

# Carbon Processing at the Seafloor

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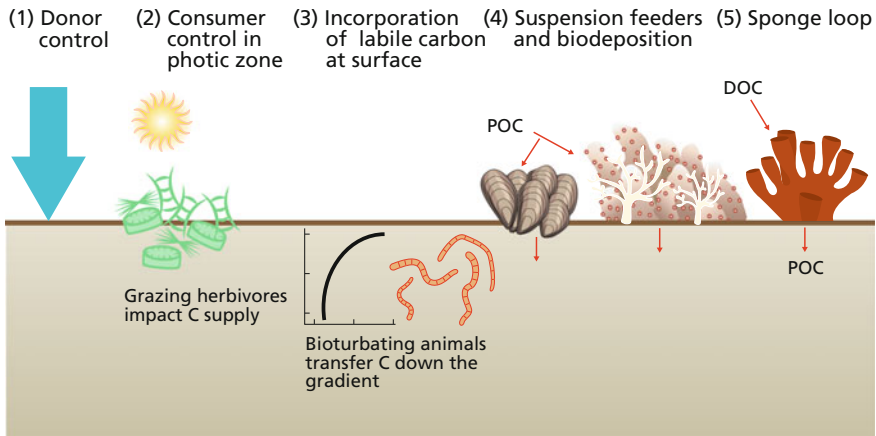
Most of the global marine primary production ( $\sim 55 \text{ Pg C y}^{-1}$ ) is consumed in the surface, sunlit ocean ( $\sim 44 \text{ Pg C y}^{-1}$ ) and ocean interior ( $\sim 8 \text{ Pg C y}^{-1}$ ) and only the remaining  $2\text{--}3 \text{ Pg C y}^{-1}$  reaches the sediment floor. Globally most of the organic carbon delivered to sediments ( $\sim 90\%$ ) is degraded because organic carbon burial is low ( $\sim 0.2\text{--}0.4 \text{ Pg C y}^{-1}$ ) and mainly occurs in rapidly accumulating coastal sediments.

In this chapter, we will first discuss organic matter delivery to the sediments, then the processes and organisms involved in organic matter degradation and close with a discussion of factors governing organic carbon burial.

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## 4.1 Organic Matter Supply to Sediments

In Chap. 3 we have seen that organic carbon deposition on the seafloor depends primarily on water depth (Fig. 3.4), as a direct consequence of organic matter production in the euphotic zone and degradation of detritus during transit from the sunlit layer to the bottom of the ocean with more time for degradation in deep-water settings than in coastal settings. Consequently, deep-sea sediments receive little organic matter, while coastal sediments receive much. This water depth dependency of organic matter delivery rates is articulated by lateral differences in ocean primary production (production in shallow coastal systems is generally higher than that in the open ocean). Marine sediments are therefore often considered donor-controlled, i.e. the organic matter consuming benthic communities have no control over their food resources. While such a donor-controlled view applies to most deep-sea environments, there are other carbon delivery routes for sediments within the euphotic zone and for sediments inhabited by animals and these carbon transfers to sediments are (partly) mediated by the consuming communities, i.e. under consumer control (Fig. 4.1; Middelburg 2018).



**Fig. 4.1** Organic matter supply to sediments (Middelburg 2018). (1) Organic matter settling from the water column is deposited at seafloor (donor control; fixed flux upper boundary condition). (2) Sediments in the photic zone are inhabited by benthic microalgae that produce new organic matter in situ and grazing animals can impact the growth of these primary producers. (3) Bioturbating animals transfer labile carbon from the sediment surface layer to deeper layers in the sediments. (Vertical axis is depth; horizontal axis is concentration, see Fig. 4.2) (4) Suspension-feeding organisms enhance the transfer of suspended particulate matter from the water column to the sediments (biodeposition). (5) Sponge consume dissolved organic carbon and produce cellular debris that can be consumed by benthic organisms (i.e., the sponge loop)

Intertidal sediments and coastal sediments within the euphotic zone may support microbial photoautotrophs (microphytobenthos). Gattuso et al. (2006) showed that globally about 1/3 of sediments within the coastal ocean receive sufficient light for photosynthesis. This primary production at the seafloor represent a source of  $\sim 0.32 \text{ Pg C yr}^{-1}$  that is not only directly available for consumption, but it is also of high quality, because there has been no pre-depositional processing of organic matter. This benthic primary production input thus supports about 10–15% of global sediment respiration. Moreover, the grazing by micro, meio and macrofauna controls the biomass of the primary producers and in this way grazing animals control food supply for themselves, as well as for microbes living on the exudates and detritus of microphytobenthos (Middelburg et al. 2000; Middelburg 2018).

Macrophytes such as seagrasses in the subtidal euphotic zone and marsh plants and mangroves in the intertidal zone enhance carbon inputs to sediments in two ways. They locally produce new organic matter that is used for respiration, invested in leaves and stems, allocated to below-ground tissues for nutrient (and water) uptake, anchoring and storage. All this tissue can be consumed by microbes and animals, although the degradability of structural carbohydrate rich macrophyte material is often lower than that of protein-rich microphytobenthos and phytoplankton material (Duarte and Cebrian 1996; Fig. 3.10). Macrophyte communities stabilize the sediments and impact the local hydrodynamics with the consequence that suspended particles, including particulate organic matter, are trapped within

their canopies. This trapped organic matter is often derived from adjacent ecosystems or phytoplankton from within the system and makes a substantial contribution to sediment organic carbon pools in salt marshes (Middelburg et al. 1997) and seagrass meadows (Gacia et al. 2002; Kennedy et al. 2010). Moreover, the trapped phytodetritus often is more readily degradable than locally produced macrophyte material (Barrón et al. 2006).

Suspension feedings worms, bivalves, corals and sponges consume particulate organic matter suspended in the water column. Part of the carbon is used for growth and maintenance, another part is excreted as faeces and pseudofaeces, which in turn are available for microbes and animals in the underlying and nearby sediments. Some organisms passively filter water, whereas others actively filter water to obtain their resources. Clearance rates ( $\text{m}^3$  of water cleared from food per unit time) can be very high, and grazing by benthic suspension feeders often represents the largest loss term of phytoplankton in tidal systems (Heip et al. 1995). While some suspension feeders are spatially distributed rather homogeneously, many others (e.g. oysters, mussels, coral reefs) occur in specific areas at high densities because of local favourable hydrodynamic conditions or positive feedbacks between community density, performance and local hydrodynamics (Herman et al. 1999). These suspension feeders locally enhance carbon input to underlying sediments relative to that delivered via sinking because they focus laterally available particulate organic carbon. Some of the highest carbon inputs to sediments have been reported for mussel and oyster beds. Moreover, benthic suspension feeders within the euphotic zone directly impact phytoplankton growth and dynamics (Koseff et al. 1993).

Sandy sediments cover about 50% of the continental shelf seafloor and about 4% of the total ocean floor. Their high permeability allows flow of water through the connected pore network of these sediments. These flows are driven by current or wave induced pressure differences, which may be enhanced through biological structures. Active flows of seawater with suspended particles result in additional transport of particulate organic matter to sediments. Part of the suspended particulate matter entering into these sediments with the water is trapped or utilized by organisms (Huettel et al. 2014), thus supplementing the particulate organic matter supply to these sediments. This additional organic carbon is highly reactive, and particulate organic carbon stocks in permeable sediments are very low (Boudreau et al. 2001).

Another organic carbon provision pathway to sediments involves organisms that consume dissolved organic carbon and use it to form particulate organic carbon (biomass and excretion products), which can be used by other consumers living at the sediment-water interface or within the sediments. This mechanism has been documented for encrusting sponges that consume large quantities of dissolved organic carbon and rapidly convert this into detritus for benthic consumers (i.e. sponge loop, de Goeij et al. 2013).

It is important to realize that some of these additional pathways involve truly new organic carbon (benthic primary production), while the others either convert widely available, but poorly useable, dissolved organic carbon into a particulate pool (sponge loop) or focus particulate organic matter delivered to a wide area for

deposition into small areas inhabited by suspension feeding animals or plants. The latter category locally enhances organic matter decomposition at the expense of adjacent areas or water-column degradation. Finally, even in donor-controlled sediments, animals enhance the transfer of labile organic matter to subsurface microbial communities by bioturbation (Box 4.1) and in that way stimulate the overall degradation of organic matter (Middelburg 2018). This mechanism will be presented in detail below; we will first introduce the consuming organisms.

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## 4.2 The Consumers

Organic matter delivered to the sediments represents the major resource for the heterotrophic consumers living in the sediments. These organic carbon consumers are usually partitioned into size classes: microbenthos (<32  $\mu\text{m}$ ), meiobenthos (32  $\mu\text{m}$ –0.5/1 mm) and macrobenthos (>0.5/1 mm), the actual size class division depending on the environment (smaller for deep-sea than coastal studies). The microbenthos includes small eukaryotes (Protists), but is by far dominated by prokaryotes (Bacteria and Archaea). The meiobenthos is often dominated by nematodes, but foraminifera (protists) also contribute. The macrobenthos comprises many different animal groups. The number of organisms declines with size: from  $10^9$  bacteria per ml of sediments (i.e.  $10^{14}$  cells in the top 10 cm of  $1 \text{ m}^2$ ),  $10^6$  meiofauna  $\text{m}^{-2}$  to  $10^4$  macrofauna  $\text{m}^{-2}$  in estuarine sediments (Herman et al. 1999). The distances between individuals is thus of the order 10  $\mu\text{m}$ , 1 mm and 1 cm for microbes, meiofauna and macrofauna, respectively. Microbes are much smaller than typical pore sizes of silty and sandy sediments, meiofauna can live within these pores, while macrofauna are much larger and consequently move particles when active. The mixing of particles and solutes by animals living in sediment is called bioturbation (Box 4.1) and has major consequences for carbon processing in sediments (Meysman et al. 2006; Middelburg 2018).

The organic carbon consumed by benthic heterotrophs is used for maintenance, growth and reproduction. The relative importance of the different size classes to carbon consumption scales more or less with their contribution to biomass. In coastal sediments, macrofauna typically accounts for 10–25% of the total biomass and respiration, with microbes accounting for the remaining, except for a small (few %) contribution of protists and meiofauna. Macrofauna number and size (and thus biomass) decline strongly with water depth compared to those of meiofauna and in particular microbes (Snelgrove et al. 2018). Carbon consumption in deep-sea sediments is almost entirely due to microbes. Accordingly, organic matter consumption is normally attributed to sedimentary microbes, and the consumption of organic matter by animals is therefore ignored in most biogeochemical studies (Middelburg 2018).

### 4.3 Organic Carbon Degradation in Sediments

Organic carbon degradation in sediments is a highly efficient process because most of the incoming organic carbon is degraded and only a small fraction eventually escapes mineralization to be buried with the accumulating sediments. This fraction is often quantified in terms of the burial efficiency (BE):

$$BE = \frac{F_B}{F_C} = \frac{F_B}{(F_B + R)} \quad (4.1)$$

where  $F_C$  is the incoming carbon flux,  $F_B$  is the rate of carbon burial and  $R$  is the total mineralization rate. Burial efficiencies are often presented as a percentage and range from a fraction of a percent in deep-sea sediments up to tens of a percent in rapidly accumulating coastal sediments (Canfield 1994; Aller 2013). In most oceanic sediments,  $R \gg F_B$ , and total respiration is a reliable proxy for quantifying the organic carbon delivery rate to sediments ( $F_C$ ).

This high efficiency of organic matter degradation within in sediments might seem paradoxical because sediments receive organic matter that has already been processed extensively before deposition. Pre-depositional processing of organic matter not only lowers the amount of organic matter delivered, but also the quality because of the preferential use of labile organic carbon by organisms (Fig. 3.9). However, when particulate organic matter is transferred from the water column, with a typical residence time of weeks to months, to the top layer of sediments, the time available for degradation changes by orders of magnitude ( $10^3$ – $10^4$  years). This increase in time available for processing organic matter more than compensates for the loss of reactivity during particle settling; hence, organic matter degradation resumes.

To understand the dynamics and distribution of organic matter in sediments we will again use the simple diffusion-advection-reaction model introduced in Box 1.1. Modelling the distribution and dynamics of organic carbon in sediments is rather challenging because the transport of organic carbon, as well as its production and consumption, are biologically controlled, and we cannot resort to physics-based laws for transport. Moreover, we are dealing with a two-phase problem (particles and water). The first simplification is that we only consider particulate organic carbon. For a sediment with a porosity (volume water/total volume) of 0.7, a particulate organic carbon content of 1 wt% and a very high pore-water dissolved organic carbon concentration (1 mM), dissolved organic carbon contributes about 1% to the sediment carbon stock. Moreover, the reactivity of dissolved organic carbon is relative low. Two, gradients in porosity due to compaction and bioturbation are ignored. Three, organic carbon degradation follows first-order kinetics (one-G model, Berner 1964; Box 3.1). Four, electron acceptors are abundant and their nature does not impact organic carbon degradation. Five, solid-phase organic carbon is transported by bioturbation (Box 4.1) and by the net accretion of sediment.

Transport of particulate organic carbon due to animal activity is the dominant transport process in sediment inhabited by animals. The transport resulting from bioturbation can usually be well described by diffusion (Goldberg and Koide 1962; Berner 1980), in particular when the benthic community is diverse (Meysman et al. 2006, 2010). It is only in sediments where chemical conditions (e.g. lack of oxygen, pollution) or physical conditions (e.g. unstable sediments that are repetitively disturbed by waves/tides) restrict macrofauna that bioturbation can be ignored and organic carbon transport due to sediment accretion dominates. Finally by assuming steady-state, the resulting equation for organic carbon ( $G$ ) is:

$$0 = D_b \frac{d^2G}{dx^2} - w \frac{dG}{dx} - kG \quad (4.2)$$

where  $G$  is labile particulate organic carbon,  $x$  is depth (positive downwards),  $D_b$  is the bioturbation coefficient ( $\text{cm}^2 \text{yr}^{-1}$ ),  $w$  is the sediment accumulation rate ( $\text{cm yr}^{-1}$ ) and  $k$  is a first-order rate constant ( $\text{yr}^{-1}$ ). Considering that all labile organic carbon is eventually consumed (at depth), we can solve the equation for specific conditions at the sediment-water interface ( $x = 0$ ). It is instructive to distinguish between sediments that are strictly donor-controlled (i.e. a fixed flux upper boundary) and sediments with a fixed concentration in the top layer. The former applies to most sediments, while the latter would represent coastal sediments with multiple deposition–resuspension events and lateral particulate organic transport pathways (Rice and Rhoads 1989). If we know the concentration of organic carbon at the sediment-water interface ( $G_0$ ), the solution is (see Box 1.1):

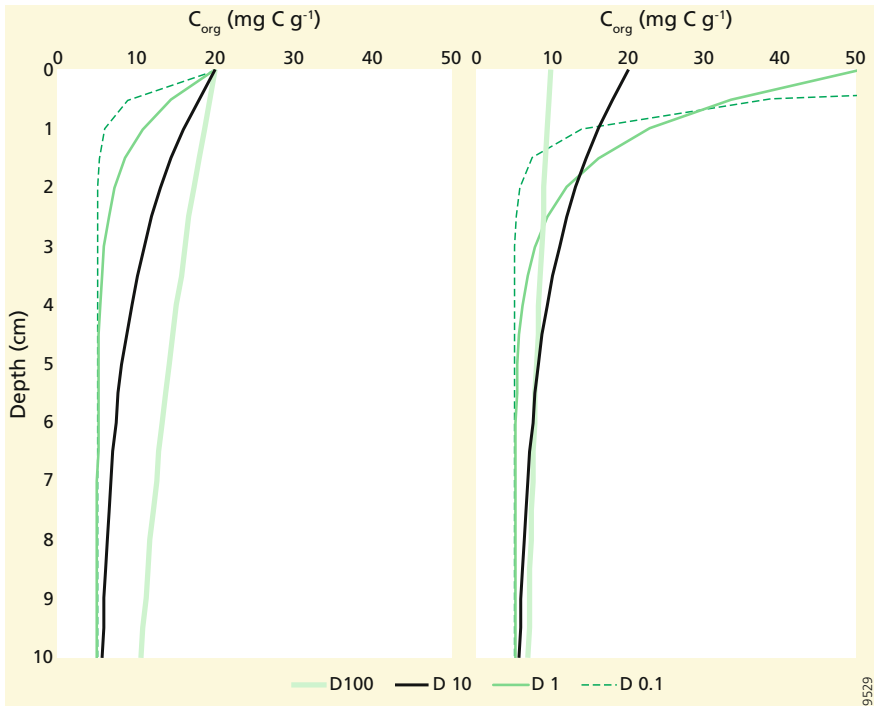
$$G = G_0 e^{\alpha x} \quad \text{with} \quad \alpha = \frac{w - \sqrt{w^2 + 4kD_b}}{2D_b} \quad (4.3)$$

Alternatively, if the flux of organic carbon delivered to the sediment ( $F$ ) is known the solution is:

$$G = \frac{F}{-D_b \alpha + w} e^{\alpha x}, \quad (4.4)$$

where  $\alpha$  is the same as in Eq. 4.3.

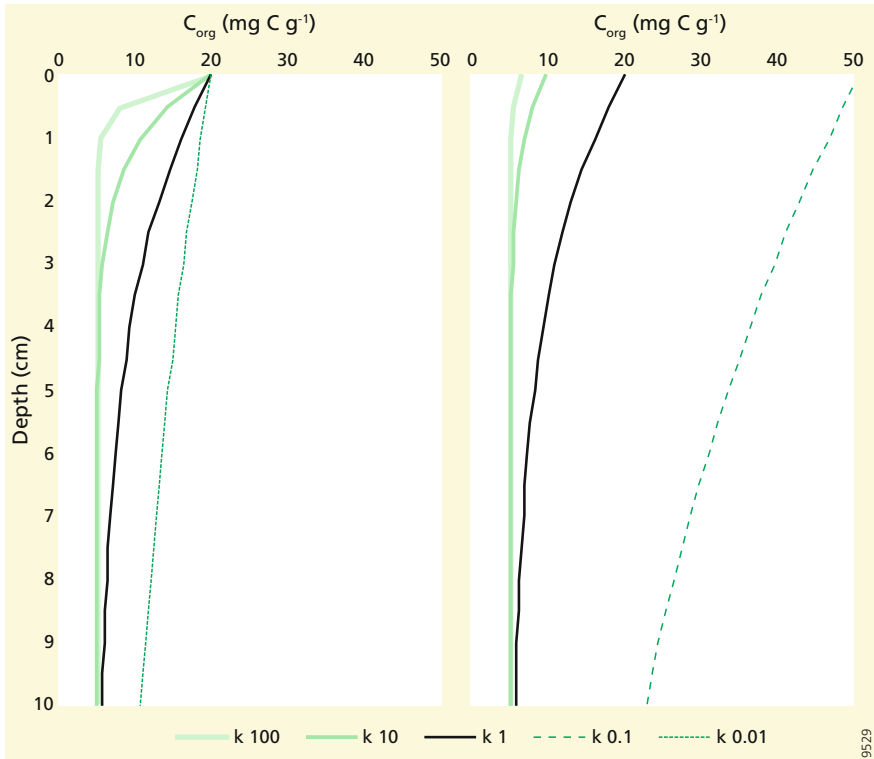
Figure 4.2 shows the distribution of organic carbon as a function of sediment depth, for a fixed reactivity and sediment accumulation rate, and for different bioturbation coefficients. The distribution of organic carbon declines exponentially with depth and the attenuation is to a first-approximation governed by  $\sqrt{\frac{k}{D_b}}$ , i.e. more mixing (higher  $D_b$ ) will flatten organic carbon concentration versus depth profiles (because the contribution of  $w$  to the attenuation coefficient  $\alpha$  is very small). In other words, particle mixing by moving animals will transfer organic carbon to larger depths. This is articulated in sediments with a fixed concentration in the top layer. For these sediments bioturbation will increase the total amount of organic



**Fig. 4.2** Organic carbon concentration versus depth profiles for different bioturbation coefficients (0.1, 1, 10, 100  $\text{cm}^2 \text{yr}^{-1}$ ) for a fixed concentration of 20  $\text{mg C g}^{-1}$  (left) and a fixed flux of 36  $\text{mg C cm}^{-2} \text{yr}^{-1}$  (right). The imposed flux has been tuned to generate an identical concentration at the sediment-water interface for a  $D_b$  of 10  $\text{cm}^2 \text{yr}^{-1}$ . Model parameters:  $k = 1 \text{ yr}^{-1}$ ;  $w = 0.1 \text{ cm yr}^{-1}$

matter available for the benthic community. In other words, animals have, to a certain extent, control over their food supply. The other major factor governing organic matter profiles in sediments is the reactivity of organic matter. More reactive organic matter is degraded shallower and does not penetrate as deep into the sediment as refractory organic matter (Fig. 4.3). Moreover, the inventory of organic carbon in surface sediments is higher when the reactivity of organic matter is lower, in particular for a fixed amount of carbon supplied per unit time.

Evidently, when applying this type of models, it is important to select the appropriate upper boundary conditions. While deep-sea sediments can best be described by an organic carbon flux boundary condition, the proper upper boundary condition for coastal sediments is not clear. A fixed concentration upper boundary conditions may be more appropriate for shelf systems in which lateral organic carbon fluxes dominate, e.g. due to a combination of resuspension-deposition cycles and residual tidal flow. Animals collecting organic matter in the surface sediment layer and bioturbating it to deeper layers make thus additional organic matter of high quality available to microbes. Moreover, first-order reactivity



**Fig. 4.3** Organic carbon concentration versus depth profiles for different first-order reactivity coefficients (0.1, 1, 10, 100  $\text{yr}^{-1}$ ) for a fixed concentration of 20  $\text{mg C g}^{-1}$  (left) and a fixed flux of 36  $\text{mg C cm}^{-2} \text{yr}^{-1}$  (right). The imposed flux has been tuned to generate an identical concentration at the sediment-water interface for  $k = 1 \text{ yr}^{-1}$ . Model parameters:  $D_b = 10 \text{ cm}^2 \text{yr}^{-1}$ ;  $w = 0.1 \text{ cm yr}^{-1}$

constants ( $k$ ) vary over orders of magnitude (Fig. 3.9) and unfortunately cannot be directly measured; they have to be derived by fitting a model to observations. This approach is problematic for a number of reasons. One, fitting of a model to observed organic carbon versus depth profiles allows constraining the depth attenuation coefficient  $\sqrt{\frac{k}{D_b}}$ , but not  $k$  or  $D_b$  individually (Soetaert et al. 1998; an iconic example of an identifiability problem). Two, both the organic matter reactivity and bioturbation coefficient may depend on depth within sediment. The former because organic matter at depth has on average been exposed longer to degradation and the latter due to the depth distribution of infauna that results in a depth gradient in mixing intensity.

The depth of the bioturbated zone ( $L$ ), the reactivity of organic carbon ( $k$ ) and the mixing intensity ( $D_b$ ) are all related (Boudreau 1998). If we assume that the depth of bioturbation is governed by the availability of food for animals and set a lower limit for organic carbon at depth  $L$  ( $G_L$ ) at 1% of the organic carbon at the surface ( $G_0$ ):



$$\frac{G_L}{G_0} = 0.01 = e\sqrt{\frac{k}{D_b}}L \quad (4.5)$$

Making use of  $\ln(0.01) \approx 4.6$ , this equation can be re-arranged to

$$L = 4.6\sqrt{\frac{D_b}{k}}. \quad (4.6)$$

The depth of the mixed layer is thus directly related the reactivity of the organic matter and the mixing intensity. This equation is highly similar to the more elaborate result of Boudreau (1998)  $L = 4\sqrt{\frac{9D_b}{8k}}$  that is based on a resource-feedback model. Figure 4.4 shows the depth of the bioturbated zone as a function of organic matter reactivity and bioturbation intensity. The observed range of  $D_b$  and  $k$  in marine sediments is also indicated. Bioturbation depth in marine sediments vary between 1 and 20 cm, with a global average of about 10 cm (Boudreau 1998). This can be obtained either by high mixing, if organic matter is highly reactive as in coastal sediments, or by low mixing, with less reactive matter in the deep sea.

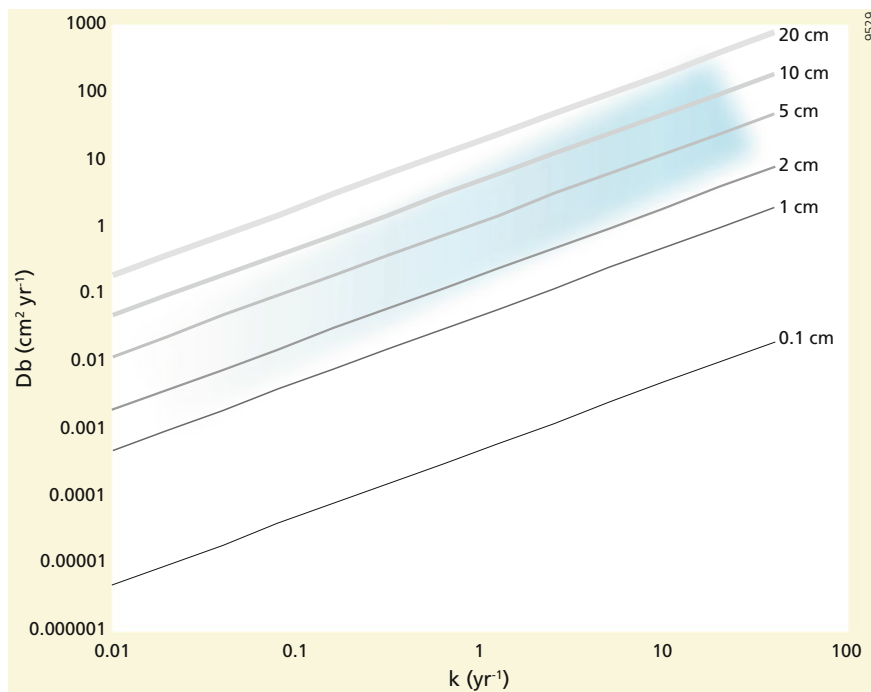
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#### 4.4 Consequences for Sediment Biogeochemistry

Degradation of organic carbon to inorganic carbon requires an electron acceptor, e.g. oxygen. In the water column, oxygen supply is usually sufficient to accept all electron released during respiration, but in sediments solutes such as oxygen are transported primarily by molecular diffusion, and oxygen supply rates often do not match oxygen consumption rates with the consequence that most sediments become anoxic at some depth. In the absence of oxygen, organic matter is either respired anaerobically or fermented. Fermentation refers to an internal redistribution of electrons among carbon atoms with the result that carbon dioxide and methane are formed.



Anaerobic respiration and fermentation of particulate organic matter involves multiple steps in a complex network: hydrolysis and fermentation of larger molecules to smaller molecules and finally the use of alternative electron acceptors (Jørgensen 2006). These intermediate products include short-chain fatty acids such as formate, acetate, propionate and butyrate, and hydrogen. The latter has a high turn-over (minutes) because of rapid production and consumption, e.g. during hydrogenotrophic processes such as carbon dioxide reduction to methane (e.g. Beulig et al. 2018).



**Fig. 4.4** Relationship between organic carbon reactivity ( $k$ ) and particle mixing ( $Db$ ) for a number of bioturbation layer depths (0.1, 1, 2, 5, 10 and 20 cm). Sediments receiving reactive organic material are more intensively mixed than those receiving refractory organic matter (blue background box). The global average bioturbation depth is about 10 cm (Boudreau 1994)

The most important alternative terminal electron acceptors are nitrate and nitrite, manganese and iron oxides and hydroxides, and sulphate, and they are used in this sequence largely because of multiple factors, including energy yield. Table 4.1 provides the overall reaction for organic carbon respiration based on nitrate, manganese oxide, iron oxide and sulphate and the corresponding change in Gibbs free energy.

The Gibbs free energy change declines from aerobic respiration to denitrification (nitrate reduction to dinitrogen gas) and metal oxide reduction to sulfate reduction because of the formation of reduced compounds (metabolites) such as ammonium, manganese (II), iron (II), hydrogen sulphide and methane (Fig. 4.5). These reduced metabolites contain a substantial amount of energy that was originally part of the organic matter. Once produced these reduced metabolites can react (after diffusion upward) with an electron acceptor (higher in the redox cascade). This re-oxidation of reduced metabolites guarantees that sediments efficiently utilize all organic matter energy delivered (Fig. 4.5). For instance, methane generated at depth can be oxidized anaerobically with sulphate, metal oxides and nitrate/nitrite and aerobically. Some of the metabolites generated (e.g. sulphide) may react with sedimentary iron containing minerals. The iron sulphide formed may be buried, but the majority

**Table 4.1** Standard gibbs free energy change of organic matter degradation pathways (based on Berner 1980)

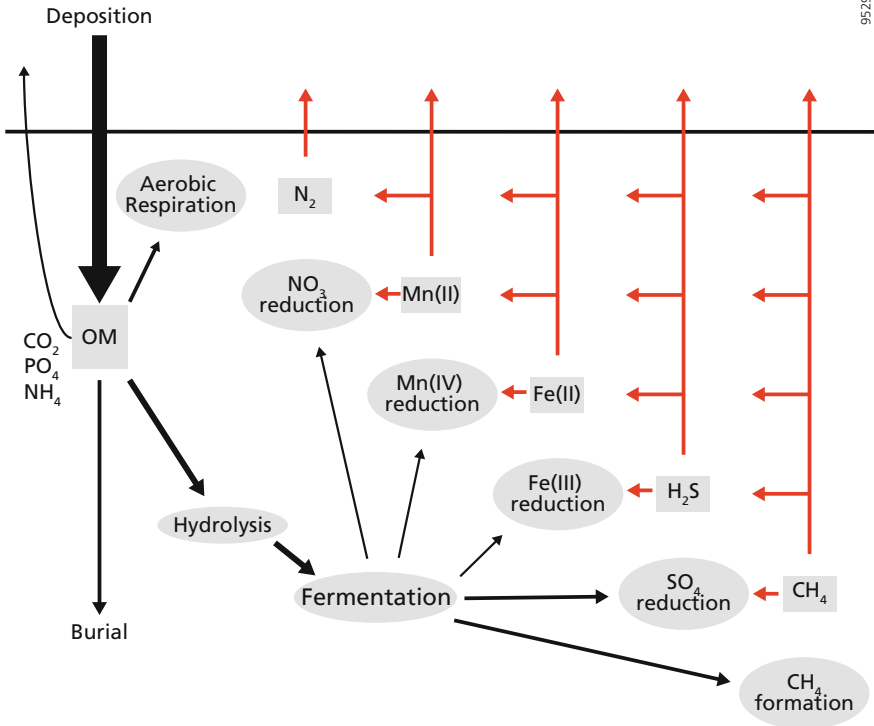
Degradation pathway	Reaction	$\Delta G^0$ (kJ mol <sup>-1</sup> of CH <sub>2</sub> O)
Aerobic respiration	$\text{CH}_2\text{O} + \text{O}_2 \Leftrightarrow \text{CO}_2 + \text{H}_2\text{O}$	-475
Denitrification	$\text{CH}_2\text{O} + 0.8 \text{NO}_3^- \Leftrightarrow 0.4 \text{N}_2 + 0.8 \text{HCO}_3^- + 0.2 \text{CO}_2 + 0.6 \text{H}_2\text{O}$	-448
Manganese oxide reduction	$\text{CH}_2\text{O} + 3 \text{CO}_2 + 2 \text{MnO}_2 + \text{H}_2\text{O} \Leftrightarrow 2 \text{Mn}^{2+} + 4 \text{HCO}_3^-$	-349
Iron(hydr)oxide reduction	$\text{CH}_2\text{O} + 7 \text{CO}_2 + 4 \text{Fe(OH)}_3 \Leftrightarrow 4 \text{Fe}^{2+} + 8 \text{HCO}_3^- + 3 \text{H}_2\text{O}$	-114
Sulfate reduction	$\text{CH}_2\text{O} + 0.5 \text{SO}_4^{2-} \Leftrightarrow 0.5 \text{H}_2\text{S} + \text{HCO}_3^-$	-77
Methanogenesis	$\text{CH}_2\text{O} \Leftrightarrow 0.5 \text{CO}_2 + 0.5 \text{CH}_4$	-58

The decrease in Gibbs free energy of the reaction results from the accumulation of energy in the reaction products, i.e. the metabolites

is usually re-oxidized after bioturbation to surface layers where oxygen or nitrate are present (Jørgensen 1977; Berner and Westrich 1985). Oxidation of these reduced metabolites often involves multiple reactions: e.g. hydrogen sulphide is oxidized to intermediate compounds such as elemental sulfur, thiosulfate and sulphite, which may then be oxidized further or disproportionated (i.e. splitted into a more reduced and more oxidized compound).

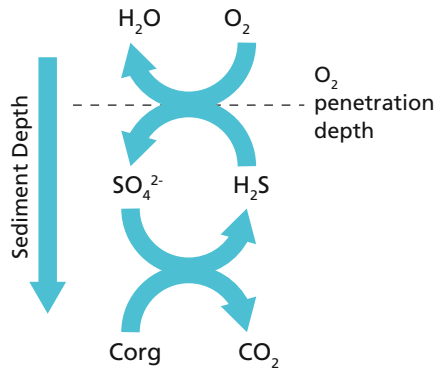
This efficient re-oxidation of reduced metabolites has two important consequences for studying the sedimentary carbon cycle. First, the energy released during re-oxidation reactions can be used to fix inorganic carbon, i.e. it supports chemolithoautotrophic processes in sediments. Chemolithoautotrophy in marine sediments is still poorly constrained, but likely on the order of 0.3–0.4 Gt C yr<sup>-1</sup> (Middelburg 2011). Secondly, total oxygen consumption is not only linked to aerobic respiration, but also includes oxygen consumption during re-oxidation processes. In organic-carbon limited sediments in the deep-sea, oxygen supply by diffusion is sufficient and all organic matter mineralization occurs aerobically, and oxygen use is primarily due to oxidation of organic carbon to carbon dioxide and nitrification (oxidation of ammonium to nitrate). In sediment with high carbon loadings, most of the oxygen consumption is due to the oxidation of reduced sulfur, iron, manganese and methane, and total oxygen consumption provides an excellent proxy for total sediment respiration irrespective of actual respiration occurred aerobically or anaerobically (Fig. 4.6). In fact, total respiration of sediments is equal to total oxygen consumption minus the burial of reduced iron and sulphide and the escape of nitrogen gas over the sediment-water interface. These contributions are usually limited to a few percent and oxygen consumption can, therefore, be used as a measurable proxy for total respiration without the need to study all microbiological reduction and oxidation processes in detail.

Oxygen distributions in sediments are normally modelled with a simple model balancing the consumption of oxygen with the diffusive supply:



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**Fig. 4.5** Conceptual model of organic matter (OM) degradation and reoxidation pathways (based on Jørgensen 2006, and Middelburg and Levin 2009). The red arrows reflect the fate of (energy-rich) substrates released during anaerobic mineralization



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**Fig. 4.6** Conceptual model of tight coupling sulfate utilization for respiration of organic carbon and sulphide oxidation by oxygen, with the net result that one mole of oxygen use corresponds with one mole of organic carbon oxidized to carbon dioxide (after Aller 1994)

$$D_s \frac{d^2 O_2}{dx^2} = R_0 \quad (4.7)$$

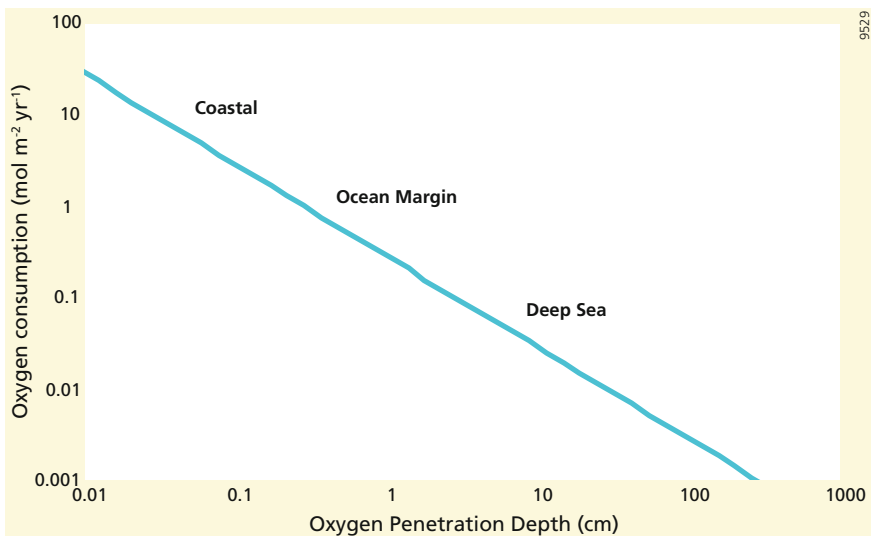
where  $O_2$  is the oxygen concentration,  $D_s$  is the diffusion coefficient of oxygen in sediments and  $R_0$  is the consumption of oxygen. Oxygen consumption rates can be described with a depth and oxygen concentration independent rate because re-oxidation is the dominant oxygen sink. The solution for this zero-order kinetics equation with a fixed concentration at the sediment-water interface ( $C_0$ ) is (Bouldin 1968):

$$C = \frac{R_0}{2D_s} x^2 - \left( \sqrt{\frac{2C_0 R_0}{D_s}} \right) x + C_0 = C_0 \left( 1 - \frac{x}{\delta} \right)^2 \quad (4.8)$$

where  $\delta$  is the oxygen penetration depth:

$$\delta = \sqrt{\frac{2C_0 D_s}{R_0}} \quad (4.9)$$

This relation shows that the oxygen penetration depth is inversely related to the total respiration. High respiration rates in coastal sediment result in shallow oxygen penetration (mm scale), while low respiration rates in organic carbon starved deep-sea sediments allow oxygen penetration to meters (Fig. 4.7). Moreover, oxygen penetration depth exhibits a square-root dependence on bottom-water oxygen levels ( $C_0$ ).



**Fig. 4.7** The relationship between oxygen consumption and oxygen penetration depth. High fluxes of oxygen into sediments imply shallow penetration. Oxygen penetration varies from <1 mm in coastal sediments to >1 m in deep-sea sediment receiving low carbon loadings

## 4.5 Factors Governing Organic Carbon Burial

Following active carbon degradation in the water column and continued mineralization in surface sediments, at some depth in the sediment all labile organic matter has been utilized and a background level of organic carbon remains (Figs. 4.2 and 4.3). This organic carbon is buried down with the accretion of sediments. Organic carbon burial is, thus, the product of sediment accumulation and organic carbon content:

$$F_B = w(1 - \phi)\rho_s G \quad (4.10)$$

where  $w$  is the sediment accumulation rate ( $\text{cm yr}^{-1}$ ),  $\phi$  is the porosity,  $\rho_s$  is the dry density ( $\text{gr cm}^{-3}$ ),  $G$  is the concentration of organic carbon ( $\text{g C gr}^{-1}$ ), with  $F_B$  expressed in  $\text{g C cm}^{-2} \text{yr}^{-1}$ . It is important to realize that  $w$  refers to the long-term accumulation rate at depth and not the rate of sediment deposition at the surface. The concentration of organic carbon should theoretically be at the depth where no further degradation occurs. Such a depth would not exist if organic matter decay follows a reactive continuum: organic matter is reactive on all timescale. However, in most sediments organic carbon concentration rapidly declines with depth and then remains almost invariant. The precise reference depth is not so important as long the gradient can be neglected.

Differences in organic carbon burial are primarily determined by differences in sediment accumulation and carbon contents, and only secondarily by differences in porosity and density. Sediment porosities vary 0.4–0.8 and dry sediment densities from  $2.6 \text{ gr cm}^{-3}$  for mineral to  $\sim 2.0 \text{ gr cm}^{-3}$  for peaty sediment. Organic carbon concentrations depend on the carbon input to sediments and the extent of decay before burial. Any process that enhances organic carbon input or impedes degradation elevates organic carbon concentration at depth and consequently carbon burial. These two factors relate directly to the old discussion on whether high export production (carbon delivery to sediment) or an oxygen related effect on preservation governs burial of organic carbon. The idea is that organic matter degradation in the presence of oxygen is more efficient than without (Box 4.2).

The by far most important factor governing organic carbon burial is the delivery of inorganic particles that results in sediment accretion. Sediment accumulation in the ocean vary about four to five orders of magnitude, from less than 0.1 cm per thousand year in the deep-sea to centimetres per year in rapidly accumulating coastal sediments (Aller 2013). Most organic carbon burial, therefore, occurs in coastal sediments. An increase in inorganic particle deposition should, in principle, not increase carbon burial, because the organic carbon will just be diluted, but observations show otherwise. In nature, particulate organic carbon is mainly associated with mineral surfaces and the higher the accumulation of minerals, the more mineral surfaces, with associated organic matter, are buried. Vegetated coastal sediments are another site of high organic carbon burial for two reasons. First, the presence of macrophytes stabilizes sediment and enhances deposition via canopy trapping of particles. Secondly, the net ecosystem carbon balance of these

communities results in the accumulation of plant derived organic matter. The following flux balance can be used to investigate the impact of sediment accretion and net ecosystem production on the burial of organic carbon in vegetated sediments:

$$w(1 - \phi)\rho_s C_{\text{external}} + \rho_{\text{organic}} C_{\text{toM}} \text{NEP} = w(1 - \phi)\rho_s C_{\text{buried}} \quad (4.11)$$

where  $w$  is sediment accumulation rate ( $\text{cm yr}^{-1}$ ),  $\phi$  is the porosity,  $\rho_s$  is the dry density of bulk sediment ( $\text{gr cm}^{-3}$ ),  $C_{\text{external}}$  is the concentration of organic carbon ( $\text{g C gr}^{-1}$ ) in deposited sediments remaining after degradation,  $\rho_{\text{organic}}$  is the density of plant organic material,  $C_{\text{toM}}$  converts organic C to organic matter, and  $C_{\text{buried}}$  is the concentration of buried organic matter. Primary production in cordgrass habitats is very high ( $\sim 2 \text{ kg C m}^{-2} \text{ yr}^{-1}$ ) with net carbon accretion of  $\sim 0.3 \text{ kg C m}^{-2} \text{ yr}^{-1}$  (Middelburg et al. 1997). If all that cordgrass detritus is retained in the system, marsh sediment accretion would be  $\sim 0.5 \text{ mm}$  per year, not enough for keeping pace with accelerated global sea-level rise ( $>2 \text{ mm}$  per year) and a mineral starved, peaty marsh may therefore drown. The combined effect of enhanced particle trapping and retention and macrophyte derived organic matter are the reason that vegetated coastal sediments represent a major term in global marine carbon burial, i.e. blue carbon (Duarte 2017).

#### Box 4.1: Bioturbation

Bioturbation refers to the reworking of sediments (particles and water) due to the activities of organisms, in particular animals (Meysman et al. 2006). This reworking has many consequences, including the creation of a three-dimensional, heterogeneous distribution of sediment properties. In fact, this animal induced heterogeneity is clear from sediments deposited during the last 0.5 billion years and palaeontologists have therefore named this period Phanerozoic, after the old greek words *phanerós* (visible) and *zōé* (life). Moreover, the small-scale heterogeneity stimulates biogeochemical and biological diversity. It also has consequences for porosity, permeability, sediment stability and roughness.

Besides these effects on sediment properties and characteristics, animal activities have a major impact on the transport of particles and solutes. Particle mixing, bioturbation *sensu stricto*, occurs through the construction and maintenance of structures such as burrows and the movement of particles while feeding (ingestion and defecation). Particles are moved vertically and horizontally, but the consequences are usually more prominent vertically because most sediment characteristics show strong vertical gradients. The particles dispersed may be reactive or unreactive minerals, organic matter as well as organisms and their cysts, eggs and remains. Many animals construct and live in burrows and ventilate these with overlying oxygenated water for respiration or food supply. In permeable sediments, this burrow water can enter the sediments and in permeable and non-permeable sediments diffusive exchange occurs between burrows and adjacent sediments because of

concentration gradients. Many animals are involved in particle mixing and ventilation. Particle mixing is pivotal for optimal functioning of sediments: organic matter and solid-phase oxidants such as iron oxides are mixed downwards, while reduced substance such as iron sulphides are mixed upwards. Bio-irrigation enhances exchange of oxygen, nutrients and other substances between water and sediment.

Particle mixing is the result of multiple activities of a diverse assemblage of large animals. While the behaviour of certain species may cause a distinct particle transport pattern, the net result of many particle mixing events can normally be described very well as diffusion. Bioturbation is then quantified in terms of a biodiffusion coefficient for particles ( $D_b$ ;  $\text{cm}^2 \text{yr}^{-1}$ ). This biodiffusion coefficient can be derived from modelling concentration versus depth profiles of a tracer A with a known reactivity (e.g. radioactive decay). Equation 4.12 balances transport due to sediment accumulation and biodiffusion with radioactive decay at steady state:

$$0 = D_b \frac{d^2 A}{dx^2} - w \frac{dA}{dx} - kA \quad (4.12)$$

where  $w$  is the sediment accumulation rate ( $\text{cm yr}^{-1}$ ) and  $k$  is the radioactive decay constant ( $\text{yr}^{-1}$ ). These macroscopic empirical  $D_b$  values can be decomposed into discrete particle properties step length ( $\lambda$ ) and the period between two displacements ( $\tau$ ) (Meysman et al. 2010):

$$D_b = \frac{\lambda^2}{2\tau} \quad (4.13)$$

The step length of particle displacement scales with organism size, and it is for this reason that meiofauna and similarly sized organisms contribute little to particle displacement.

#### Box 4.2: Oxygen and Organic Matter Preservation

The impact of oxygen on organic matter degradation and preservation has been studied extensively because of its relevance for the formation of oil and gas source rocks, the reconstruction of paleoenvironments, and the projection of carbon cycling in the future warmer, low oxygen ocean. Although most of the evidence is correlative, there is now consensus that more organic carbon is preserved under low oxygen conditions (Middelburg and Levin 2009). Experimental studies have shown that oxygen has little if any impact on microbial organic matter degradation, but is needed for the degradation of the



most refractory fraction of sediment organic carbon (Hulthe et al. 1998). Natural experiments provided by turbidite deposition and cyclic de-oxygenation events have revealed that organic matter preserved under anoxic conditions can be re-activated when exposed to dissolved oxygen (Moodley et al. 2005). Bottom-water oxygen levels have been shown to increase the carbon burial efficiency and the amount of carbon preserved per unit area of reactive surface area (Canfield 1994; Hartnett et al. 1998). Lack of oxygen not only increases the quantity of organic carbon buried, but also its nature. Organic carbon buried under anoxic conditions is usually less degraded and that is reflected in organic matter proxies (see Chap. 6), such as hydrogen index and the amino-acid degradation index (Middelburg and Levin 2009). Elevated organic carbon burial under anoxic conditions is a negative feedback in Earth System dynamics.

Although the impact of dissolved oxygen on carbon preservation has been well documented, and we have made progress studying the implications, there is still little understanding of why there is more organic carbon burial under anoxic conditions. Most organic matter is buried in ocean margin and coastal sediments that are anoxic below a few mm to cm, irrespective of the presence of oxygen in the bottom waters. This implies that the dissolved oxygen effect should be either pre-depositional or related to the changes in the benthic community processing the delivered organic matter. There is evidence for both. Organic carbon flux attenuation in an anoxic water column is less than that in an oxic water column, perhaps due to the absence of zooplankton under anoxic conditions, and the organic matter delivered to anoxic sediments appears to be less reactive towards degradation (Keil et al. 2016). Changes in bottom-water oxygen levels have consequences for the benthic community composition because of the decrease or disappearance of animals (Jessen et al. 2017). Benthic animals play a major role in sediment ecosystem functioning, through their interactions with microbes: particle mixing delivers labile organic carbon to microbes living at depth and bio-irrigation provides microbes with fluctuating oxygen levels, so that they can efficiently process organic matter (Aller 2013).

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