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Degradation and Preservation of Organic Matter in Marine Sediments

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Abstract Organic matter that is deposited in aquatic sediments is subject to an intense diagenetic reactor that determines how much organic carbon is eventually preserved in sediments. The balance between organic matter degradation and preservation has immense consequences for the global carbon and oxygen cycles. A diverse set of hypotheses regarding the controls on organic matter degradation/preservation have received considerable attention over the past decade, most often revolving around the relative roles of bottom water and pore water oxygen and the rate of organic matter delivery to the sediments. These overriding hypotheses have in turn spawned numerous other hypotheses on specific topics. In this review, we discuss four important controls that impact on the degradation and subsequent preservation of organic matter in aquatic sediments. Our focus areas are: (1) the chemical nature of the organic substrate; (2) the potential influence of matrix on preservation; (3) the role of redox effects in degradation; and (4) the effects of physical mixing of sediments. Although we have divided our discussion under these headings, it will immediately become apparent that these subsections are at best arbitrary and that the four factors are indeed intimately related.

Keywords Diagenesis · Organic carbon · Organic carbon preservation · Organic carbon degradation · Redox oscillation · Co-metabolism

1 Introduction

Aquatic sediments serve as an intense reactor through which organic matter moves from the overlying water column toward sedimentary rocks [1]. The reactions taking place are largely mediated by sedimentary microorganisms that efficiently degrade ~ 99% of the organic matter that rains down onto the water/sediment interface in open ocean settings. Ultimately, only ~ 1% of this organic rain is preserved in underlying deep-ocean sediments to become part of the sedimentary record. Burial efficiencies in continental margin sediments may be substantially greater, and in some cases up to 40% of the input flux may be preserved. The consequences of this efficient reactor are profound. The organic matter that is eventually preserved is the source of fossil fuels and provides insight into the Earth's history. The balance between loss by remineralization, preservation by burial, and weathering of uplifted kerogen-containing sedimentary rocks inextricably links the global carbon, oxygen, and sulfur cycles [2–4]. Achieving a better understanding of the fate of organic matter during early diagenesis is also of practical importance, because of the use of biomarkers and other proxies in paleoenvironmental studies and the reconstruction of past environmental changes.

It is these global implications that drive the need to understand the biogeochemical processes that determine the character and quantity of organic matter that is either degraded or preserved. Over the past decade, theories regarding the dominant control(s) on organic matter preservation in marine sediments have revolved around the competing roles of water column production and organic matter delivery to the sediment versus bottom water oxygen content [5–12]. Related factors include organic matter source, molecular character and selective preservation of recalcitrant molecules [13–15], sediment accumulation rate [16], effects of bioturbation [17], oscillating redox conditions [18, 19], oxygen exposure time [20, 21], microbial dynamics [22–24], sorptive preservation on mineral surfaces [4, 25, 26], and protective encapsulation within macromolecular organic matrices [27, 28].

In this chapter, we review four important controls on organic matter degradation and preservation in marine sediments, building on concepts developed in the past and using new results to refine the ideas and theories that have been put forward. These four focus areas are: (1) substrate character; (2) matrix effects; (3) redox controls; and (4) sediment mixing regime. Although we have divided our discussion under these four headings, they are by no means the only important factors that may come into play nor are they mutually exclusive. In fact, as we will show, these four factors are closely interrelated.

2 Substrate Character

The classic "multi-G" model of Berner and coworkers for organic matter degradation in sediments [29–31] describes sedimentary organic matter as composed of many fractions, each with different susceptibilities to degradation. Implicit in this model is that each type of organic matter degrades independently of both other types of organic matter and the overall metabolic activity of the sediment. Middelburg [32] and Boudreau and Ruddick [33] have developed "continuous multi-G" models that have a continuous spectrum of G-types and a continuum of rate constants. In a further refinement, Canfield [34] described a "pseudo-G" model in which the metabolic activity of the sediment was controlled by degradation of the most labile fraction. In this model, two or more types of organic matter are present, and once the most labile fraction is consumed, the next most reactive form controls the overall metabolic activity of the sediment.

Degradation of the more refractory components is linked to the decay of the labile components, and high overall metabolic activity enhances the decomposition of refractory organic matter. This linked "co-metabolism" results from a relationship between the degradation of refractory organic matter and sediment metabolic activity [23, 35], where some metabolic activity in highly microbially active sediments is channeled into the oxidation of compounds that on their own would be resistant to decay. Ultimately, the key to both aerobic and anaerobic decomposition is the nature of the organic substrate [34]. In fact, Canuel and Martens [36] developed an approach for determining in situ decomposition rates by following the behavior of individual compounds within parcels of sediment of known age, rather than relying on down-core profiles obtained from a sediment core. Their analysis provides convincing evidence that organic matter reactivity changes with time (and burial), as apparent decomposition rates were substantially higher at the sediment surface than in deeper horizons (Fig. 1).

That there is a continuum of reactivities for organic matter comes as no surprise to organic geochemists. Polysaccharide components of vascular plants have been shown to be degraded two to five times faster than lignin components of vascular plants [37]. Similarly, in a study of the comparative geochemistries of lignins and carbohydrates in an anoxic fjord, Hamilton and Hedges [38] showed that neutral sugars were consistently the most reactive class. Among early studies of lipid biomarker distributions in sediments were observations that compounds displayed a range of stabilities. For instance, Cranwell [39] reported that reductions in abundance for various lipids indicated an order of stability: *n*-alkanes > alkan-2-ones > sterols > *n*-alkanoic acids > *n*-alkanols > *n*-alkenoic acids, and that within classes, shorter-chained components apparently were lost more rapidly than longer-chained ones. In part, variability in degradation rate may be due to mo-

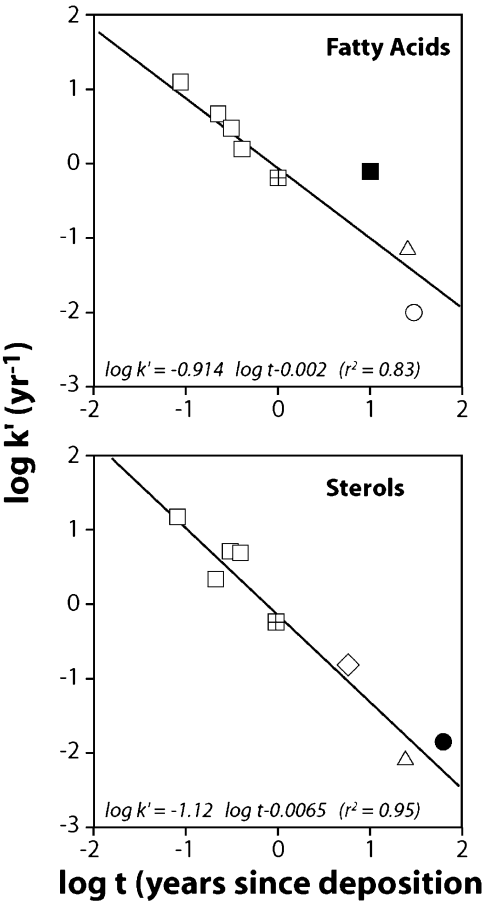

Fig. 1 Rate constants (k') for total fatty acids and total sterols for surficial sediments as a function of time since deposition. Key: ◇ Peru; •, ○ Buzzards Bay; △ Black Sea; □, ⊞ Cape Lookout Bight. After Canuel and Martens [36]

lecular structural features, i.e., short-chain lipids are more reactive than long chain lipids, unsaturated bonds are more reactive than saturated ones, and numerous recent studies confirm these trends in lipid reactivity [36, 40–44].

Arnosti [45–47] has studied polysaccharide hydrolysis and demonstrated that rates of extracellular enzyme hydrolysis vary considerably as a function of polysaccharide substrate (Fig. 2), with differences resulting from a mismatch between substrate structure and extracellular enzyme availability and activity for hydrolysis steps. Similarly, among major biochemical classes, such as amino acids and carbohydrates, differential degradation is common. Harvey et al. [48], for example, conducted laboratory experiments to evaluate the decomposition of algal organic matter and found carbohydrates to be more reactive than protein under oxic conditions, but the reverse under anoxic con-

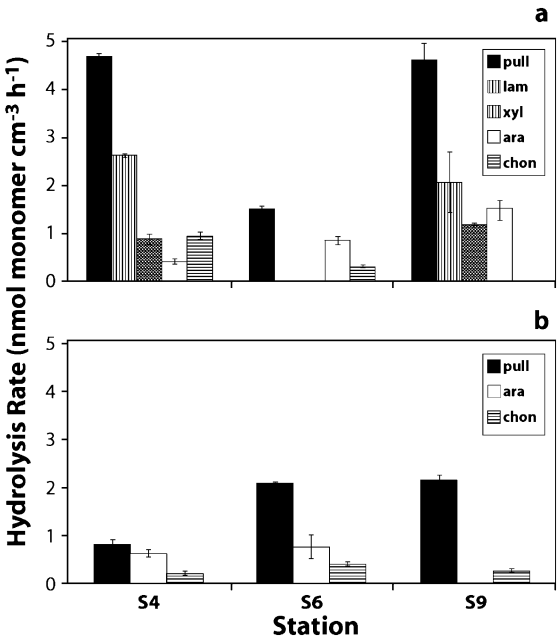

Fig. 2 **a** Hydrolysis of polysaccharides in homogenized surface (0–3 cm: S4; 0–1 cm: S6 and S9) sediments. **b** Hydrolysis of substrates in homogenized subsurface (3–6 cm) sediments. Pull – pullulan; lam – laminarin; xyl – xylan; ara – arabinogalactan; chon – chondritin sulfate. Error bars are for triplicate incubations. After Arnosti and Holmer [47]

ditions. Lignin is remarkably stable in sediments because there are relatively few enzymes produced by aquatic organisms that are capable of hydrolyzing the lignin macromolecule [49–51], but it can in fact be degraded under both oxic and anoxic conditions (review by Gough et al. [52]). These diverse studies point out that highly disparate views of organic matter degradation may arise, depending on what substrates are being examined and the environment in which they are being studied.

Despite numerous laboratory simulations and measurements in natural settings showing that individual (or specific) organic matter classes and compounds behave differently toward degradation, susceptibility to diagenetic alteration is clearly not related to molecular structure alone. Concentrations of compounds susceptible to degradation and total organic carbon often never drop to zero in sediments; organic molecules of identical structure often occur in both labile and relatively refractory forms (e.g., extractable and bound). It is thus likely that environmental conditions and/or protective matrices must be involved in determining the fate of organic matter. These physically protected forms may be relatively rare in fresh, undegraded organic material, and/or they may be concentrated in geochemical samples as the bulk and more labile organic substrates are extensively and preferentially degraded.

Since long carbon chain lipids tend to be derived largely from terrigenous vascular plant tissues whereas short-chained compounds generally originate from algae and bacteria, and since allochthonous compounds appear more refractory during diagenesis than autochthonous lipids, carbon chain length has been widely used to distinguish between allochthonous and autochthonous sources. Terrigenous compounds are generally considered to be more refractory, and thus better preserved, than algal compounds, based on changes in relative abundance in sediments [11, 36, 44, 53–55]. But is reactivity a function of molecular structure, or is it a function of differential packaging?

In an experiment by Reiley et al. [56], lipids of the vascular plant, *Fagus salvatica*, were found to be more resistant than lipids of the alga, *Isochrysis galbana*. Potentially, the difference observed by Reiley and coworkers may be due to differences in cellular and structural materials in their susceptibility to degradation, and/or different cellular matrices for vascular plants and this alga. As long as bacterial lipids remain associated with the membranes of bacterial cells, their constituent fatty acids are protected from degradation, but once the cells die and are subject to disruption, autolysis and further decomposition are rapid [57, 58]. Individual lipids common to two marine phytoplankton, the diatom *Thalassiosira weissflogii* and the cyanobacterium *Synechococcus* sp., showed different patterns of decay in a decomposition experiment, suggesting that factors other than molecular structure might be active [41]. Structural polysaccharides are less subject to diagenetic decomposition and are thus preferentially preserved compared to quickly degraded storage polysaccharides [59]. In addition, when allochthonous materials are delivered to aquatic environments, they may be sorbed to clays or sediment particles, providing additional protection from degradation (see below).

Over a decade ago, Tegelaar et al. [13] reappraised the processes involved in the formation of kerogen. In the condensation/humification scenario [60], simple biochemicals, generated by hydrolysis of complex substances, abiotically condense to produce complex assemblages (Fig. 3) that are difficult to define structurally [15]. Recent evidence [61] continues to indicate that some refractory sedimentary organic matter with a melanoidin-type structure is indeed formed by a degradation–recondensation of products derived mainly from polysaccharide and proteinaceous material. Intermolecular incorporation of inorganic sulfur with functionalized lipids [62] leads to complex and biologically resistant macromolecular material; this mechanism is still the subject of intense research [63]. An alternate theory, the preferential preservation mechanism, relies on the preservation of abundant hydrolysis-resistant biomacromolecules that are now known to be present in vascular plants and some algae [13, 14, 64] and that can be traced into sediments and kerogens [65, 66]. Hydrolysis-resistant biomacromolecules including algaenans, sporopollenins, cutans, suberans, and lignin, among others (see review by de Leeuw and Largeau [14]) are highly cross-linked and highly aliphatic in nature, often being associated with cell wall and/or structural organelles

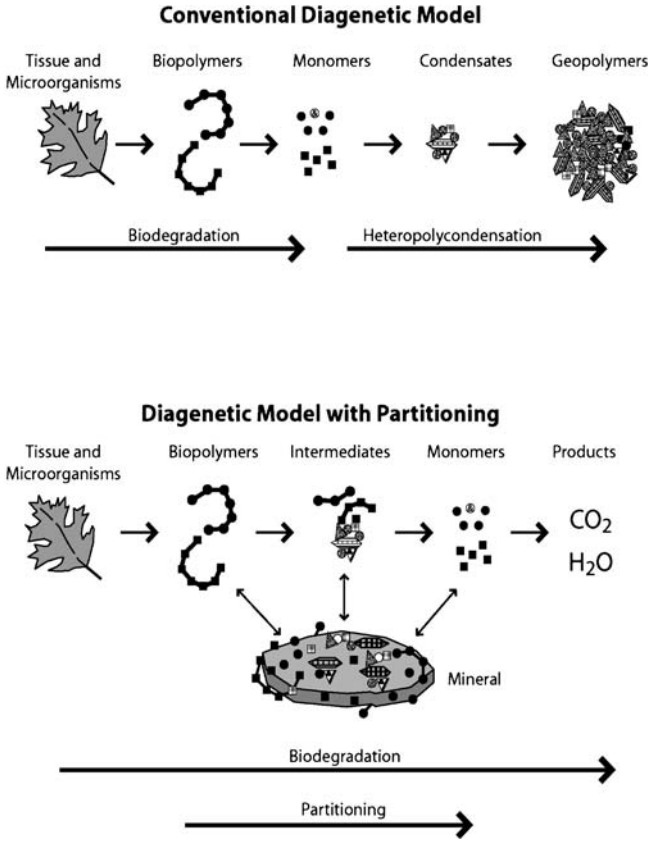

Fig. 3 Illustrations of the conventional biodegradation/repolymerization model (*top*) and the alternate biodegradation/sorption model for organic matter diagenesis and preservation (*bottom*). After Hedges and Keil [111]

of plants. Preferential preservation of these biomacromolecules results from their surviving microbial decomposition during early diagenesis (Table 1).

3 Matrix Effects

Organic matter is associated with mineral particles [67–69] and this association slows decomposition [70–72]. Distributions of "free" (released by solvent extraction) and "bound" (released by some hydrolysis step) compounds are often different [73–75], suggesting that this association is not equal for all molecular structures. Suess [76] observed a correlation between mineral surface area and organic carbon content of calcite-rich marine sedimentary particles. He found that the organic carbon (OC) loading per unit of surface

Table 1 Inventory of presently known biomacromolecules, their occurrence in extant organisms, and their potential for survival during sedimentation and diagenesis[a]

Biomacromolecules	Occurrence	"Preservation potential"[b]
Starch	Vascular plants; some algae; bacteria	–
Glycogen	Animals	–
Fructans	Vascular plants; algae; bacteria	–
Laminarans	Mainly brown algae; some other algae and fungi	–
Poly-β-hydroxyalkanoates (PHA)	Eubacteria	–
Cellulose	Vascular plants; some fungi	– /+
Xylans	Vascular plants; some algae	– /+
Pectins	Vascular plants	– /+
Mannans	Vascular plants; fungi; algae	– /+
Galactans	Vascular plants; algae	– /+
Mucilages	Vascular plants; (seeds)	+
Gums	Vascular plants	+
Alginic acids	Brown algae	– /+
Fungal glucans	Fungi	+
Dextrans	Eubacteria; fungi	+
Xanthans	Eubacteria	+
Chitin	Anthropods; copepods; crustacea; fungi; algae	+
Glycosaminoglycans	Mammals; some fish; Eubacteria	– /+
Proteins	All organisms	– /+
Extensin	Vascular plants; algae	– /+
Mureins	Eubacteria	+
Teichoic acids	Gram-positive Eubacteria	+
Teichuronic acids	Gram-positive Eubacteria	+
Lipoteichoic acids (LTA)	Gram-positive Eubacteria	+
Bacterial lipopolysaccharides (LPS)	Gram-negative Eubacteria	++
DNA, RNA	All organisms	–
Glycolipids	Plants; algae; Eubacteria	+/++
Polyisoprenols (rubber and gutta)	Vascular plants	+
Polyprenols and dolichols	Vascular plants; bacteria; animals	+
Resinous polyterpenoids	Vascular plants	+/++

[a] After de Leeuw and Largeau [14]

[b] Preservation potential ranges from – (extensive degradation under depositional conditions) to ++++ (no degradation under any depositional conditions)

Table 1 continued

Biomacromolecules	Occurrence	"Preservation potential"[b]
Cutins, suberins	Vascular plants	+/++
Lignins	Vascular plants	++++
Tannins	Vascular plants; algae	+++/++++
Sporopollenins	Vascular plants	+++
Algaenans	Algae	+++
Cutans	Vascular plants	++++
Suberans	Vascular plants	++++
Cyanobacterial sheaths	Cyanobacteria	+

[a] After de Leeuw and Largeau [14]
[b] Preservation potential ranges from – (extensive degradation under depositional conditions) to ++++ (no degradation under any depositional conditions)

area was similar to that for single layers of protein associated with interfaces, and suggested that the calcite-rich sediments under study consisted of highly irregular particle surfaces. The significance of OC–mineral associations was extended by Mayer [25, 26], who reported a widespread relationship between OC concentration and mineral surface area that approximated a monolayer of adsorbed OC on mineral surfaces (a "monolayer equivalent"). This led to the hypothesis that there was a surface area control on the stabilization and burial of OC in sediments, especially those on continental shelves. Further work led to a refined hypothesis, that OC saturates adsorption sites within small pores ("mesopores") on mineral surfaces that are small enough to exclude hydrolytic enzymes and hence protect otherwise intrinsically labile organic matter against biological attack. Several subsequent studies [77–81] support aspects of these hypotheses.

Mayer's "sorptive preservation" hypotheses [25, 26] have been the subject of considerable testing. Hedges and Keil [4] synthesized the early evidence in favor of the sorptive preservation hypothesis (Fig. 3). However, recent microscopic analyses [81] showed that organic matter distributions on mineral surfaces were patchy, discrete, and discontinuous rather than the continuous distributions that the monolayer equivalent hypothesis would imply. This study revealed that the vast bulk of OC in sediments is not in direct contact with the mineral surface, and that more attention needs to be directed toward understanding the relationships between mineralogy and surface area [82]. Bock and Mayer [83] determined pore size distributions of organic–clay aggregates and found most surface area to be within small mesopores (< 10 nm in width) that consist of interparticle slitlike spaces between clay grains rather than intraparticle dissolution features. The implication of this observation is that the formation of these aggregates involves an organic "glue" rather

than a physical adsorption. Observations such as these have led Mayer [84] to recast the sorptive preservation hypothesis, recognizing that most organic matter is not adsorbed in a monolayer and that mineral surfaces are largely uncoated, with the result that most sediments in the ocean are actually naked aluminosilicate surfaces.

There is general agreement that a continuum of reactivity exists based on the chemical structure of the organic substrate, and that this continuum can be altered by interactions with minerals which can stabilize labile organic matter [85], leading to the well-established correlation between organic carbon content and mineral surface area (Fig. 4). But what are the molecular implications of organic–mineral associations? Compositional differences between sediment size and density fractions are well known [77, 79, 80], but more work is needed in order to characterize the relative lability of specific organic substances associated with these different fractions. Organic matter that is incorporated into silicate and carbonate tests during biological deposition of these minerals is better preserved than cellular organic matter: mineral-bound amino acids are well protected from diagenesis and remain relatively unaltered chemically [86, 87] compared to cellular amino acids. In a study of opal-rich Southern Ocean sediments, Ingalls et al. [88] showed that the proportion of silica-bound amino acids increased significantly with increasing depth in the sediments, reaching > 50% of total hydrolyzable amino

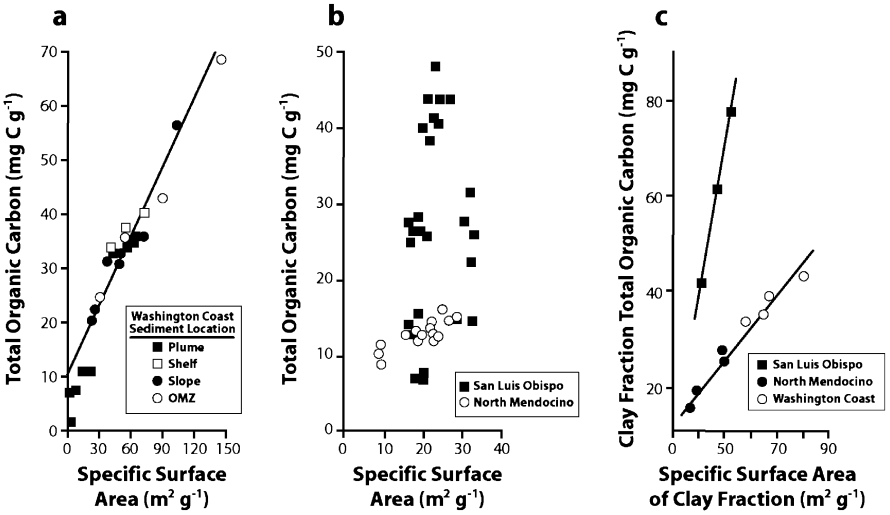

Fig. 4 Correlation between mineral surface area and total organic carbon content of marine sediments collected from **a** the Washington continental margin and **b** the California continental margin. **c** The relationship between the total organic carbon content of the clay fraction and surface area of the clay fraction of the Washington and California continental margin sediments. After Baldock and Skjemstad [85]

acids compared to negligible amounts in the diatom-rich plankton in overlying surface waters. Compositions also changed between mineral-bound and nonmineral-bound amino acids with increased depth.

Mineral associations are apparently not a prerequisite for organic matter preservation. While proteinaceous material can be preserved by interactions with mineral surfaces [89, 90], there is mounting evidence that proteinaceous material survives in systems where minerals are absent or in low abundance. This observation led Knicker and Hatcher [27] to study organic matter diagenesis in Mangrove Lake, Bermuda, an environment characterized by sapropelic sediments with low mineral content. Using ^{15}N NMR, Knicker and Hatcher [27] determined that since amide N was the dominant form of N in diagenetically altered 4000-year-old sapropel, and that there was little contribution from heterocyclic N, the refractory organic N could not derive from heterocyclic aromatic N compounds formed via condensation and polymerization of monomeric or oligomeric hydrolysis products of bacterial degradation. Rather, this organic N must survive via some interaction with other refractory macromolecular organic matter, whereby proteins become sandwiched or "encapsulated" between highly aliphatic macromolecular layers during diagenesis.

In follow-up studies, Harvey and coworkers [91–93] provided further support for the encapsulation hypothesis. Zang et al. [91] conducted dual-labeling experiments using ^{13}C and ^{15}N to follow the degradation of *Botryococcus braunii*, a prolific producer of biopolymeric algaenan. They found that biologically labile proteins and carbohydrates were preferentially lost during the time course of the experiment, but proteinaceous material remained the major form of organic N even after 200 days. Again, there was no evidence of formation of heterocyclic N compounds via depolymerization–recondensation reactions. Nguyen and Harvey [92] reported that noncovalent associations, such as hydrophobic interactions and hydrogen bonding, of protein could enhance preservation by stabilizing structures that are resistant to degradation. Nguyen et al. [93] used pyrolysis gas chromatography–mass spectrometry and ^{13}C NMR to show the preferential loss of intracellular material during degradation of *B. braunii* coupled with preservation of cell wall material. Furthermore, there were significant differences in degradation rates as a function of phytoplankton species (Fig. 5), implying distinctly different cell wall matrices. The highly aliphatic macromolecular fraction was refractory and the intrinsically labile proteinaceous material was protected against degradation.

The consideration of matrix effects on organic matter preservation now comes full circle when considered along with condensation, and in fact Collins et al. [94] contended that the two mechanisms work in concert with one another. The condensation pathway for kerogen formation [60] is based on the condensation of labile biomolecules, but condensation of organic compounds from solution is thermodynamically unfavorable. On the other hand, the process of selective adsorption represents a mechanism for concentrating the

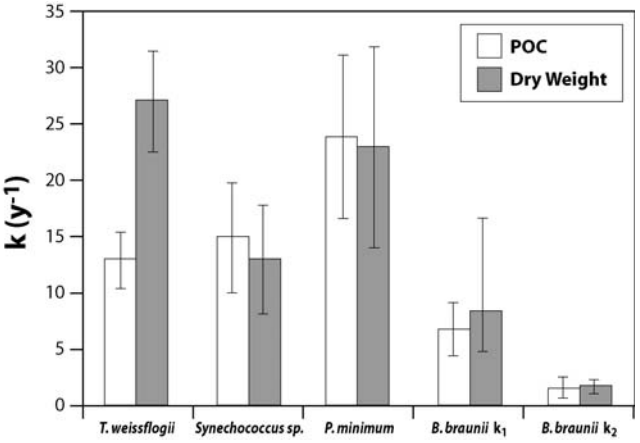

Fig. 5 Comparison of first-order decay constants (k) for particulate organic carbon (POC) and dry weight during oxic degradation of four phytoplankton species: *Thalassiosira weissflogii* (diatom), *Synechococcus* sp. (cyanobacterium), *Prorocentrum minimum* (dinoflagellate), and *Botryococcus braunii* (green alga). After Nguyen et al. [93]

labile organic compounds as mineral coatings, protects them from biodegradation, and provides a monolayer template that can irreversibly incorporate labile organic matter into an evolving macromolecule. Condensation reactions between adsorbed compounds leads to the formation of strongly bound macromolecules, which could lead to unexpected preservation of labile compounds in an organomineral phase that effectively transfers the compounds into the realm of the "molecularly uncharacterized component" [15].

4 Oxygen/Redox Control of Aerobic and Anaerobic Degradation

Considerable effort over the past decade has gone toward determining the relative efficiency of microbial decomposition operating through aerobic or anaerobic metabolic pathways. Traditionally, aerobic oxidation has been accepted as being more important because energy yields for aerobic decomposition are generally greater than those for anaerobic decomposition reactions. Oxygen serves two functions in organic matter degradation [95]: that of terminal electron acceptor during oxidation of organic carbon, and as a reactant in the oxygenase-catalyzed primary attack on substrate molecules. The first function may be transferred to other oxidized compounds (sulfate, nitrate) in the absence of oxygen, but there is no equivalent to O_2 that can fulfill its function as a reactant. Limitations in the ability of anaerobes to hydrolyze certain structurally complex compound types result in slower rates of decomposition in anoxic zones. This may also be due to the fact that the organic matter has

already been partially decomposed by aerobic bacteria, and the anaerobes are exposed to the "leftovers" that tend to contain higher proportions of refractory, residual material. Thus, substrate lability and apparent decomposition rates usually decrease rapidly with depth in the sediment.

In addition, aerobic metabolism is generally more direct than anaerobic metabolism. Aerobic decomposition involves diverse enzymes, many of which are specific to individual types of organic functional groups, and each substrate is often rapidly and completely metabolized to CO_2 and biomass by a single microorganism [34]. Anaerobic heterotrophs, in contrast, are unable to degrade most polymeric compounds [96, 97] and must rely on slow hydrolytic and fermentative bacteria using various oxidized inorganic compounds (NO_3^-, Fe, Mn, and SO_4^{2-}) as electron acceptors for the supply of metabolizable low molecular weight substrates. The result is that anaerobic degradation often involves a consortium of cooperating organisms.

There is considerable molecular evidence from laboratory simulation experiments and natural settings addressing redox effects on organic matter degradation/preservation (Table 2). These studies have shown that the residence times for organic compounds present in marine sediments can vary as a result of environmental conditions such as bioturbation, physical mixing, and the presence or absence of oxygen and other electron acceptors. Some evidence indicates significant differences in degradation rates when comparing oxic and anoxic experimental conditions [43, 98–101], and field measurements also suggest an oxygen effect [42, 53, 55]. Other observations suggest that anoxic decomposition may not be intrinsically slower than oxic decomposition [22, 102], at least for simple substrates and at the onset of diagenesis. But, as discussed above, anaerobes often must deal with the more refractory substrates that have already survived attack by aerobes.

Teece et al. [100] reported that initial rates of degradation of lipids from *Emiliania huxleyi* were rapid for both oxic and anoxic conditions, but that rates for anaerobic decomposition slowed significantly, and initial rates of decay poorly reflected the overall extent of degradation. One implication of this study is that experiments of anaerobic decomposition need to be carried out over longer timescales to more accurately assess the long-term effect of anaerobic decomposition. Furthermore, Teece et al. [100] observed that since decomposition patterns were different under the two anoxic conditions examined, sulfate reduction and methanogenesis, the specific anaerobic pathways involved also needed to be considered rather than simply the overall anoxic state. A recent study by Lehmann et al. [101] tracking changes in $\delta^{13}C$ and $\delta^{15}N$ in incubation experiments showed similar rates of decomposition for reactive organic matter under oxic and anoxic conditions, again supporting the idea that aerobic and anaerobic metabolic pathways are capable of degrading labile components. However, this study showed that once the labile component was degraded, the proportion of organic matter resistant to degradation was lower under oxic than anoxic conditions.

Table 2 Comparison of turnover times for organic compounds in marine sediments

Location	Bottom water	Sediment interface	τ (days)	Refs.
Bioturbated				
Carteau Bay, Mediterranean Sea (surface sediments)	Oxic	Oxic	*n*-alkenes: 23–28 *n*-alkyl diols: 55–100 sterols: 40–59 acids: 21–76	[43]
Long Island Sound, NY (surface sediments)	Oxic	Oxic	sterols: 24–50 acids: 11–17 acids: 8–50 TOC (reactive): 51 TOC (nonreactive): 365	[118] [98] [31]
York River, VA (33–84 cm; ~ 30–40 years in age)	Oxic	Oxic	sterols: 28×10^3 acids: 22×10^3 TN: 243×10^3 TOC: 166×10^3	[55]
Physically mixed				
York River, VA (41–54 cm; ~ 30–40 years in age)	Oxic	Oxic	sterols: 20×10^3 acids: 21×10^3 to 30×10^3 TN: 54×10^3 TOC: 64×10^3	[55]

Table 2 continued

Location	Bottom water	Sediment interface	τ (days)	Refs.
Nonbioturbated				
Cape Lookout Bight, NC (surface sediments)	Oxic	Dysoxic/anoxic	sterols: 11–170 acids: 11–17 *n*-alkanes: 14–45	[36]
			TOC: 33–379	[119]
			TN: 68–456	[120]
Cape Lookout Bight, NC (0–1 m)			acids: 250–2500	[40]
Chesapeake Bay (0–3 m)	Oxic/seasonally hypoxic or anoxic	Oxic/seasonally hypoxic or anoxic	TOC: 14×10^3 to 33×10^3	[121]
Peru upwelling (surface sediments)	Dysoxic	Dysoxic	br alkene: 2300 *n*-alkanols: 2100–6100 sterols: 680–2400	[122]
Black Sea (surface sediments)	Anoxic	Anoxic	br alkene: 8900 *n*-alkyl diols: 26 000–33 000 sterols: 16 000–26 000 acids: 6500–14 000	[42]

Because the most energetically favorable metabolic pathways for bacteria involve oxygen as the electron acceptor, it follows that organic carbon degradation (and preservation) in sediments is strongly controlled by the average time that organic matter is exposed to oxygen, or the oxygen exposure time, OET [20, 21]. In a transect across the Washington continental margin, slope, and adjacent abyssal plain, measurements of the penetration of O_2 into surface sediment along with sediment accumulation rates allowed calculation of the oxygen exposure time [21]. There was a marked increase in OET in the further offshore sediments that corresponded to decreased OC concentrations and OC/surface area ratios and increased molecular indications of organic matter degradation. Studies of deep-sea turbidites characterized by an oxidation front (the Madeira abyssal plain (MAP) turbidites) clearly implicate molecular oxygen as a key agent in organic matter degradation [103–105]. As the MAP turbidites were laid down, the slumping sediment was thoroughly mixed mineralogically and presumably chemically. Following deposition, the upper half-meter of the turbidite was exposed to bottom water oxygen before being "capped" by the next deposit that returned the turbidite to a suboxic state. There was marked degradation—orders of magnitude reduced concentrations—of organic carbon and biomarkers in the oxidized zone compared to the unoxidized zone, producing sharp organic gradients across the redox front. In addition, there were significantly different apparent degradation rates for individual compounds and classes across the oxidation fronts. Prolonged exposure of sedimentary organic matter to oxygen not only led to greater alteration of that organic matter than occurred for sulfate reduction only, but also resulted in marked changes in absolute and relative distributions of biomarkers. Further evidence for the importance of both oxygen exposure and variable effects on different molecular structures comes from the work of Sinninghe Damsté et al. [11], who investigated the biomarker record in sediments of the Arabian Sea that had been exposed to varying oxygen exposure times (Fig. 6). Under anoxic conditions, a much larger fraction of biomarker flux accumulated than under oxic conditions, and it was apparent that different biomarkers were subject to differences in the degree of degradation, and hence variable preservation. Compositional changes such as these could substantially compromise our ability to use biomarkers for paleoenvironmental reconstructions.

Given that oxygen plays a significant role in organic matter degradation/preservation, and since intrinsic molecular character also plays a role, Hedges and Keil [4] built on previous work (references cited above) showing that organic matter does not degrade as a single pool but rather as a composite of multiple rates among the various classes of organic components. In the oxygen-sensitive organic matter model of Hedges and Keil [4] there are (at least) three forms of organic matter in sediments. Materials such as charcoal are totally refractory. An oxygen-sensitive fraction, lignin for example, degrades slowly in the presence of oxygen, but not at all under anoxic con-

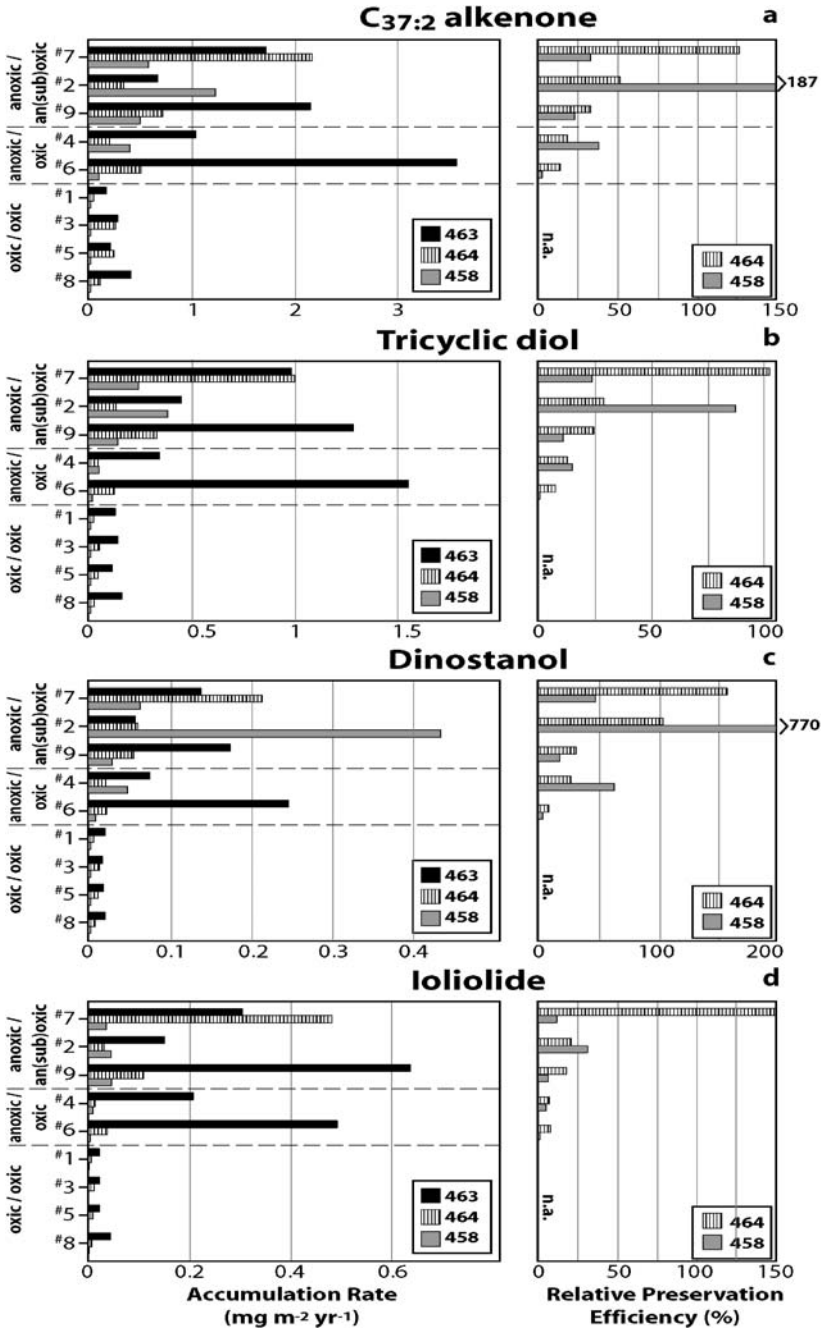

Fig. 6 Accumulation rates and preservation efficiencies for biomarkers in sediment cores from the Arabian Sea, grouped according to the degree of oxygen depletion in bottom and pore waters at the time of sediment deposition. After Sinninghe Damsté et al. [11]

ditions. Hydrolyzable molecules such as proteins and polysaccharides are readily degraded regardless of conditions. Some combination of remineralization of these three types of OC, albeit on very different timescales, is additive in proportion to their abundance, generating the profiles observed in sediments. Note that the oxygen-sensitive organic matter model relies on molecular properties as a key determinant of organic degradation rates, whereas the sorption model is largely based on sediment surface area, although the two are certainly not mutually exclusive.

Hulthe et al. [106] have provided a synthesis of concepts developed by, among others, Mayer [25, 26], Kristensen et al. [95], and Hedges and Keil [4], in terms of mineral association and oxygen effects. Hulthe et al. [106] suggest that aerobic and anaerobic degradation rates are fundamentally similar for fresh organic matter because the organic matter has yet to attach to mineral grains; that is, both aerobes and anaerobes are equally adept at leaching and hydrolyzing organic matter. As time and depth increase in sediments, a greater fraction of the organic matter becomes associated with mineral surfaces, and anaerobic bacteria have increasing difficulty with its hydrolysis. Over time, apparent rates of aerobic decomposition become faster than rates for anaerobic decomposition because aerobes have the capability of producing stronger oxidizing agents, such as H_2O_2, which penetrate into mesopores where enzymes cannot reach. As sorption increases, aerobic degradation becomes progressively more effective than anaerobic degradation. However, some mechanism, such as physical mixing, bioturbation, or redox oscillations, is required to continually reintroduce dissolved O_2 into subsurface sediments that have higher proportions of protectively sorbed organic material.

5
Sediment Mixing Regime

Most organic matter decomposition occurs in bioturbated sediments underlying oxygenated waters [18]. Whereas many laboratory investigations have been designed to study decomposition under strictly oxic or anoxic conditions, extrapolation to natural environments can be problematic if there is heterogeneity in the bioturbated zone. Mobile benthos burrow and irrigate sediment and then often move on, allowing oxygen to penetrate into the upper sediments, but then as the oxygen is consumed by aerobic processes, the sediments may return to an anoxic state. These redox oscillations also lead to oscillations in aerobe–anaerobe communities and decomposition processes that may be distinct from the aerobic and anaerobic end-members. As the size of the pool of organic carbon that is preserved in sediments depends on the delivery rate, the rate of degradation, the nature of the organic carbon available, and the length of time the substrates are exposed to a particular

degradation mechanism, processes that prolong exposure to oxygen will enhance degradation and decrease preservation, in keeping with the oxygen exposure time hypothesis. The overall effect of bioturbation in sediments is suggested in a study by van der Weijden et al. [8], who found that the depth of bioturbation significantly influenced the accumulation of organic carbon in sediments across the oxygen minimum zone in the Arabian Sea (Fig. 7).

The abundance of aerobic infauna capable of bioturbation thus may be an important control on carbon decomposition and subsequent preservation, because they may provide a mechanism for renewing the oxygen content of pore waters and for transporting organic material up into the oxygenated zone where material resistant to anaerobic degradation is exposed to aerobic metabolism or "primes" co-metabolism. Laboratory experiments have now shown that decomposition rate constants for algal lipids [99] and chlorophyll *a* [107] are proportional to the abundance of subsurface-deposit feeders, such as *Yoldia limatula* (Fig. 8). In an earlier study where Bianchi et al. [108] studied the effects of macrofauna on the degradation of chloropigments, the conversion of chlorophyll *a* to phaeophorbide *a* was enhanced in sediments containing either the bivalve, *Macoma balthica* (surface-deposit feeder), or the polychaete, *Leitoscoloplos fragilis,* compared to controls with no macrofauna. In addition to the physical mixing of sediments, deposit-feeding animals can regulate the dynamics of bacterial growth. In the experiments conducted by Sun et al. [99], *Yoldia* grazing on bacteria limited the accumulation of bacterial fatty acids in the sediments, and presumably this

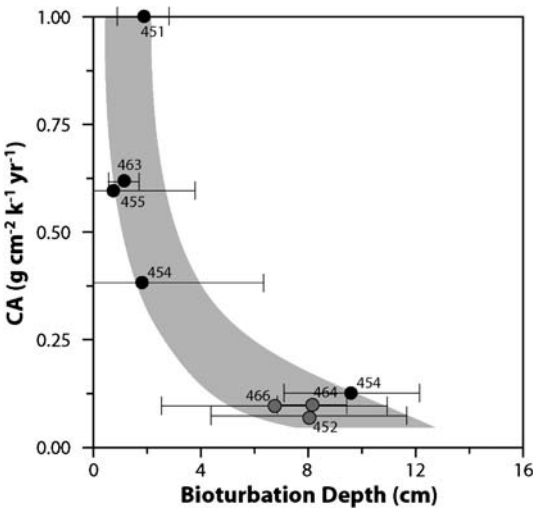

Fig. 7 Accumulation rates of organic carbon vs bioturbation depth estimated from differences in ^{14}C ages between organic carbon and foraminiferal carbonates for sediments crossing the oxygen minimum zone of the Arabian Sea. After van der Weijden et al. [8]

reduced the extent of bacterial decomposition. This observation supports the hypothesis of Lee [22] that predation on bacterial biomass, either by protozoa as suggested by Lee or by macrofauna [99, 107], would reduce bacterial decomposition and enhance carbon preservation. Aller [18] suggested that in a similar manner, periodic catastrophic death of a portion of a microbial population due to rapid redox change might significantly alter the net efficiency of remineralization.

Redox oscillation in nature is undoubtedly a highly variable event both temporally and spatially. Sun et al. [109] conducted microcosm experiments using ^{13}C- and ^{15}N-labeled algae to assess the effects of the frequency of oxic–anoxic oscillation on the rates and pathways of degradation of algal lipids in surface sediments. These experiments, carried out in the absence of bioturbating macrofauna, clearly show that the degradation of lipids is faster when redox oscillation is more frequent and, as a result, exposure to oxygen diffusing into the sediments from the overlying bottom waters is longer in duration (Fig. 9). Fatty acid analysis also indicated that redox oscillations strongly affected net synthesis of bacterial biomass, and that turnover of this biomass was faster under continuously or occasionally oxic conditions than under continuously anoxic conditions.

In addition to bioturbation, physical mixing, such as during large tidal excursions and storm events, can alter the redox environment of sediments or redistribute organic matter into different redox zones. Such physical mix-

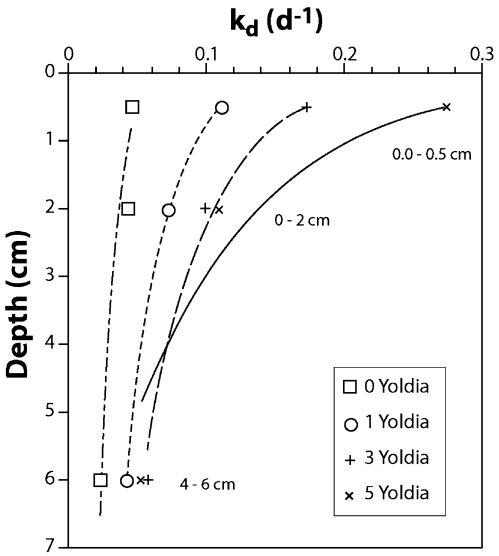

Fig. 8 Relationships between the decay constant (k_d) of chlorophyll *a* and depth interval for laboratory experiments involving varying abundances of *Yoldia*. After Ingalls et al. [107]

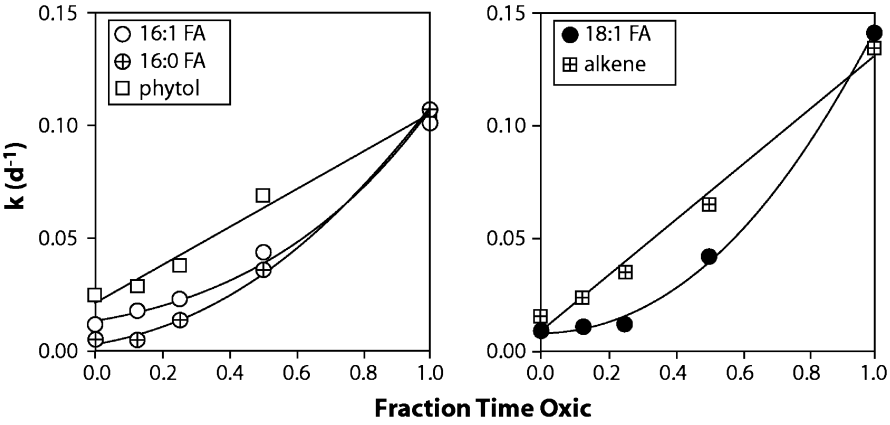

Fig. 9 Relationships between degradation constants for cell-associated ^{13}C-labeled algal lipids and the fraction of time of exposure to oxygen in redox oscillation experiments. After Sun et al. [99]

ing is more important in highly dynamic estuarine, deltaic, and coastal areas than in quiescent lagoonal or deep-sea environments. In these active depositional environments, even the relatively refractory terrestrial component may be susceptible to rapid degradation [110, 111]. Aller [112] provided an explanation for this scenario: mobile deltaic and continental shelf muds, driven by fluvial energy, estuarine circulation, tidal energy, coastal upwelling, and wind-driven waves. In environments such as the continental shelves off the Amazon River and the Fly River, Papua New Guinea, muds act as fluidized-bed reactors due to exposure to repetitive redox successions, the availability of electron acceptors, and the supply of planktonic organic carbon. Together, these conditions result in efficient remineralization of both labile marine and refractory terrestrial material under oxic and suboxic conditions. Sorbed organic matter may be released as readily degradable dissolved organic carbon [78] and the introduction of new labile substrates likely stimulates co-metabolism. Bioturbation is not a prerequisite for the intense mixing of these highly mobile muds, and in fact biomass of benthic communities tends to be significantly reduced compared to less strongly mixed sediments [112]. The decreased importance of macrofauna in these environments may be due to the disturbance regime [112, 113].

A recent study examined the effects of physical mixing, although perhaps not to the extremes of the Amazon and Fly River deltas, on the fate of organic matter in sediment cores obtained from sites representing contrasting mixing conditions in the York River (USA) estuary [55, 114]. The sites differed in the extent and mechanism by which they were mixed: one station was characterized by the confluence of tidal and fluvial energy leading to resuspension, erosion, and episodic disturbances to the upper 50–100 cm

(Dellapenna et al. [115]); in contrast, the second site experienced lower bottom currents, but was dominated by bioturbation in the upper 10–15 cm. Calculated residence times for organic carbon and total nitrogen were two to four times higher at the physically mixed site than the bioturbated site (Table 2). Consistent with the Lehmann et al. [101] and Hulthe et al. [106] studies, apparent rate constants for labile compounds (e.g., diatom-derived fatty acids) were similar under the two mixing regimes, while rate constants for more stable compounds (*n*-alcohols, sterols, and long-chain fatty acids) were higher in the physically mixed sediments. Arzayus and coworkers [114] also found evidence for the degradation of quite stable compounds such as polycyclic aromatic hydrocarbons in sediments at the physically mixed site through differences in isomer ratios.

The influence of physical mixing of sediments on diagenesis reported by Arzayus et al. [55, 114] contrasts with a microcosm experiment conducted by Sun et al. [109]. Three different mixing regimes were simulated in the study by Sun and coworkers: bioturbated, episodically physically mixed, and no mixing. Algal lipids degraded at different rates under the different mixing conditions, with slow degradation under episodic physical mixing. The interpretation put forward by Sun et al. [109] was that the mechanical stirring that constituted the physical mixing moved otherwise labile substrates into the subsurface anoxic zone where anaerobic metabolism was slow. Degradation rates of lipids subjected to oscillating redox conditions via bioturbation were similar to those of unmixed cores in which aerobic decomposition dominated at the sediment surface. As suggested further by Arzayus and Canuel [114], part of the difference between the field and microcosm findings could derive from the very different timescales relevant to the two investigations, and to the fact that field conditions represent "open" systems while laboratory experiments are "closed".

6 Concluding Remarks

Despite the progress we have made in recent years, there are still considerable gaps in our understanding of the mechanisms by which physical and biogeochemical processes control organic matter degradation in marine sediments. In addition to further developments in the areas highlighted in this review, there are several new areas in which studies should be developed. The first of these is investigation of the role of suboxic processes (e.g., denitrification, reduction of iron and manganese oxides) on organic matter diagenesis. Recent studies [55, 114, 116] have illustrated the potential importance of suboxic processes, but additional studies are needed to explore the specific role metal oxyhydroxides play in enhancing rates of degradation of bulk carbon as well as specific biomolecules. Efforts in this area should be directed to deltaic and

coastal regions where the delivery of manganese and iron oxide species is greatest. In addition, future work should attempt to tease apart the roles of sulfate reduction and methanogenesis in anoxic systems [100].

A second area for future investigations involves the study of co-metabolism. Co-metabolism is a process whereby the mixing of labile organic matter may enhance the degradation of refractory organic matter (i.e., terrestrial organic matter, or anthropogenic compounds such as polycyclic aromatic hydrocarbons). Coastal and deltaic regions are characterized by high rates of primary production due to human-induced nutrient loading. These regions are also affected by terrestrial and anthropogenic carbon inputs. Future studies should examine the role of co-metabolism in carbon diagenesis in these regions.

A third area in which additional studies are needed is in bridging the gap between benthic ecology and organic geochemistry. To date, studies in this area have involved laboratory experiments in which usually a single macrofaunal species has been manipulated. In the future, there is a need for field-based experiments in which complex benthic communities are manipulated to better understand the role of the microbial and macrofaunal communities in diagenesis. Additional areas of focus should include studies of benthic diversity and trophic processes on sediment organic carbon dynamics [117].

Finally, organic geochemists should pursue studies bridging the fields of organic geochemistry and molecular ecology. As tools in molecular ecology develop, biomarker information coupled with molecular (genetic) data will provide new insights about specific sediment microbial communities and their effects on sediment organic matter. An excellent example of this linkage comes from recent work on the anaerobic oxidation of methane in sediments (AOM; reviewed by Hinrichs and Boetius [123]). A variety of lipid biomarkers constructed of isoprenoid backbones derived from ether lipids similar to those of cultured methanogenic archaea have been identified in methane-rich sediments that are characterized by high rates of AOM. In the absence of culturable methanotrophic archaea, the presence of these biomarkers and their extremely depleted $\delta^{13}C$ values (often – 100‰ or less) have been taken as biosynthetic products of anaerobic microorganisms using isotopically depleted methane as a carbon source. Parallel studies of the phylogeny of microorganisms in sediments with high rates of AOM and biomarkers associated with AOM reveal two groups of archaea, designated ANME-1 and ANME-2, involved in AOM. Phylogenetic analyses of archaeal ribosomal rRNA sequences place the ANME-1 and ANME-2 groups near the methanogenic *Methanosarcinales*. Fluorescent in situ hydribization (FISH) further shows that ANME-2 archaea occur in a syntrophic association with sulfate-reducing bacteria of the *Desulfosarcina/Desulfococcus* lineages, suggesting that a consortium of archaea–sulfate-reducing bacteria is involved in AOM. Subsequent biomarker analyses have now shown that some biomarkers derived from sulfate-reducing bacteria in methane-rich sediments are indeed

strongly depleted in ^{13}C [123, 124]. Similar cross-disciplinary work should be quite fruitful in future studies of the impact that microorganisms have on organic geochemistry.

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