arrived at a uniform calibration for the global ocean from 60°N to 60°S. The resulting relationship,

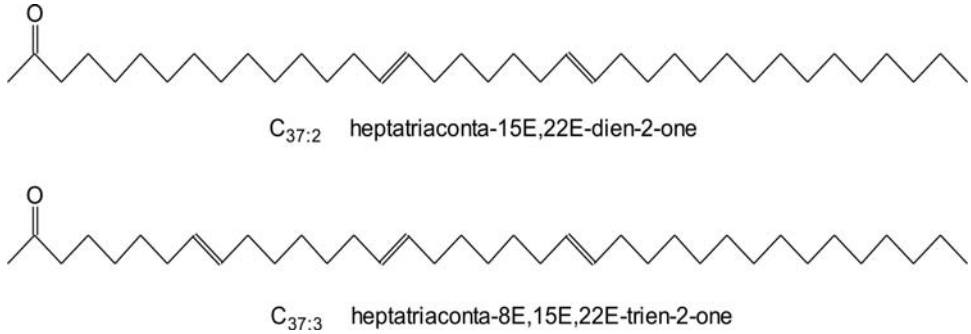

Fig. 4.17 Structural formulae of long-chain alkenones used for paleo-sea surface temperature assessment.

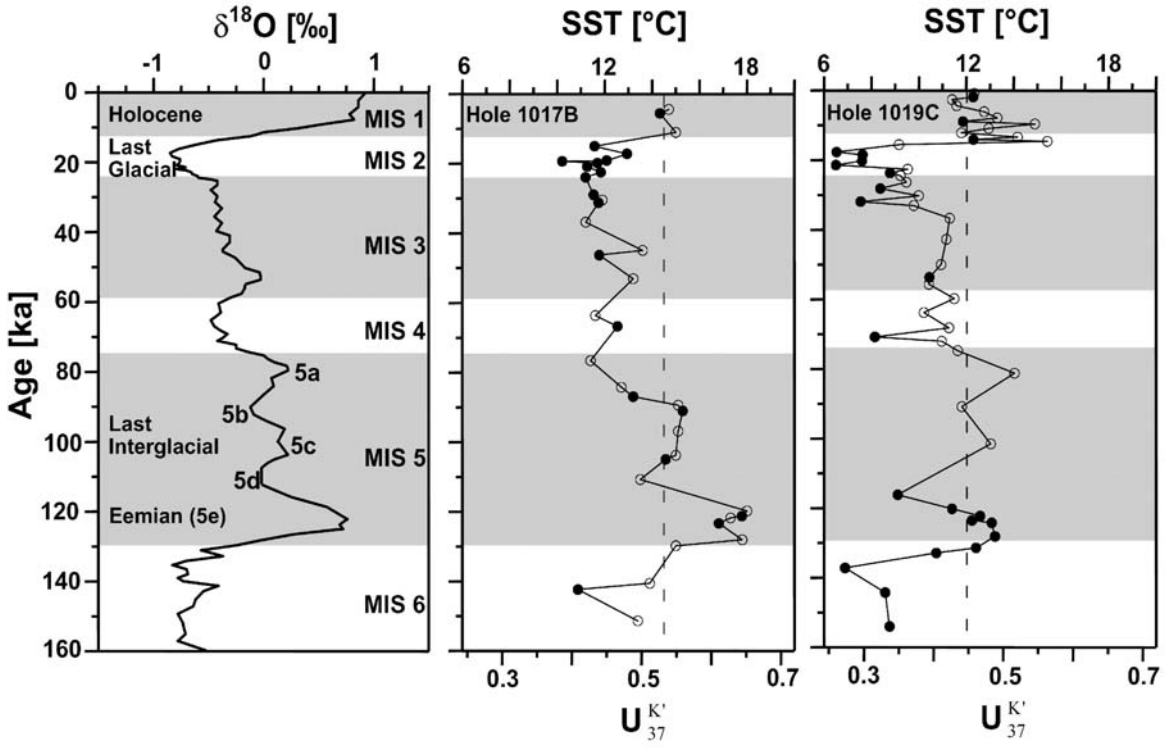

Fig. 4.18 Alkenone-based sea-surface temperature (SST) reconstruction of two sediment sections from Ocean Drilling Program (ODP) Holes 1017B (Southern California, 50 km west of Point Arguello) and 1019C (Northern California, 60 km west of Crescent City in the Eel River Basin) on the California continental margin (after Mangelsdorf et al. 2000) compared to the global $\delta^{18}O$ chronostratigraphy (SPECMAP; after Martinson et al. 1987). MIS = Marine isotope stage.

$$U^{K'}_{37} = 0.033T + 0.044 \qquad (4.12)$$

is identical within error limits with the widely used calibrations of Prahl and Wakeham (1987) and Prahl et al. (1988) based on *Emiliania huxleyi* cultures ($U^{K'}_{37} = 0.033T + 0.043$). Müller et al. (1998) also found that the best correlations were obtained using ocean water temperatures from 0 to 10 m water depth, suggesting that the sedimentary $U^{K'}_{37}$ ratio reflects mixed-layer temperatures and that the production of alkenones within or below the thermocline was not high enough to significantly bias the mixed-layer temperature signal. Regional variations in the seasonality of primary production also have only a negligible effect on the U signal in the sediments. Furthermore, the strong linear relationships obtained for the South Atlantic Ocean and the global ocean indicate that U values of the sediments are neither affected to a measurable degree by changing species compositions nor by growth rate of algae and nutrient availability, other than expected from culture experiments. Significant effort was undertaken to intercalibrate the analysis of the alkenone parameter world-wide (Rosell-Melé et al. 2001). Continuing research on the alkenone parameter, however, still reveals additional calibrations for extreme environments (e.g. Sicre et al. 2002) or the temperature range over which the alkenone index can be applied (Pelejero and Calvo 2003).

The alkenone index presently is one of the most frequently used molecular organic geochemical parameters in the geosciences. A simple example of an application is shown in Figure 4.18. The global oxygen isotope stratigraphy (SPECMAP; after Martinson et al. 1987) is compared with the sea-surface temperature curve reconstructed from the sedimentary alkenone ratio ($U^{K'}_{37}$) for two holes drilled by the Ocean Drilling Program into deep-sea sediments off the coast of California (Mangelsdorf et al. 2000). The temperature follows the variations of the $\delta^{18}O$ values reasonably well. They both illustrate the repetitive change from cold to warm climatic stages and *vice versa*. It is also noteworthy that the absolute temperatures, as expected from the oceanographic setting, are higher at the location of Hole 1017B (50 km west of Point Arguello, just north of the Santa Barbara Channel) than at the Northern Californian location 60 km west of Crescent City in the Eel River basin (Hole 1019C).

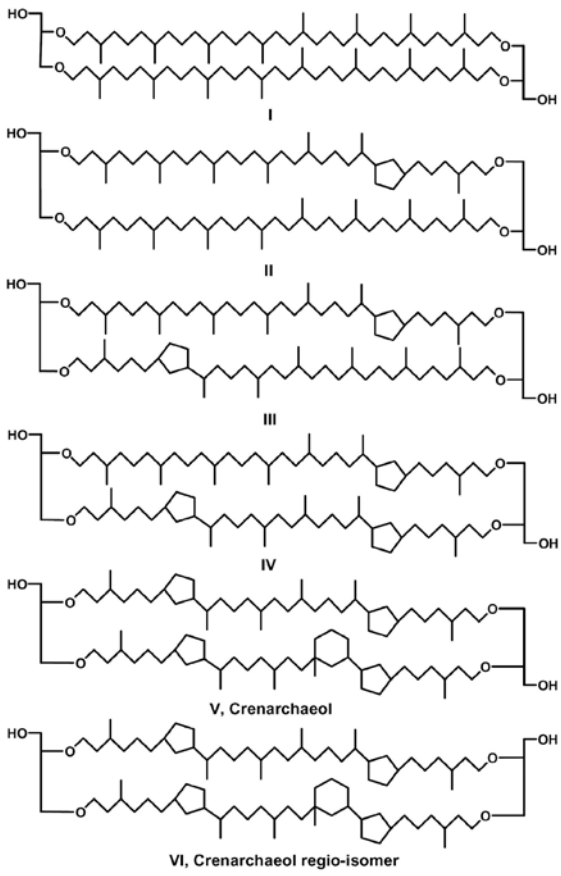

Fig. 4.19 Crenarchaeotal membrane lipid moieties used for TEX_{86} paleothermometry (after Schouten et al. 2002).

TEX_{86} Paleothermometry

Recently, a new geochemical temperature proxy, the TEX_{86} index, was introduced by Schouten et al. (2002). It is based on the number of cyclopentane moieties in the glycerol dialkyl tetraethers (GDGTs; Fig. 4.19) of the membrane lipids of a group of marine archaea called Crenarchaeota, which changes as a response to temperature in the growth medium as demonstrated both by core top samples of marine sediments (Schouten et al. 2002) and in culture experiments (Wuchter et al. 2004). It is defined as follows:

$$TEX_{86} = (III + IV + VI)/(II + III + IV + VI) \qquad (4.13)$$

where the Roman numbers represent the relative contents of four different membrane lipids (Fig. 4.19). With increasing temperature, the number of cyclopentane rings in the Crenarchaeotal membrane lipids increases. The TEX_{86} index showed a significant linear correlation with growth temperature in the incubation experiments (Eq. 4.14) and with the annual mean sea-surface temperature in the surface sediments (Eq. 4.15).

$$TEX_{86} = 0.015 \cdot T + 0.10 \quad (r^2 = 0.79) \qquad (4.14)$$
$$TEX_{86} = 0.015 \cdot T + 0.29 \quad (r^2 = 0.92). \qquad (4.15)$$

Both equations exhibit identical slopes but differ slightly in the intercept with the y-axis. Two additional aspects make this new proxy parameter particularly promising. The temperature range (0-35 °C) for the TEX_{86} appears to be wider than for the alkenone index (5-28 °C), and the Crenarchaeota are likely to significantly predate the first occurrence of the alkenone-producing haptophytes in Earth history.

ACL Index Based on Land Plant Wax Alkanes

In marine sediments, higher-plant organic matter can be an indicator of climate variations both by the total amount indicating enhanced continental run-off during times of low sea level or of humid climate on the continent and by specific marker compounds indicating a change in terrestrial vegetation as a consequence of regional or global climatic variations. Long-chain *n*-alkanes are commonly used as the most stable and significant biological markers of terrigenous organic matter supply (e.g. Eglinton and Hamilton 1967). The odd carbon-numbered C_{27}, C_{29}, C_{31} and C_{33} *n*-alkanes are major components of the epicuticular waxes of higher plants. These terrestrial biomarkers are often preferentially enriched in the marine environment, particularly under oligotrophic surface waters, because the compounds are protected by the resistant character of the plant particles and in part by the highly water-insoluble nature of the waxes themselves (Kolattukudy 1976).

The carbon number distribution patterns of *n*-alkanes in leaf waxes of higher land plants depend on the climate under which they grow. The distributions show a trend of increasing chain length nearer to the equator, i.e. at lower latitude (Gagosian et al. 1987), but they are also influenced by humidity (Hinrichs et al. 1998). In addition, waxes of tree leaves have molecular distributions different from those of grasses with either the C_{27} or the C_{29} *n*-alkane having the highest relative concentration in trees and the C_{31} *n*-alkane in grasses (Cranwell 1973). Poynter (1989) defined an Average Chain Length (ACL) index to describe the chain length variations of *n*-alkanes,

$$ACL_{27\text{-}33} = (27[C_{27}] + 29[C_{29}] + 31[C_{31}] + 33[C_{33}]) / ([C_{27}] + [C_{29}] + [C_{31}] + [C_{33}]) \qquad (4.16)$$

in which [C_x] signifies the content of the *n*-alkane with x carbon atoms. Poynter (1989) demonstrated the sensitivity of sedimentary *n*-alkane ACL values to past climatic changes. In Santa Barbara basin (offshore California) sediments from the last 160,000 years, Hinrichs et al. (1998) found the highest ACL values in the Eemian climate optimum (about 125,000 yr B.P.). Over the entire sediment section, the ACL values were higher in homogeneous sediment layers deposited in periods of more humid climate than in laminated sediments deposited under a semi-arid continental climate like that of today (Fig. 4.20). The sedimentary ACL variations most probably recorded the climatic changes on the continent for the following two reasons:

- Vegetation patterns on the continent responded rapidly to climatic oscillations, which were often characterized by drastic changes of temperature and precipitation. During relatively warm and dry periods when mainly laminated sediments were accumulated in the Santa Barbara basin, smaller proportions of grass-derived biomass may have contributed to the sedimentary organic matter.
- Changes in continental precipitation significantly affected the degree of erosion and the transport of terrigenous detritus to the ocean, enhancing the proportion of biomass from other source areas (probably over longer distances from higher altitudes). This explains best the almost parallel and abrupt changes of oceanic conditions (e.g. bottom-water oxygen concentrations affecting sediment texture) and terrestrial signals recorded in the sediments (e.g. ACL indices).

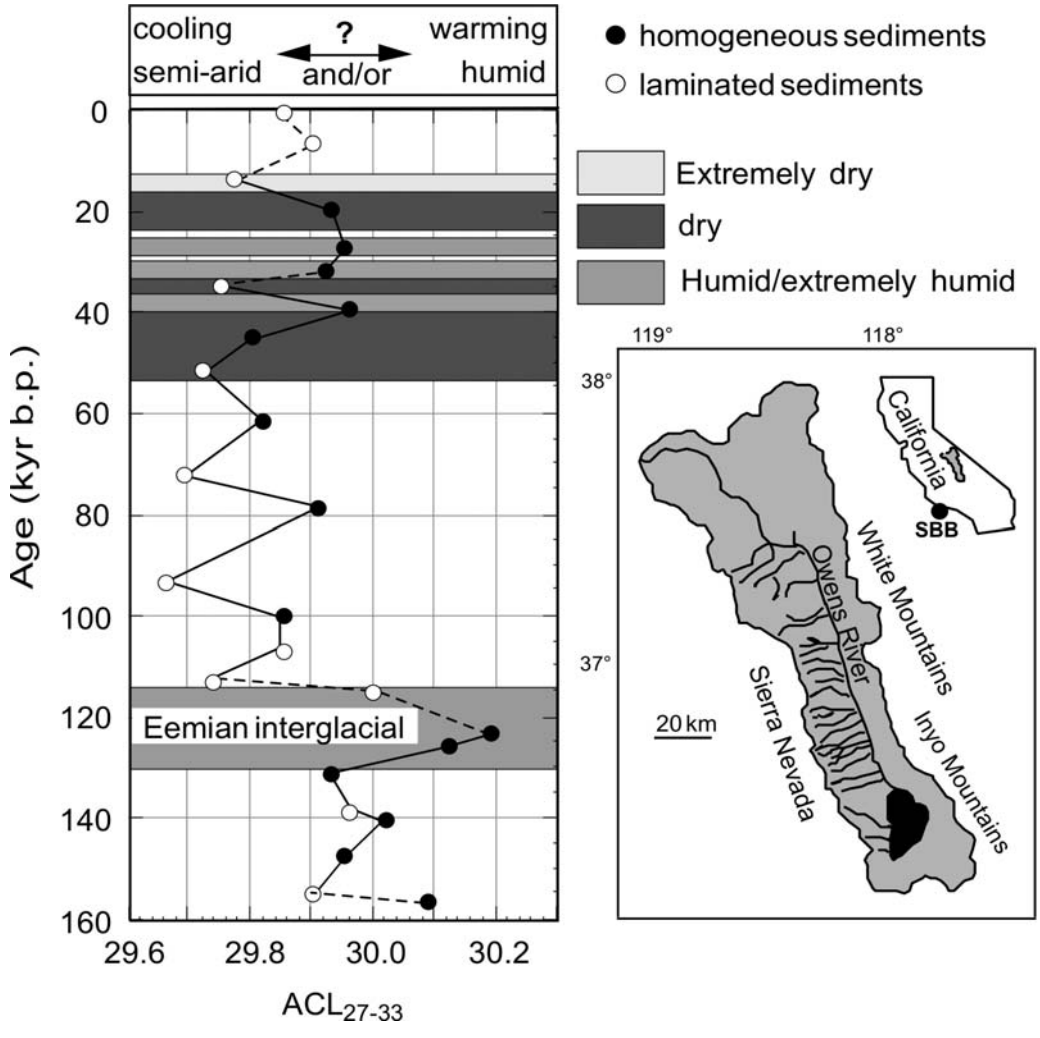

Fig. 4.20 Average chain length (ACL) time-series in relation to sediment texture (homogeneous versus laminated) for a core in the central Santa Barbara basin offshore California (after Hinrichs et al. 1998). Information on continental humidity from a sediment core in the Owens Lake basin was taken from Benson et al. (1996).

4.5 Analytical Techniques

Organic geochemical analyses of marine sediments may range from the rapid determination of a few bulk parameters to a high level of sophistication if trace organic constituents are to be investigated at the molecular level. The analytical scheme in Figure 4.21 is one of many that are currently being used in different laboratories. It is certainly not complete nor is it fully applied to each sample, particularly not when large series are studied. For example, the analysis of amino acids (e.g. Mitterer 1993), sugars (Cowie and Hedges 1984; Moers et al. 1993), lignin (Goñi and Hedges 1992), or humic substances (Brüchert 1998; Senesi and Miano 1994; Rashid 1985) requires a modification of the scheme in Figure 4.21. Other than in inorganic geochemical analysis, where modern instrumentation allows the simultaneous determination of a wide range of element concentrations, the millions of possible organic compounds require an *a priori* selectivity, but even the analysis of selected lipids can be quite time-consuming. In addition, the amount of sample material required for molecular organic geochemical studies is higher than for many other types of analyses, and this limits stratigraphic (time) resolution.

4.5.1 Sample Requirements

Most organic geochemical methods require a well homogenized, pulverized sample aliquot. An exception is reflected-light microscopy in organic petrography where the association of organic matter with the sediment matrix can be quite informative and is, therefore, preserved. Before homogenization, the sample needs drying either at ambient temperature or by freeze-drying. Higher temperatures are to be avoided due to the thermal lability of the organic matter. For the same reason, sediments – particularly those of young

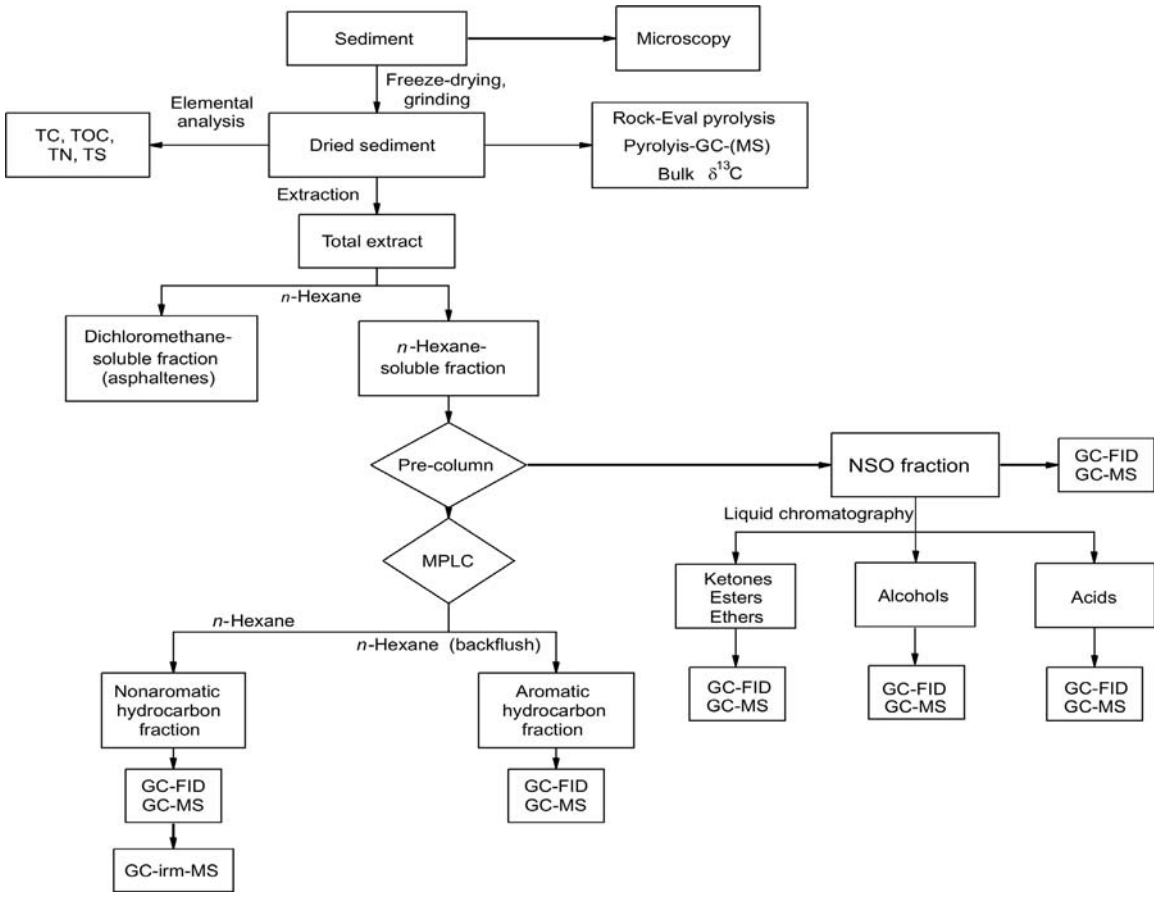

Fig. 4.21 Example of an analytical scheme of organic geochemical analyses of marine sediments comprising bulk and molecular parameters.

age in which bacteria may still be active – should be stored deep-frozen (-18°C or lower) between sampling and analysis. Grinding can be done by mortar and pestle or in an electrical ball or disc mill, but excessive grinding should be avoided due to the associated rise in temperature in the sample.

4.5.2 Elemental and Bulk Isotope Analysis

The basic parameter determined in most organic geochemical studies is the total organic carbon (TOC, C_{org}) content. Most marine sediments and sedimentary rocks contain carbon both as carbonates (C_{inorg}, C_{carb}, C_{min}) and as organic matter. There are numerous methods for quantifying carbon, most of them are based on heating solid samples in an oxygen atmosphere and detection of the evolving CO_2 by coulometric or spectrometric techniques or by a thermal conductivity detector. Commonly used instruments are elemental analyzers, which determine carbon, nitrogen, hydrogen (only applicable to pure organic matter), and sulfur (CHN, CNS, CS analyzers). Organic carbon is either determined directly, after destruction of carbonate with mineral acids before combustion in the elemental analyzer, or as the difference between total carbon (combustion) and mineral carbon (measurement of CO_2 released upon acid treatment).

For the determination of bulk stable carbon isotope ratios ($^{13}C/^{12}C$) the organic matter is converted to carbon dioxide by oxidation following digestion of the sediment with mineral acid to remove carbonates. Traditionally, oxidation of organic matter was performed off-line, CO_2 was separated from other gaseous oxidation products, and the purified gas introduced into an isotope ratio mass spectrometer. Modern instruments provide on-line combustion isotope-ratio measurement facilities. In this case, an elemental analyzer is connected to an isotope ratio mass spectrometer *via* a special interface that allows removal of gases other than CO_2. This configuration can also be used to separate sulfur and nitrogen oxides which, after on-line conversion to a suitable single species (SO_2 and N_2, respectively), can be used to determine stable sulfur ($^{34}S/^{32}S$) and nitrogen ($^{15}N/^{14}N$) isotope ratios. A special technical configuration of the mass spectrometer is required for hydrogen isotope ($^{2}H/^{1}H$) ratio measurement. Isotope ratios are not determined directly, but relative to an internationally accepted standard. The results are reported in the delta notation ($\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$, $\delta^{2}H$ [or commonly δD for deuterium]) relative to this standard. For details see, e.g., Fogel and Cifuentes (1993) and references therein.

4.5.3 Rock-Eval Pyrolysis and Pyrolysis Gas Chromatography

Rock-Eval pyrolysis (Espitalié et al. 1985) is conducted using bulk sediment samples to determine, (1) the amount of hydrocarbon-type compounds already present in the sample (S1 peak [mg hydrocarbons per g sediment]; compounds released at low temperature and roughly equivalent to the amount of organic matter extractable with organic solvents), (2) the amount of hydrocarbon-type compounds generated by pyrolytic degradation of the macromolecular organic matter during heating up to 550°C (S2 peak [mg hydrocarbons per g sediment]), (3) the amount of carbon dioxide released from the organic matter up to 390°C, i.e. before carbonates decompose (S3 peak [mg CO_2 per gram sediment]), and (4) the temperature of maximum pyrolysis yield (Tmax [°C]). The Hydrogen Index (HI) and Oxygen Index (OI) derived from the S2 and S3 values correspond to the pyrolysis yield normalized to the content of organic carbon (mg hydrocarbons and mg CO_2 per g TOC, respectively). The results of Rock-Eval pyrolysis are usually displayed in a van-Krevelen-type diagram of HI *versus* OI values which roughly corresponds to an H/C versus O/C atomic ratio van Krevelen diagram (see Fig. 4.11; Tissot and Welte 1984).

One of the methods of studying the composition of macromolecular sedimentary organic matter in more detail is the molecular analysis of pyrolysis products. For this purpose, the pyrolysis products are transferred to a gas chromatographic column and analyzed as described for extractable organic matter in Sect. 4.5.5, with or without the combination with a mass spectrometer. Both flash pyrolysis (Curie-point pyrolysis; samples are heated on a magnetic wire by electrical induction almost instantaneously, e.g., to 610°C) or off-line pyrolysis at various heating rates have been applied to geological samples (see Larter and Horsfield 1993 for an overview of various pyrolysis techniques).

4.5.4 Organic Petrography

Organic petrography is the study of the macroscopically and, more importantly, microscopically recognizable organic matter components initially of coal, but meanwhile more generally in sediments and sedimentary rocks. Organic-matter-rich rocks and coal are usually studied as

polished blocks in reflected light under a petrographic microscope. When sediments are lean in organic matter, the organic particles have to be concentrated by dissolution of the mineral matrix in consecutive treatments with hydrochloric and hydrofluoric acid. The concentrates are then analyzed as smear slides in transmitted light or embedded in araldite® resin and subsequently studied as polished blocks similar to whole-rock samples.

Organic particles visible under the microscope (>1 μm) are called macerals. The most important groups in the order of increasing reflectance are liptinite, vitrinite and inertinite. Liptinites are lipid-rich parts of aquatic (e.g. alginite) or land plants (e.g. cutinite, suberinite, sporinite, resinite), the terms indicating the origin of these organoclasts. Many liptinites are probably related to nonhydrolyzable, highly aliphatic biopolymers found in algae (algaenan) and land plants (cutinan, suberan) (see Sect. 4.3.3). These biopolymers serve as cell wall components of the organisms and their stability allows the morphological shapes of plant material to be preserved after sedimentation and burial so that they can be identified under the microscope. Vitrinites derive from the woody parts of higher plants. Inertinites are highly reflecting particles of strongly oxidized or geothermally heated organic matter of various origin, most commonly from higher plants. Non-structured, often (incorrectly) called amorphous, organic matter is known as bituminite or sapropelinite. Lipid-rich organic matter, even if finely dispersed, can be recognized under the microscope after UV irradiation by its bright fluorescence.

In addition to maceral distribution, organic petrographers determine vitrinite reflectance as a measure of geothermal evolution of sedimentary organic matter. For more details of microscopic analysis see Taylor et al. (1998).

4.5.5 Bitumen Analysis

The larger part of sedimentary organic matter is insoluble in organic solvents. The proportion of the soluble fraction (bitumen) can be relatively high in surficial sediments, then decreases in amount with increasing depth of burial due to formation of humic substances and kerogen. It only increases again when temperatures become high enough for thermal kerogen cracking to generate petroleum (Tissot and Welte 1984).

The most common solvent used for extraction of bitumen from dried sediments is dichloromethane (CH_2Cl_2) with a small admixture (e.g. 1%) of methanol, although more polar mixtures like chloroform/methanol or chloroform/toluene are also used. Occasionally, when very polar lipids from surficial sediments are to be extracted, wet sediment samples are preferred, and extraction starts with acetone or methanol or a mixture of these two because they mix with water. Extraction is then repeated with dichloromethane or a solvent of similar polarity. Extraction in a Soxhlet apparatus usually takes one to two days, whereas reasonably complete extracts can be obtained within minutes with the support of ultrasonication or blending. After filtration, the solvent is removed by rotary evaporation and the total extract yield determined gravimetrically, as is commonly done for any subfraction after further separation. Internal standards for quantitation of single compounds are added either before or after extraction, occasionally only after liquid chromatographic separation (see later).

The most polar and highest-molecular-weight extract components (called asphaltenes, a term derived from petroleum geochemistry, but often also applied to surficial sediments or even biological material) may interfere with many subsequent separations and analyses. For this reason, these components are frequently removed from the total extract by dissolving it in a small amount of, e.g., dichloromethane and adding a large excess of a nonpolar solvent like *n*-hexane (or *n*-pentane, *n*-heptane). The *n*-hexane-soluble extract fraction can be further separated into compound classes (or fractions of similar polarities) either by column liquid chromatography, medium-pressure liquid chromatography (MPLC: Radke et al. 1980; HMPLC: Willsch et al. 1997), high-performance liquid chromatography (HPLC), or thin-layer chromatography (TLC), depending on the sample quantity used and the sophistication of the separation required. In MPLC separation, as indicated in Figure 4.21, the polar lipids are withheld by a pre-column filled with deactivated silica gel, and only the hydrocarbons are separated on the main silica gel column into nonaromatic and aromatic hydrocarbon fractions. Because the main separation system is only operated with *n*-hexane, the difficult separation between the two hydrocarbon fractions is very reproducible, an important prerequisite for some applications, particularly in petroleum geochemistry. The polar lipids can be removed from the pre-column with a polar solvent. If emphasis is placed on the subfractionation of the polar heterocompounds, then HMPLC may be the method of choice. There are, however, many variations of this separation scheme. The nature of the geological samples and the scientific objectives will determine the type and extent of separation required.

Total extracts and/or liquid chromatographic subfractions are then analyzed by capillary column gas chromatography using a flame ionization detector. Except for hydrocarbon fractions, derivatization is commonly applied to render polar lipids more volatile in order to reduce gas chromatographic retention times and to improve peak shape at the detector. Carboxylic acids are usually transformed into their methyl esters, and hydroxyl or amine groups into their trimethylsilyl ether derivatives. Alternatively, both acid and hydroxyl groups can be silylated. Acetate formation is another common derivatization method. A variety of derivatization reagents are commercially available for this purpose.

Only a few major compound series can be recognized at the level of their molecular structures based on relative retention times and distribution patterns by gas chromatography alone. This applies to *n*-alkanes in the nonaromatic hydrocarbon fraction, *n*-fatty acids in the carboxylic acid fraction and in some cases *n*-alkanols in the neutral polar fraction. High abundance of a few single compounds (pristane, phytane, long-chain alkenones) sometimes also allow their direct identification from gas chromatograms.

The most powerful technique for assigning molecular structures to constituents of complex mixtures as they are found in the lipid extracts of geological samples is the combination of capillary column gas chromatography and mass spectrometry (GC-MS). Although the expression "identification" is frequently used, GC-MS alone is insufficient to fully characterize a new compound whose gas chromatographic and mass spectrometric behavior has not been described before. Normally, GC-MS analysis relies on a comparison with GC and MS data published in the (geochemical) literature or with data of standards, commercially available or synthesized in the laboratory, or on the interpretation of mass spectral fragmentation patterns following common empirical rules (e.g. McLafferty and Turecek 1993). Unfortunately, there is no comprehensive compilation of mass spectra of geochemically relevant organic compounds, although a significant number of spectra was recently published by de Leeuw (2004). Peters et al. (2005) have provided a detailed coverage of hydrocarbons and selected polar compounds of significance in petroleum geochemistry and other fields of organic geochemistry.

The youngest, revolutionary development in analytical organic geochemistry is the on-line coupling of a gas chromatograph to an isotope ratio mass spectrometer via a combustion interface (GC-irm-MS; Hayes et al. 1990; Freeman et al. 1994). This instrument allows the determination of stable carbon and hydrogen isotope ratios of single organic compounds in complex mixtures provided they are gas chromatographically reasonably well separated. Chemotaxonomic relations to specific precursor organisms are then possible if these are distinct from other organisms in their carbon isotope fractionation behavior during photosynthesis and biosynthesis. Sample preparation and analysis are similar to those for GC-MS analysis with the provision that the isotopic composition of derivatizing agents is accounted for in data interpretation.

4.6 The Future of Marine Geochemistry of Organic Matter

The evolution of organic geochemistry has always been closely connected to the developments in instrumental techniques for the analysis of organic compounds in geological samples. Now that the instrumentation has reached a high level of sophistication and particularly sensitivity, one of the future targets will certainly be higher stratigraphic (time) resolution which is particularly important for climate research. Advancement in the fundamental understanding particularly of the early part of the geological organic carbon cycle will depend on the cooperation between organic geochemists and microbiologists. They will have to refine the knowledge of the biological effects on the early diagenesis of organic matter arriving at the sediment-water interface and becoming buried in the uppermost sediment. It will be necessary to broaden the natural product inventory of microorganisms, both of sedimentary bacteria and archaea and of unicellular algae, protozoans and other organisms at the lower end of the food chain in order to arrive at solid chemotaxonomic relationships between source organisms and molecular fossils.

Carefully designed laboratory simulation experiments together with high-resolution field studies will refine the mass balance approaches of organic matter exchange between sediment and water column related to early diagenetic processes. Finally, mathematical modeling of transport and reaction processes will become an increasingly important tool in marine geochemistry of organic matter.

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4.7 Problems

Problem 1

What are the factors influencing organic matter preservation in marine sediments?

Problem 2

What are the main electron acceptors in the metabolization of organic matter during early diagenesis?

Problem 3

What is meant with selective preservation of organic matter?

Problem 4

What is the biological marker concept?

Problem 5

Can you name a few applications of (molecular) organic geochemistry?

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