

5.09 Estuarine and Coastal Sediments – Coupled Biogeochemical Cycling

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Abstract

A variety of macroscopic physical and biological forcing functions act on estuarine and coastal sediments across a range of time and space scales, and can have a profound effect on the processes associated with the remineralization of sedimentary organic matter. These interactions exert a strong influence on the cycling of biogeochemically reactive elements (C, N, S, P and trace metals such as Mn and Fe), and result in linkages between and within these cycles that are far more complex than once envisioned. Biogeochemical processes in estuarine and coastal sediments also have implications on benthic–pelagic coupling in estuaries and the coastal ocean, and on some global oceanic cycles and biogeochemical budgets.

5.09.1 Introduction

Estuarine and coastal marine sediments are impacted by a wide range of macroscopic physical and biological forcings that occur over a broad range of time and space scales. These include, for example, bioturbation and bioirrigation by benthic macrofauna, pore-water advective exchange driven by near-seabed pressure gradients, oxygen input through macrophyte roots, and large-scale physical mixing (reworking) of the sediments by tides, surface currents, or storms. The interplay between these forcings and biological (largely microbial)

processes directly or indirectly associated with the remineralization of sedimentary organic matter has a significant impact on the biogeochemical cycling of elements such as carbon, nitrogen, phosphorus, sulfur, and many trace metals, including manganese and iron. Furthermore, because estuarine and coastal systems are relatively shallow, biogeochemical processes that occur in the underlying sediments tend to have a greater overall impact on the dynamics of estuaries and the coastal ocean as a whole.

With this in mind, the goal of this chapter is to present an integrated view of estuarine and coastal sediment

biogeochemistry, focusing on these considerations. First, the chapter briefly describes the key biogeochemical processes that occur in these sediments, using the biogeochemical zonation model (Claypool and Kaplan, 1974; Froelich et al., 1979) as the framework for the discussion. Next, it discusses how an understanding of the physical and biological forcings outlined above can be used to characterize estuarine and coastal sediments based on their functional diagenetic characteristics (e.g., Aller, 2004). The remaining sections then link these two discussions together to provide a unified discussion of the coupled biogeochemical processes that occur in estuarine and coastal sediments.

5.09.2 Introduction to Biogeochemical Processes in Sediments

This discussion largely focuses on bacterial metabolism, in part, because there is a much greater diversity of metabolic processes among prokaryotes than there is among eukaryotes. (As used here, the term 'bacteria' is synonymous with 'prokaryotes'. Except where specifically noted, it therefore includes organisms in the group *Archaea*, cyanobacteria, and true bacteria or eubacteria, i.e., organisms in the group *Bacteria*.) Most bacterial processes that impact sediment biogeochemistry result from dissimilatory metabolism (energy-acquiring processes), although assimilatory processes (i.e., production of new bacterial biomass) may be important in some aspects of sediment organic carbon remineralization and preservation (Burdige, 2006).

Bacterial biomass dominates the total benthic biomass in many, but not all, marine sediments (Aller, 1998; Alongi, 1998; Fenchel et al., 1998). Furthermore, because of their relatively large surface-to-volume ratio as compared to higher, eukaryotic organisms, bacterial metabolic processes (on a per organism volume basis) can have a much greater impact on overall sediment metabolism, even if they represent only a few percent of the total benthic biomass (Nealson, 1997). Additional aspects of this problem are discussed in Section 5.09.5

All of these considerations are most pronounced in anoxic (oxygen-deficient) sediments, since only a few protozoans and fungi are capable of anaerobic metabolism. Thus, in most estuarine and coastal sediments, which are anoxic within a centimeter or two (or less) below the sediment–water interface, bacterial metabolism dominates organic matter remineralization and, therefore, drives most of the biogeochemical cycles that will be discussed here.

5.09.2.1 Organic Matter Remineralization Processes

The occurrence of specific organic matter remineralization (respiratory) processes in any natural system appears to be controlled by the free energy yield per mole of organic carbon oxidized by a specific individual electron acceptor (Claypool and Kaplan, 1974; Froelich et al., 1979). Based on this biogeochemical zonation model, the oxidant that provides the greatest amount of free energy will be utilized first, and when this oxidant is depleted then the next most efficient oxidant will be used (Table 1). In principle, this will continue until either all available oxidants are consumed or all oxidizable (metabolizable) organic carbon is utilized (e.g., Aller and Mackin, 1984).

On much of the Earth's surface and in the oceans, the amount of oxygen is sufficient relative to the amount of reduced (oxidizable) organic carbon, and aerobic respiration predominates. (Note, however, that this is not necessarily the case in all estuaries and coastal waters (see Chapter 5.05 for details).) However, in many estuarine and coastal settings, the flux of reactive organic carbon to the sediments is sufficiently high relative to O₂ transport into the sediments, and anaerobic remineralization occurs. Anaerobic remineralization processes are often referred to as suboxic remineralization (organotrophic denitrification, Mn and Fe reduction) and anoxic remineralization (sulfate reduction and methanogenesis), although strictly speaking suboxic remineralization occurs under anoxic conditions (e.g., in sediments that are devoid of oxygen; see Canfield and Thamdrup, 2009 for an alternate view of this classification scheme for remineralization processes). If we define denitrification in a general sense as the reduction of combined nitrogen (nitrate or nitrite) to gaseous end-products (predominantly N₂), then organotrophic denitrification is a process that couples this reduction to the oxidation of organic matter (e.g., Devol, 2008). Recent studies have also shown that denitrification can be coupled with a number of other oxidative processes (Hulth et al., 2005), hence the need for a more complete description of denitrifying processes.

Under most, but not necessarily all, circumstances, anoxic sediments are defined as those in which sulfate reduction and methanogenesis occur. The biogeochemical zonation illustrated in Table 1 can also be looked from the standpoint of the redox or half cell potential (E_H) of the reduction of each of these terminal electron acceptors. This then leads to their being a gradient from positive E_H values (oxidizing conditions) in

Table 1 Standard state free energy changes for the major organic matter remineralization processes^a

Process	Chemical reaction	ΔG° (kJ mol C ⁻¹) ^b
Aerobic respiration	$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$	-471
Organotrophic denitrification	$5C_6H_{12}O_6 + 24NO_3^- \rightarrow 12N_2 + 24HCO_3^- + 6CO_2 + 18H_2O$	-444
Organotrophic manganese reduction	$C_6H_{12}O_6 + 18CO_2 + 6H_2O + 12\delta\text{-MnO}_2 \rightarrow 12Mn^{2+} + 24HCO_3^-$	-397
Organotrophic iron reduction	$C_6H_{12}O_6 + 42CO_2 + 24Fe(OH)_3 \rightarrow 24Fe^{2+} + 48HCO_3^- + 18H_2O$	-131
Sulfate reduction	$2C_6H_{12}O_6 + 6SO_4^{2-} \rightarrow 6H_2S + 12HCO_3^-$	-76
Methanogenesis	$2C_6H_{12}O_6 \rightarrow 6CH_4 + 6CO_2$	-49

^a Data for C₆H₁₂O₆, δ-MnO₂, and Fe(OH)₃ are for glucose, fine-grained vernadite, and amorphous ferric oxide, respectively. Values of standard free energies of formation are from Stumm and Morgan (1996).

^b To convert the values listed here to kJ mol⁻¹ of glucose, multiply by 6.

oxic regions where aerobic respiration occurs, to negative E_H values (reducing conditions) in anoxic sediments where sulfate reduction (or methanogenesis) occurs.

Many pore-water profiles, particularly in deep-sea (pelagic and hemi-pelagic) sediments, appear, to a first approximation, to be consistent with this biogeochemical zonation model (Froelich et al., 1979; Burdige, 1993). However in estuarine sediments, particularly those that are bioturbated and/or bioirrigated (Section 5.09.4.1), the distribution of biogeochemical processes in the sediments is more complex than that predicted by this relatively simple conceptual model. These systems will be referred to here as mixed redox sediments (Aller, 1994a; Burdige, 2001), although in the literature they are sometimes discussed in terms of the exposure of the sediments to redox oscillations (see Section 5.09.3 for details).

It is also important to recognize that the biogeochemical zonation model is not necessarily meant to provide specific information about the controls on organic carbon remineralization and preservation in sediments (see Postma and Jakobsen, 1996), with the possible exception of the role that oxygen may play in controlling organic carbon remineralization in some sediments (Emerson et al., 1985; Calvert and Pedersen, 1992; Canfield, 1994; Burdige, 2007). Rather, the model provides information on the occurrence of different terminal electron acceptor (or respiratory) processes that comprise sediment organic carbon remineralization. Such information is of some interest since the occurrence of these specific reductive processes leads both directly and indirectly to a whole host of other processes that play important roles in the overall biogeochemistry of marine sediments. Therefore in spite of its limitations, the biogeochemical zonation model has proved to be quite useful for understanding many aspects of marine sediment biogeochemistry.

5.09.2.1.1 The anaerobic food chain for organic matter remineralization

The anaerobic decomposition of organic matter in sediments occurs in a stepwise manner, involving a consortium of several different functional groups of bacteria (Laanbroek and Veldkamp, 1982; Capone and Kiene, 1988; Fenchel et al., 1998). During this sequence the end product of one process becomes the reactant for the next process, such that in each reaction in the sequence the responsible organism acquires only a portion of the total energy available from the substrate being utilized, passing on the remaining energy in the end products it produces. Because these microbial processes are tightly coupled, the net reaction (i.e., the sum of these processes) can be expressed by the equations in Table 1, despite the fact that the terminal respiration process (e.g., sulfate reduction) is only responsible for the last portion of the overall decomposition sequence (see Burdige (2006) for additional discussions of this anaerobic food chain).

The first process here involves the breakdown (by solubilization, hydrolysis, or oxidative cleavage) of particulate organic matter, followed by processes such as fermentation that produce and consume dissolved organic matter (DOM) compounds of increasingly smaller molecular weights. This eventually leads to the production of a limited number of LMW-DOM compounds, primarily short chain fatty acids such as acetate and formate. These compounds, along with H_2 (also a fermentation end product), are then consumed by

the terminal respiratory organisms in the sediments. Competition for these key substrates also provides the kinetic mechanism by which the thermodynamic basis of the biogeochemical zonation model expresses the observed zonation of processes. For example, significant amounts of methane production occur only in the absence of sulfate, and based on lab and field studies, this occurs because sulfate reducers outcompete methanogens for acetate and H_2 , key substrates that are used by both groups of organisms (Crill and Martens, 1986; Fauque, 1995; Winfrey and Zeikus, 1977).

This anaerobic food chain model and competition for key substrates also appear to explain the zonation of iron reduction, sulfate reduction, and methanogenesis in freshwater sediments (Lovley and Phillips, 1987; Lovley, 1991), and may describe, in general, the zonation of all suboxic and anoxic processes in estuarine and marine sediments (see discussions in Thamdrup, 2000). However, this latter observation is not well tested.

5.09.2.2 Chemolithotrophic Reactions

In addition to organic matter respiration (i.e., redox reactions involving reduced organic carbon substrates), redox reactions involving only inorganic substances also occur in sediments. Many of these reactions are microbially mediated, by organisms generally referred to as chemoautotrophs or chemolithotrophs. For the most part, these organisms are autotrophs, and use the chemical energy obtained from these reactions to fix carbon and produce new biomass. However, some of these organisms can also assimilate fixed (reduced) carbon compounds from the environment for biomass production.

5.09.2.2.1 Aerobic processes

During anaerobic respiration, a number of reduced end products are produced whose oxidation by O_2 is thermodynamically favored (i.e., the reaction has a negative ΔG°). These compounds include ammonium, methane, reduced iron, and manganese, and several reduced forms of sulfur (e.g., sulfide and elemental sulfur).

Aerobic methane oxidation (methanotrophy) is an important process in many sediments (see Hanson and Hanson, 1996 for a review), and the balance between methane oxidation (both aerobic and anaerobic; see Section 5.09.9) and methanogenesis plays a key role in regulating the methane flux to the atmosphere from aquatic environments (Reeburgh, 2007). Ammonium oxidation, or nitrification, is an extremely common process in nature, both in sediments and in the water column (Ward, 2008). It occurs in two steps, with ammonium first being oxidized to nitrite by one group of organisms, and nitrite to nitrate by another group. The ammonium used in nitrification generally comes from particulate organic nitrogen that is regenerated during aerobic respiration. However in many types of sediments, ammonium produced at depth in the sediments by anoxic remineralization can then be nitrified in the oxic portion of the sediments (see Burdige, 2006 for details). While much of this nitrate may be subsequently consumed by organotrophic denitrification in the sediments, recent work on the anammox reaction (see reaction 1 in Table 2) suggests that the specific mechanism(s) of ammonium loss from sediments needs further examination

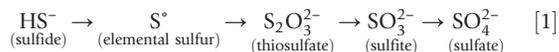
Table 2 Some possible anaerobic (non-O₂ utilizing) oxidation reactions that may occur in marine sediments^a

Process	Chemical reaction	ΔG (pH = 7)	ΔG (pH = 8)
<i>Reactions coupled to NO₃⁻ reduction (units: kJ mol nitrate⁻¹)</i>			
1. Anammox	NH ₄ ⁺ + NO ₂ ⁻ → N ₂ + 2H ₂ O	-302	-302
1a. Anammox ^b	5/3NH ₄ ⁺ + NO ₃ ⁻ → 4/3 N ₂ + 3H ₂ O + 2/3H ⁺	-421	-425
2. Denitrification coupled to sulfide oxidation	NO ₃ ⁻ + 5/8FeS + H ⁺ → 1/2N ₂ + 5/8SO ₄ ²⁻ + 5/8Fe ²⁺ + 1/2H ₂ O	-419	-413
3. Denitrification coupled to Fe ²⁺ oxidation	NO ₃ ⁻ + 5Fe ²⁺ + 12H ₂ O → 5Fe(OH) ₃ + 1/2N ₂ + 4 H ⁺	-319	-370
4. Denitrification coupled to Mn ²⁺ oxidation	5/2Mn ²⁺ + NO ₃ ⁻ + 2H ₂ O → 5/2MnO ₂ + 1/2N ₂ + 4H ⁺	-49	-71
<i>Reactions coupled to manganese reduction (units: kJ mol MnO₂⁻¹)</i>			
5. Anoxic nitrification	4MnO ₂ + NH ₄ ⁺ + 6H ⁺ → 4Mn ²⁺ + NO ₃ ⁻ + 5H ₂ O	-44	-35
6. Mn reduction coupled to oxidative N ₂ production	3/2MnO ₂ + NH ₄ ⁺ + 2H ⁺ → 3/2Mn ²⁺ + 1/2N ₂ + 3H ₂ O	-150	-141
7. Mn reduction coupled to complete sulfide oxidation	2H ⁺ + MnO ₂ + 1/4FeS → Mn ²⁺ + 1/4SO ₄ ²⁻ + 1/4Fe ²⁺ + H ₂ O	-148	-137
8. Mn reduction coupled to partial sulfide oxidation	3H ⁺ + MnO ₂ + HS ⁻ → Mn ²⁺ + S ⁰ + 2 H ₂ O	-136	-119
9. Mn reduction coupled to iron oxidation	MnO ₂ + 2Fe ²⁺ + 4H ₂ O → Mn ²⁺ + 2Fe(OH) ₃ + 2H ⁺	-42	-127

^a The following conditions were used to calculate ΔG values: $T = 25$ °C; [NO₃⁻] = 5 μ M; [NO₂⁻] = 5 μ M; [NH₄⁺] = 25 μ M; pN₂ = 0.791 atm.; [Mn²⁺] = 100 μ M; [Fe²⁺] = 5 μ M; [SO₄²⁻] = 24 mM; [H₂S] = 25 μ M; [HS⁻] = 5 μ M. Activity coefficients were assumed to be 1. Values for the standard free energies of formation (ΔG°) were taken from Stumm and Morgan (1996).

^b Although anammox organisms appear to use nitrite (rather than nitrate) as the electron acceptor, the source of this nitrite in natural systems is generally the reduction of nitrate (see Section 5.09.6.1 for details). Hence, the biogeochemistry of this process is often thought of in terms N₂ production via nitrate reduction coupled to ammonium oxidation. Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton; and Hulth, S., Aller, R.C., Gilbert, F., 1999. Coupled anoxic nitrification/manganese reduction in marine sediments. *Geochimica et Cosmochimica Acta* 63, 49–66.

(see Section 5.09.6.1). The bacterial oxidation of reduced sulfur species involves several oxidation reactions that eventually produce sulfate:



This complete oxidative process may actually involve several groups of organisms, each mediating only a portion of the overall sequence, which then results in the transient production of partially oxidized intermediates such as elemental sulfur or thiosulfate. Many of these organisms (e.g., *Beggiatoa*, *Thioplaca*, and *Thiothrix*) often form mats on the sediment–water interface, allowing them to use bottom water O₂ to oxidize sulfide that diffuses upward toward the sediment surface (see Levin et al., 2009 for a recent review). These organisms are also capable of using nitrate in place of O₂ as an electron acceptor (see Section 5.09.2.2 and Schulz and Jørgensen, 2001). The cycling of many of the intermediates in eqn [1] is an important part of sulfur dynamics in some environments (Canfield et al., 2005). However in many cases, the net oxidation of sulfide to sulfate is of most geochemical significance.

The oxidation of reduced iron and manganese (Fe²⁺ and Mn²⁺) can also be biologically mediated, although at pH values typical of most marine sediments, abiotic (chemical) iron oxidation is extremely rapid (Stumm and Morgan, 1996) and likely outcompetes biological oxidation (Nealson, 1997). In contrast, Mn²⁺ is much more kinetically stable in the presence of oxygen at natural pH values, and its oxidation by O₂ is often times biologically catalyzed. The majority of the manganese oxidation occurring in sediments appears to be biologically catalyzed (Thamdrup et al., 1994b; Tebo et al., 1997), although unlike the other chemolithotrophic processes discussed in this section, evidence that manganese-oxidizing bacteria gain energy for growth at the expense of this oxidation reaction remains equivocal (Tebo et al., 1997).

5.09.2.2.2 Anaerobic processes

Field observations also suggest that a wide range of other inorganic oxidation reactions may occur in marine sediments using nitrate (or nitrite) and manganese oxides, rather than O₂, as the oxidant (Aller and Rude, 1988; Bender et al., 1989; Aller, 1994b; Luther et al., 1997; Aller et al., 1998; Hulth et al., 1999; Anschutz et al., 2000; Thamdrup, 2000; Schippers and Jørgensen, 2001; Mortimer et al., 2002; Thamdrup and Dalsgaard, 2002; Trimmer et al., 2003; Mortimer et al., 2004; Engström et al., 2005; Bartlett et al., 2008). Under natural conditions, these reactions have negative ΔG values (see Table 2), and therefore chemolithotrophic bacteria should be able to couple these reactions to carbon fixation. These reactions generally occur in the absence of oxygen (i.e., suboxic or anoxic conditions), or under what is referred to as mixed redox conditions (see Sections 5.09.2.3 and 5.09.3 for details).

While many of the geochemical studies cited above are indeed consistent with these anaerobic oxidation reactions being biologically mediated, certain of the reactions can occur abiotically. For example, manganese reduction coupled to iron oxidation (reaction 9 in Table 2) is important in other biogeochemical processes in sediments (Burdige, 2006), although its kinetics are sufficiently rapid and the process likely occurs abiotically (Myers and Nealson, 1988a; Burdige et al., 1992). At the same time, for some reactions listed in Table 2 evidence for their occurrence is equivocal; for example, recent studies in the suboxic waters of the Black Sea were unable to demonstrate the occurrence of denitrification coupled to Mn²⁺ oxidation (reaction 4 in Table 2; Schippers et al., 2005; Clement et al., 2009).

A final point to consider is that in many cases the organisms responsible for these anaerobic oxidation reactions have not yet been isolated and/or studied in pure culture. Exceptions to this do exist, that is, for denitrification coupled to Fe²⁺ oxidation (Straub et al., 1996) or to sulfide oxidation (Schulz and Jørgensen, 2001). However, such observations should not be

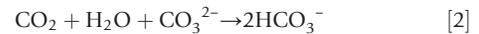
taken as evidence for lack of microbial involvement in any of these reactions, since the overwhelming majority of bacterial species thought to exist in nature have yet to be isolated in pure culture and grown in the lab. The same observation is also true of microbial phyla that have been identified in natural samples based solely on genetic sequences (16S rRNA) isolated from these samples (Schloss and Handelsman, 2004).

5.09.2.3 Linkages between Chemolithotrophic and Organic Matter Remineralization Processes

Many of the chemolithotrophic reactions described above involve the oxidation of reduced end products of anoxic and suboxic respiration. In many sediments, this leads to the internal redox cycling of these elements, such that aerobic chemolithotrophic or abiotic oxidative processes are coupled with suboxic, or anoxic, organic matter remineralization (Figure 1(a)). These processes can then be thought of as electron shuttles that bring O_2 oxidation equivalents into deeper anoxic (O_2 -devoid) portions of the sediments (Jørgensen, 1982a; Burdige and Nealson, 1986; Aller, 1994b). Thus, in a net sense O_2 appears to be the oxidant of organic matter in the sediments, despite the fact that the actual remineralization occurs by anoxic, or suboxic, metabolism (also see related discussions in Aller, 1994a and Thamdrup and Canfield, 2000). While this coupling can occur through pore-water diffusive processes, more often it is mediated by macrofaunal activity, that is, bioturbation and bioirrigation, or macrophyte O_2 input (see Sections 5.09.3, 5.09.4.1 and 5.09.4.5 for

details). This coupling implies that redox-sensitive metals such as Mn and Fe can undergo repetitive oxidation–reduction cycles before ultimately being buried in sediments (see Section 5.09.7).

This type of sulfur redox cycling also has an important impact on the sulfur isotope record in sediments and sedimentary rocks (Canfield et al., 2005), as well as on the occurrence of carbonate dissolution or authigenic carbonate precipitation in estuarine and coastal sediments. In situations where there is no net sulfate reduction (i.e., sulfate reduction and sulfide oxidation are balanced as in Figure 1(a)), net CO_2 production occurs when the acid produced during sulfide oxidation protonates the bicarbonate produced by sulfate reduction, thus forming aqueous CO_2 . This CO_2 neutralizes dissolved carbonate ion in the pore waters, according to,



and lowers the saturation state of the pore waters with respect to the most soluble carbonate mineral present in the sediments. Once the pore waters become sufficiently undersaturated with respect to this phase, continued CO_2 production then drives the dissolution of sedimentary carbonate (Burdige and Zimmerman, 2002; Burdige et al., 2008).

At the other extreme are systems where net sulfate reduction occurs, or where the couplings between chemolithotrophic and suboxic or anoxic organic matter remineralization processes are more complex (see Figure 1(b) and discussions below). Here, bicarbonate (rather than aqueous CO_2) is the ultimate dissolved inorganic carbon end product. This then leads to an alkalinity buildup that eventually results in carbonate mineral precipitation (Sholkovitz, 1973; Suess, 1979; Aller and Rude, 1988; Canfield and Raiswell, 1991a; Aller et al., 1996).

This latter situation also illustrates how anaerobic chemolithotrophic may be coupled with aerobic chemolithotrophic processes as well as suboxic or anoxic organic matter remineralization (Figure 1(b)). Here, elements such as manganese and sulfur may actually undergo more complex internal redox cycling than that described above (i.e., compare Figures 1(a) and 1(b)). The occurrence of such interactions suggests that the sediment biogeochemical cycles of Mn, Fe, N, S, C, and O_2 may be closely coupled and more complex than previously thought. These processes not only have important implications on the internal dynamics of sediment processes, but may also impact net sediment (and perhaps global) budgets of these elements.

An important consequence of these interactions is that in many cases sediment oxygen uptake (also sometimes referred to as sediment oxygen demand) results not only from aerobic respiration but also from the oxidation of reduced compounds such as sulfide (dissolved and solid FeS and FeS_2), ammonium, Fe^{2+} , and Mn^{2+} (Mackin and Swider, 1989; Sampou and Oviatt, 1991; Rysgaard et al., 1998; Berg et al., 2003; Glud et al., 2003). Furthermore, these processes are often tightly coupled, such that there is no significant net loss of reduced intermediates during this redox cycling by, for example, sulfide burial, benthic N_2 gas flux, or benthic fluxes of dissolved Mn^{2+} . Under these circumstances, sediment oxygen uptake that occurs by a combination of aerobic respiration, chemolithotrophic reactions, and/or abiotic chemical oxidation still provides a reasonably good estimate of the total (depth-integrated) rate of sediment organic carbon oxidation (i.e., oxic, suboxic plus

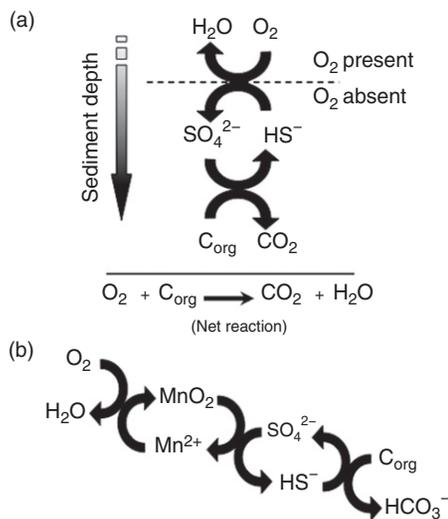


Figure 1 (a) A schematic representation of the coupling between bacterial sulfate reduction and sulfide oxidation, such that in a net biogeochemical sense O_2 appears to be the electron acceptor used in the remineralization of sedimentary organic matter. (b) A more complex coupling of oxygen, manganese, sulfur, and organic carbon redox cycling that may occur in some marine sediments. Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton based on Aller, R.C., 1994b. The sedimentary Mn cycle in Long Island Sound: its role as intermediate oxidant and the influence of bioturbation, O_2 , and C_{org} flux on diagenetic reaction balances. *Journal of Marine Research* 52, 259–295 and Burdige, D.J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. *Earth-Science Reviews* 35, 249–284.

anoxic remineralization; referred to here as R_{cox}), even though aerobic respiration is only a fraction of the total sediment oxygen uptake (Canfield et al., 1993a; Soetaert et al., 1996; Thamdrup et al., 2007). In situations where there is net loss of reduced metabolites (e.g., sulfide burial in sediments), these other processes can, however, also be quantified and incorporated (along with, e.g., sediment O_2 uptake measurements) into estimates of R_{cox} (Berelson et al., 1996; Thamdrup and Canfield, 2000). This may be particularly important in low salinity (or extremely organic-rich), estuarine sediments, where methane loss from the sediments (e.g., gas ebullition) uncouples sediment oxygen uptake and sediment organic carbon remineralization (Martens and Klump, 1984; Kelley et al., 1990; Middelburg et al., 1996a).

The discussion above pertains solely to sediments that are in steady state, based on the observation that under steady-state conditions, solute fluxes across the sediment–water interface are balanced by (i.e., are equal to) their depth-integrated rates of sediment production or consumption (see Burdige, 2006). However, the question of steady state can often be one of observational timescales, since estuarine and coastal sediments that clearly show seasonal variability in, for example, pore-water profiles or measured rates of sediment processes (i.e., the sediments are in non-steady-state on short timescales) may actually be in steady state on annual timescales (see the next section for more details as well as Klump and Martens, 1989; Martens et al., 1992; Soetaert et al., 1996; and Burdige and Zheng, 1998). One particular aspect of this behavior is that it can result in a temporal uncoupling of anoxic remineralization reactions and their corresponding (chemolithotrophic) re-oxidation reactions, leading to the seasonal in-growth and subsequent removal of reduced inorganic compounds in the sediments (Luther et al., 1991; Sampou and Oviatt, 1991; Therkildsen and Lomstein, 1993; Thamdrup et al., 1994a; Green and Aller, 1998; Thamdrup and Canfield, 2000).

In contrast, the non-steady-state conditions occurring in physically reworked margin sediments such as those on the Amazon shelf (Section 5.09.4.2) result in a more complex uncoupling of sediment O_2 uptake from the cycling of reduced metabolites. Here, estimates of sediment remineralization rates based on sediment oxygen uptake are likely to be lower limits of their true value (Aller et al., 1996; McKee et al., 2004), and such sediment systems with complex transport processes and non-steady-state diagenetic conditions require the independent determination of the rates of sediment processes to ascertain estimates of the total rates of sediment organic carbon remineralization.

5.09.2.4 Seasonality and Non-Steady-State Processes in Estuarine and Coastal Sediments

Seasonality in the rates of sediment biogeochemical processes are often observed in estuarine and coastal sediments in response to: annual changes in temperature; the composition, and reactivity of carbon deposited in the sediments; bottom water conditions; or the rates of benthic macrofaunal activity (which can themselves be, in part, a function of these other parameters; see the references cited below and, Klump and Martens, 1989; Sun et al., 1991; Therkildsen and Lomstein, 1993; Aller, 1994b; Roden et al., 1995; Canuel and Martens,

1996; Gerino et al., 1998; and Marvin-DiPasquale et al., 2003). For example, in temperate sediments an annual temperature changes of up to $\sim 20^\circ\text{C}$ between winter and summer implies that remineralization rates may vary by up to a factor of ~ 8 over an annual cycle, based on the observed temperature dependence of sediment remineralization rates (Burdige, 2006). Phytoplankton production (e.g., Kemp et al., 1997) and growth of salt marsh plants (e.g., Hines, 2006) also tend to increase from spring to fall, and can result in, for example, seasonal changes in sediment POC deposition.

Seasonality in remineralization rates expresses itself in time-varying sediment pore-water profiles of remineralization end products (e.g., ammonium or phosphate). However, on these timescales diffusion damps out any seasonal periodicity in these profiles (Lasaga and Holland, 1976), and what is generally observed are smooth, asymptotic profiles whose concentrations simply grow in and out over the annual seasonal cycle (e.g., Aller, 1980a; Klump and Martens, 1989). Seasonal changes in sediment O_2 consumption also lead to the shoaling of the oxygen penetration depth during warmer months (Rysgaard et al., 1998; Glud et al., 2003; Glud, 2008; Martin, 2009). Likewise, in the organic-rich sediments of Cape Lookout Bight, NC (where sulfate reduction and methanogenesis dominate sediment organic matter remineralization), there is a seasonal shoaling in the depth of complete sulfate removal in the pore waters, from a depth of greater than ~ 20 cm during winter to ~ 10 cm (or less) during summer (Martens and Klump, 1984).

Despite non-steady-state seasonality in such sediments, under some circumstances it is possible to assume that pore-water profiles are in quasi-steady-state over short time periods (Burdige, 2006). This then allows one to apply steady-state diagenetic models to individual, time-varying pore-water profiles to estimate instantaneous sediment remineralization rates for the times of sample collection (Martens and Klump, 1984; Soetaert et al., 1996). These are therefore snapshots of the time-varying rates at a particular point in time, and are not necessarily good estimates of the rates of sediment processes on more appropriate seasonal or annual timescales. Nevertheless, to determine seasonal- or annual-average rates, one can average these instantaneous rate estimates over a seasonal cycle (e.g., Burdige and Zheng, 1998). Alternately, one can obtain this annual average rate by fitting a temporal data set of, for example, individual pore-water profiles and/or rate measurement profiles with a time-dependent model for sediment diagenesis (Klump and Martens, 1989; Soetaert et al., 1996).

On shorter timescales, non-steady-state processes may affect biogeochemical processes in sediments in a number of different ways (see Sections 5.09.4.1, 5.09.4.3, and 5.09.4.5 for further details). Episodic (or event-driven) events such as flash floods, storms, or resuspension events (wind or current driven) can also have an impact on biogeochemical processes in sediments (Fanning et al., 1982; Chanton and Whiting, 1995; Cowan et al., 1996; Deflandre et al., 2002; Mucci et al., 2003; Tengberg et al., 2003; Kalnejais et al., 2007). For example, resuspension events which move reduced constituents from the sediments to the water column may be several times more effective at re-oxidizing these constituents than is re-oxidation mediated by diffusive benthic O_2 uptake (Glud, 2008).

5.09.3 Linkages of Biogeochemical Processes and Transport Processes and the Occurrence of Mixed Redox Conditions in Sediments

As noted above, transport processes such as bioturbation or bioirrigation (Section 5.09.4.1), permeability-driven pore-water advection (Section 5.09.4.3), and solute release from macrophyte roots and rhizomes (Section 5.09.4.5) complicate the relatively simple picture of sediment biogeochemistry predicted by the biogeochemical zonation model. In terms of this solute transport, oxygen input to sediments is of particular importance, given the impact that it has on the two- and three-dimensional redox gradients that occur in sediments. In addition, a more general observation here is that these transport processes often lead to more active and dynamic cycling of redox-sensitive elements than would occur in their absence (i.e., in more strictly diffusive systems such as those described in Section 5.09.4.1). In particular, the linked chemolithotrophic and organic matter remineralization processes discussed in Section 5.09.2.3 are often an integral part of what is referred to here as mixed redox conditions. Furthermore, while all of the processes discussed here lead (in general) to more complex sediment redox cycling, differences in, for example, the spatial and temporal scales of sediment mixing, or the mechanism of oxidant input to the sediments, can lead to very different biogeochemical expressions of these forcings (Dellapenna et al., 1998; Hines, 2006). These considerations will be discussed later, in Sections 5.09.4.2 and 5.09.4.5.

When these transport processes are thought of in the context of the biogeochemical zonation model, the zonation predicted by this model may occur, for example, radially around cylindrical animal burrows (Figure 2(b)), or near-spherically around organic matter hot spots, for example, fecal pellets, in the sediments (Figure 2(c)), rather than as simple vertical zonation (Figure 2(a)). This transforms the sediment environment into

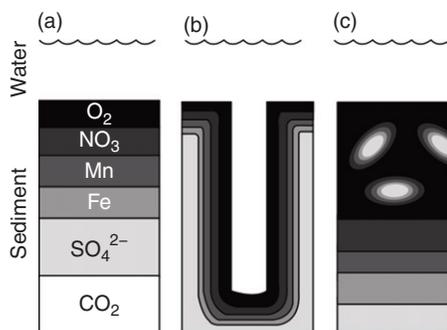


Figure 2 (a) The classical biogeochemical zonation that appears to occur in many marine sediments (e.g., based on the thermodynamic considerations in Table 1). Note the vertical redox zonation of electron acceptors that are used in these sediments. (b) A representation of the zonation of redox reactions in the microenvironment surrounding an irrigated macrofaunal burrow (or perhaps a macrophyte root). (c) A representation of the zonation of redox reactions in the microenvironment surrounding a fecal pellet in a marine sediment. From Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton. Modified from Aller, R.C., 1982. The effects of macrobenthos on chemical properties of marine sediments and overlying water. In: McCall, P.L., and Tevesz, M.J.S. (Eds.), *Animal–Sediment Relations, the Biogenic Alteration of Sediments*. Plenum Press, New York, NY, pp. 53–102.

one in which the full three-dimensional view of the sediments may need to be considered when attempting to study biogeochemical processes (e.g., Aller, 1988; Brandes and Devol, 1995).

However, even this conceptual model of mixed redox sediments is incomplete since particles and pore waters in these environments may actually be exposed to alternating oxic and anoxic condition as a result of these transport processes. In the simplest sense we think of these sediments as being periodically, or episodically, oxidized (or oxygenated), although the details of just how this occurs will vary among different environments. The timescales over which these redox oscillations occur are quite variable, ranging from minutes for bioirrigation to longer timescale characteristics of sediment mixing (also see discussions in Burdige, 2006). In some cases, these redox oscillations are asymmetrical in length, with anoxic conditions occurring for substantially longer times (10× or greater) than oxic conditions (Aller, 1994a).

Oscillating (or mixed) oxic/anoxic sediment redox conditions occur, for example, when mobile deposit feeder oxygenate the sediments as they crawl through the sediments, when burrowing organisms pump fresh (oxygenated) seawater through their burrows (Kristensen, 2001), or when wave and/or tidal action drives advective flow and exchange of anoxic pore water and oxic bottom water in permeable, sandy sediments (see Section 5.09.4.2 and Precht et al., 2004). Physical mixing (reworking) of sediments (Section 5.09.4.2) can also lead to the occurrence of such oscillating redox conditions, as can O₂ transport into sediments by the roots and rhizomes of macrophytes such as seagrasses (see Section 5.09.4.5 and e.g., Fredericksen and Glud, 2006).

Redox oscillations such as those described here also have the potential to greatly enhance organic carbon remineralization in sediments over that which might occur under more strict anoxic conditions, in spite of the often-times asymmetry between cycles or periods of anoxic versus oxic conditions (Aller, 1994a; Canfield, 1994; Hedges and Keil, 1995; Aller et al., 1996; Sun et al., 2002; Kristensen and Mikkelsen, 2003). The specific mechanisms by which this enhanced organic matter remineralization occurs under mixed redox conditions are not well characterized, although several possibilities have been discussed in the literature (see Burdige, 2007 for a recent review).

Based on all of these considerations, we see that mixed redox sediments are temporally varying, two- or three-dimensional sedimentary environments. Some degree of caution should therefore be taken in studying them assuming a one-dimensional, time-averaged perspective, as is often done in many sediment biogeochemical studies. A number of modeling approaches have begun to address these problems (Boudreau and Marinelli, 1994; Koretsky et al., 2002; Meysman et al., 2007; Miller et al., 2007; Cardenas et al., 2008), as have the use of two-dimensional optical imaging systems in laboratory mesocosm studies and in natural sediments *in situ* (e.g., Glud et al., 2001; Zhu et al., 2006).

5.09.4 The Classification of Estuarine and Coastal Sediments

Estuarine and coastal sediments can be classified into several functional types based on differences between the linkages of (and interactions between) biogeochemical processes and

transport processes in the sediments. This approach has been used previously in the examination of continental shelf sediments (Aller, 1998, 2004; McKee et al., 2004), and will be adapted here for our discussion (also see related discussions in Middelburg et al., 2005).

In an attempt to put this classification scheme into a larger conceptual framework, I have also examined the distribution of these sediment types in terms of the physical energy of each sediment type and the average grain size of the sediments (Figure 3). This is far from a perfect approach since, for example, sediment grain size is a function of both sediment sources and the physical processes acting on the sediment system. Similarly, this figure shows that certain sediment types plot in the same region of this graph because they show strong

similarities based solely on these two parameters. Here, other controlling factors not incorporated into this plot lead to the divergence in the properties of these sediments. Nevertheless, in spite of the shortcomings of this approach, we believe that it will be useful in the discussion presented here.

For several sediment types, one key factor not explicitly indicated here is the differentiation between intertidal and subtidal sediments. Subtidal sediments, being completely submerged, can exchange solutes and dissolved gases with the overlying waters continuously. In contrast, intertidal sediments can only exchange solutes during times they are submerged, and gas exchange will vary between exchange directly with the atmosphere and exchange of dissolved gases with the overlying waters. The consequences of these differences are not well

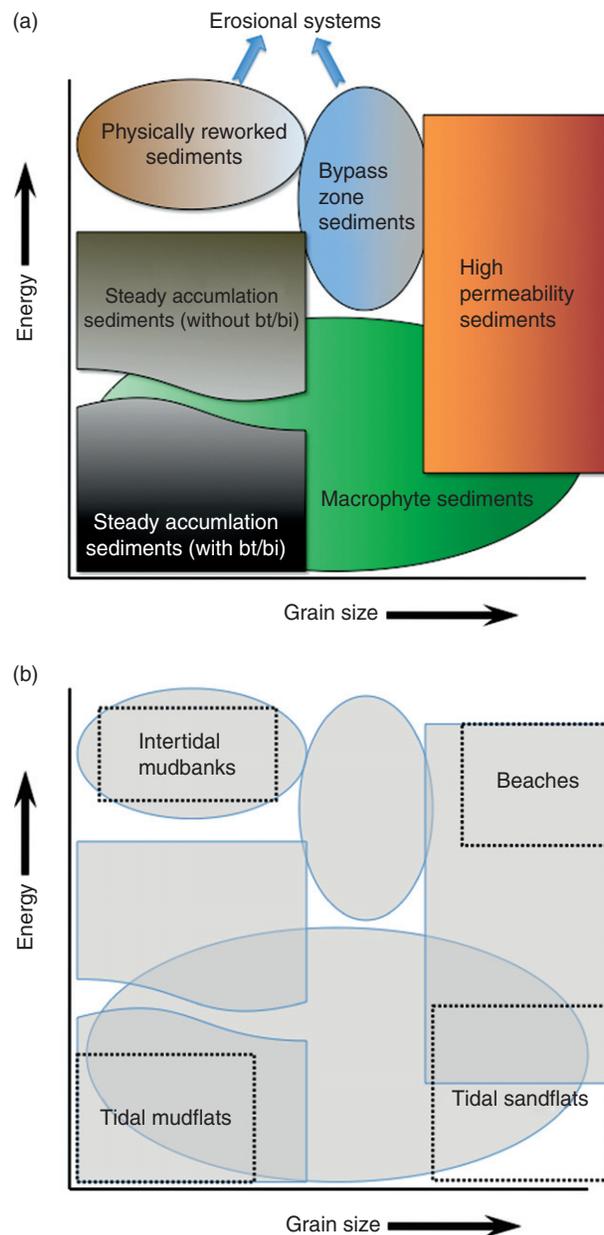


Figure 3 (a) The approximate distribution of five of the sediment types discussed in Section 5.09.4 in energy vs. grain size space. (b) An overlay of the approximate distribution of intertidal sandflats and mudflats in energy vs. grain size space on the analogous distribution for other sediment types shown in (a). bt/bi=bioturbation/bioirrigation.

understood, although for reduced gases such as methane, direct exchange with the atmosphere bypasses their possible oxidation in the water column (see Section 5.09.9 for details).

5.09.4.1 Steadily Accumulating Sediments

These subtidal sediments contain fine-grained silts and muds, and the surface zone of the sediments can be bioturbated or bioirrigated. These sediments are often referred to as depositional systems, and have been well-studied for several decades (see Boudreau, 2000 and Aller, 2004 for historical perspectives). In fact, much of what we know about biogeochemical processes in sediments stems from studies of these types of sediments.

In sediments that are not bioturbated or bioirrigated, molecular diffusion, modified by the tortuosity of the sediment matrix (Burdige, 2006), is the major transport process for solutes. Particles are added to the sediments by both vertical and lateral transport from the overlying waters, and this process is referred to as sedimentation or sediment accumulation. The occurrence of sediment accumulation implies that particles at the sediment surface are eventually buried below the surface as new material continues to accumulate. Since the sediment–water interface is defined as the frame of reference for most geochemical studies, this then implies that there is a net downward flux (or burial) of material as a result of sediment accumulation.

In many estuarine and coastal sediments (both those that are depositional and nondepositional), the upper portion of the sediments is inhabited by higher organisms as well as bacteria. The activities of benthic macrofauna and meiofauna

lead to the transport of solids and solutes in the surface sediments, and profoundly affect sediment redox conditions. These organisms therefore have a major impact on the sedimentary cycles of elements such as carbon, nitrogen, sulfur and redox-sensitive trace metals (e.g., Fe and Mn). Different aspects of benthic macrofaunal biogeochemistry from a more biological perspective are discussed in a number of monographs and review articles (Rhoads, 1974; Snelgrove and Butman, 1994; Kristensen, 2001; Schaffner et al., 2001; Kristensen et al., 2005; Dorgan et al., 2006; Levin et al., 2009), and the interested reader is urged to look in these references for this information.

There is a great variety in the types of macrofaunal activities (Figure 4). Some organisms simply crawl through the sediments or along the sediment surface in search of food, and mix sediment and sediment pore waters as a result of their activities. These organisms also ingest and subsequently defecate sediment materials. Such processes are commonly referred to as local mixing processes (Boudreau, 1986a; Meysman et al., 2005a) and more generally referred to as bioturbation. This process leads to the creation of a mixed (or bioturbated) layer in the surface sediments. (In some earlier works, the term 'bioturbation' is used in a much broader sense to describe all of the activities of benthic macrofauna in surface sediments. However, here (as in many more recent works) we will attempt to use this term in the more specific sense that is discussed in this section.) Bioturbation can, in principle, mix (and transport) both sediment particles and pore waters. However except in heavily bioturbated sediments (many of which are found in coastal and estuarine regions), rates of bioturbation are slow compared to molecular diffusion. Thus, bioturbation is largely of greatest impact in terms of particle mixing and transport in

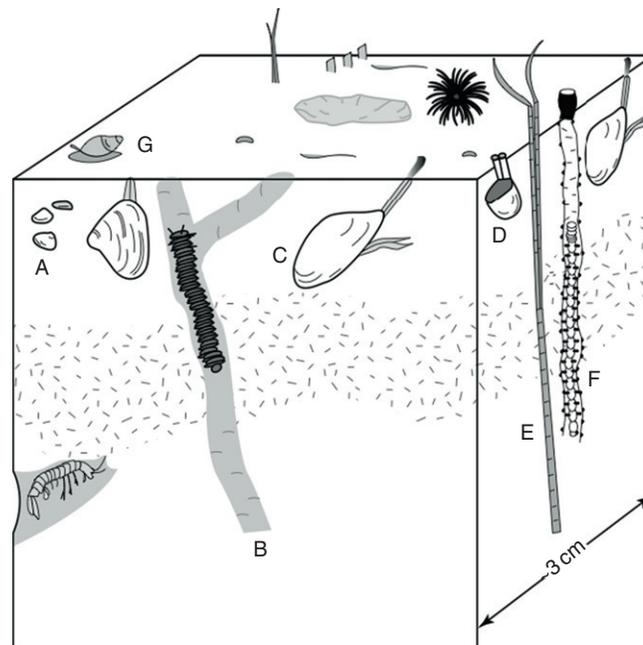


Figure 4 A schematic representation of the major benthic macrofauna found in a typical coastal marine sediment. The organisms shown here include the deposit feeding bivalves *Nucula annulata* (A) and *Yoldia limulata* (C), the suspension feeding bivalve *Mulinia lateralis* (D), the mobile burrowing polychaete *Nephtys incisa* (B), the sedentary polychaetes *Spirochaetopterus oculatus* (E) and *Clymenella* sp. (F), and the deposit feeding gastropod *Nassarius trivittatus* (G). From Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton, based on an original figure in Aller, R.C., 1980a. Diagenetic processes near the sediment–water interface of Long Island Sound, I. Decomposition and nutrient element geochemistry (S, N, P). *Advances in Geophysics* 22, 235–348.

surface sediments. An exception to this may be bioturbation by benthic meiofauna, for example, nematodes or juvenile polychaetes, in addition to, or instead of, benthic macrofauna (Berg et al., 2001). Meiofaunal bioturbation may differentially affect solutes versus solids, because of the size of these organisms, and the fact that at the relatively small (submillimeter) scales at which these organisms operate it may be easier to move pore waters rather than solids (also see Aller and Aller, 1992).

Other deposit-feeding macrofauna live in fixed sediment burrows and move material from depths a few centimeters below the sediment surface to the surface, forming burrow mounds. This process is generally referred to as conveyor-belt transport (e.g., Boudreau, 1986b; Robbins, 1986). Reverse conveyor-belt feeders carry out a similar type of transport in the opposite direction, by taking surface sediment and moving it down to some depth in the sediments (e.g., Smith et al., 2001). Both of these types of bioturbation are also referred to as nonlocal mixing (Boudreau, 1986b; Meysman et al., 2003).

Finally, a last group of macrofaunal organisms are water-column suspension feeders and tubeworms. These organisms build sediment burrows and tubes, and flush these burrows with overlying bottom waters to cleanse the burrows of potentially harmful solutes that can accumulate in the burrow due to, for example, diffusion into the burrow from the surrounding sediments. This process is generally referred to as bioirrigation, in that it does not affect transport of the surrounding sediment particles, but does enhance the exchange of pore waters and bottom waters.

The impact of bioirrigation on sediment biogeochemistry results from the fact that the occurrence of macrofaunal tubes and burrows leads to a complex three-dimensional geometry in the zone of irrigation that significantly alters the spatial (and temporal) distribution of reactions occurring in these sediments. Bioirrigation of sediments creates diffusive sources and sinks for pore-water solutes within portions of the sediments that would otherwise be isolated from exchange with the overlying waters by diffusive processes alone. Bioirrigation is therefore also a nonlocal exchange process (Aller, 1980c, 2001; Boudreau, 1984; Grigg et al., 2005). Because burrows are flushed with oxygenated bottom water, bioirrigation enhances sediment oxygen input, thus altering sediment redox conditions, promoting redox oscillations, and allowing for the occurrence of a wide range of coupled oxidative and reductive processes associated with organic matter remineralization (see discussions in Sections 5.09.2.3 and 5.09.3, as well as in Aller et al., 2001 and Glud, 2008). The sediments immediately surrounding animal burrows and tubes are often sites of elevated microbial populations and enhanced activity (Aller, 1988). As a result, macrofaunal processes can have both direct as well as indirect effects on the rates of sediment organic matter remineralization (also see Glud et al., 2003).

Irrigation rates vary among different species of benthic macrofauna, and irrigation is often times a discontinuous process (i.e., there are periods of active irrigation followed by periods of rest). This can then lead to transient (non-steady-state or time-dependent) responses in burrow-water and pore-water concentrations near the burrows. The impact this has on sediment processes and pore-water concentrations can vary depending on the type of sediment (e.g., sands vs. muds) along with the reaction kinetics (e.g., zero vs. first-order kinetics) affecting the production/consumption of a given

solute (Boudreau and Marinelli, 1994; Marinelli and Boudreau, 1996; Meysman et al., 2005b, 2006).

A variety of factors control the species distribution and abundance of benthic macrofauna in sediments (also see more extensive reviews in Rhoads, 1974; Snelgrove and Butman, 1994; Herman et al., 1999; and Schaffner et al., 2001). As a general controlling factor bottom-water oxygen appears to be quite important, at least in terms of the presence/absence of benthic macrofauna. Long-term bottom-water O_2 concentrations that are less than $\sim 5 \mu\text{M}$ generally lead to the complete absence of benthic macrofauna in the underlying sediments (Rhoads, 1974; Savrda et al., 1984; Levin et al., 2009). Studies also show that bottom water $[O_2]$ levels less than $\sim 60\text{--}70 \mu\text{M}$ begin to adversely impact benthic communities (Diaz and Rosenberg, 1995; Levin et al., 2009). (Note that in the literature a wide range of units are still used to express oxygen concentrations. For comparison, an oxygen concentration (at STP) of $1 \text{ ml} \cdot \text{l}^{-1}$ is equivalent to $44.6 \mu\text{M}$, so $5 \mu\text{M}$ is equivalent to $\sim 0.1 \text{ ml} \cdot \text{l}^{-1}$. In discussing low oxygen environments, the term hypoxia is also often used, and it is generally defined as oxygen concentrations below $2 \text{ ml} \cdot \text{l}^{-1}$, or $\sim 90 \mu\text{M}$ (Diaz and Rosenberg, 1995).)

In contrast though, many estuarine and coastal sediments are subject to episodic, or seasonal, hypoxia (or anoxia) in the bottom waters. Its effect on the distribution, abundance, and activity of benthic macrofauna is a complex function of the level, duration, and physical extent of low oxygen conditions in the bottom waters, and the impact that this has on the geochemistry of the bottom sediments (Middelburg and Levin, 2009). It is difficult to generalize these effects, and Levin et al. (2009) summarized the results from studies of benthic macrofaunal responses to bottom-water hypoxia (and anoxia) across a wide range of estuarine and coastal settings, including Chesapeake Bay, the Baltic Sea, and the northern Gulf of Mexico.

Other factors that appear to control the occurrence of benthic macrofauna include sediment type, food source, sedimentation rate, and physical disturbance (again see any of the review articles cited above for details). In the latter cases, areas of high physical disturbance (in terms of both frequency and intensity), as well as areas of high sediment deposition generally show very low abundances of macrofauna, with bacteria dominating the total benthic biomass (e.g., Aller and Aller, 2004). Of the macrofauna that are present in these sediments, small, surface dwelling polychaetes and tube-dwelling amphipods are generally most important (also see Rhoads, 1974; Snelgrove and Butman, 1994; Schaffner et al., 2001).

Benthic macrofauna tend to inhabit the upper $\sim 10\text{--}20 \text{ cm}$ of sediment, and based on radio-geochemical analyses Boudreau (1998) has suggested that worldwide, the mixed layer depth in marine sediments has a mean value of $\sim 10 (\pm 4.5) \text{ cm}$. The average thickness of the bioirrigation zone may be of similar magnitude (see Burdige, 2006 for a summary), although some studies do suggest that irrigation may occur to depths of $\sim 30\text{--}50 \text{ cm}$ (e.g., Martin et al., 2007; Jørgensen and Parkers, 2010). At the same time, many of the factors outlined in the previous paragraph may lead to bioturbation or bioirrigation depths that are shallower than 10 cm (e.g., Schaffner et al., 2001; Smith and Rabouille, 2004).

5.09.4.2 Sediments Subject to Extensive Physical Reworking

These sediments are highly mobile deposits, in which physical processes both resuspend sediments and redistribute them horizontally. As a result, the sediments appear to act as a massive, non-steady-state suboxic fluidized bed reactor (see Section 5.09.7 for details). The biogeochemical consequences of this type of large-scale sediment mixing contrast with the more small-scale, mixed redox conditions (oxic → anoxic) associated with biological mixing, that is, bioturbation (see discussions in Dellapenna et al., 1998).

This type of physical reworking of sediments has been best studied in muddy continental margin deltas such as the Amazon continental shelf or the Gulf of Papua/Fly River complex (Papua New Guinea), as well as in mobile tropical mud belts such as the Amazon-Guianas mud belt of coastal French Guiana (Alongi, 1995; Aller, 1998; Zhu et al., 2002; Aller et al., 2004a, 2008; Corbett et al., 2004; McKee et al., 2004). On the Amazon shelf, the upper ~0.5–2 m of sediment is eroded by shelf currents and tides, re-oxidized by brief resuspension into the bottom waters, and then re-deposited (McKee et al., 2004). This physical reworking occurs on daily to seasonal timescales (also see DeMaster and Aller, 2001).

An important aspect of these continental margin settings is that they occur in association with major rivers that have relatively high freshwater discharge rates. As a result, estuarine processes, which would normally take place in a physically confined estuary, take place offshore, on the adjacent continental shelf. These large rivers also have high suspended sediment loads, and the river-dominated ocean margins receive large inputs of both lithogenic and biogenic material (McKee et al., 2004; Bianchi and Allison, 2009). These continental margin settings therefore represent the major repositories for the deposition and burial of the material transported by rivers to the oceans (also see Berner and Berner, 1996).

The physical reworking of these sediments has a profound impact on both sediment carbon cycling (i.e., preservation vs. remineralization) and nitrogen cycling on both local and global scales (see the references cited above, as well as Burdige, 2005). These processes also impact the oceanic cycles of elements such as U, F, and K, by, for example, promoting the occurrence of authigenic mineral formation, or reverse weathering (e.g., Michalopoulos and Aller, 2004).

Analogous types of physical reworking of sediments also appear to occur in estuarine environments, albeit on smaller spatial scales (Dellapenna et al., 1998; Schaffner et al., 2001; Galler and Allison, 2008). They may occur, for example, in the maximum turbidity zone of tidal estuaries, where there are fine-grained materials and sufficient energy for physical reworking of the surface fluid muds. While the biogeochemical significance of this type of physical reworking in estuarine sediments is not as well documented as it is in deltaic or offshore continental margin mobile muds, results to date suggest some degree of commonality (Abril et al., 1999, 2000; Robert et al., 2004; Arzayus and Canuel, 2005; Palomo and Canuel, 2010).

5.09.4.3 High Permeability, Sandy Sediments

Because of their grain size these sediments have the capacity to allow advective flow through them in response to an external pressure gradient (e.g., Lerman, 1979). This phenomenon is

referred to as sediment permeability. In contrast, more fine-grained silts and muds have a low permeability, and allow for little advective flow; diffusion is therefore the dominant non-biological transport process for solutes. High-permeability, sandy sediments occur on ~70% of all continental shelves globally, often as nonaccumulating, well-sorted relict sands that were deposited during the low stand of sea level during the last Ice Age (Emery, 1968). Sandy sediments also occur in some estuarine settings on-, and just off-shore, most beaches (see Sections 5.09.4.4–6), and on shallow water carbonate platforms such as the Bahamas Bank.

The near-seabed pressure gradients that drive advective flow in these sediments have several possible sources. In shallow waters and intertidal regions, pressure gradients may result from wave and tide action (Shum and Sundby, 1996; Falter and Sansone, 2000) that can be thought of as pumping overlying waters into the sediments. Tidal forcing such as that described here has also been examined in recent years in terms of submarine groundwater discharge to the oceans, based on the recognition that some fraction of what is referred to as groundwater being discharged into the coastal ocean is actually seawater that has been recirculated through the underlying sediments (e.g., Martin et al., 2007). By analogy with a surface estuary, Moore (1999) has referred to the reaction zone of fresh (terrestrial) ground water and recirculated seawater as a subterranean estuary. There is increasing recognition that reactions occurring in this subterranean estuary may be of geochemical significance (e.g., Charette and Sholkovitz, 2006; Johannesson and Burdige, 2007; Roy et al., 2010), although sampling difficulties coupled with the complexity of water circulation in these systems have made quantification of these processes difficult (Burnett et al., 2006).

Advective exchange in permeable sediments also occurs through interactions between bottom currents and surface structures, for example, physical surface roughness, sand ripples, and biogenic structures such as animal mounds (e.g., Huettel and Webster, 2001). Larger structures such as seagrass canopies (Section 5.09.4.5) can similarly impact bottom-water flow and lead to near-seabed pressure gradients (Jumars et al., 2001; Ghisalberti and Nepf, 2002; Koch et al., 2006). These latter interactions are complex and not fully understood, although past studies suggest that the most important factors include canopy architecture (shoot density and leaf length). Also important here is the type of flow (e.g., unidirectional tidal currents vs. wave-dominated flow) and its impact on the motion of individual leaves (also see Koch and Gust, 1999; Peterson et al., 2004). Wind-driven Langmuir cells that extend over the full depth of shallow water columns may similarly result in oscillatory bottom water flow that can generate large (and changing) areas of increased and decreased pressure on the seafloor (Gargett et al., 2004; Tejada-Martinez and Grosch, 2007). This then represents another physical process that may drive advective pore-water exchange across the sediment–water interface in shallow environments (see related discussion in Dierssen et al., 2009).

In examining the relative importance of different transport processes in sediments, it has been suggested that pressure-driven pore-water advection is likely to be important when permeabilities (k) exceed $\sim 1\text{--}2 \times 10^{-12} \text{ m}^2$ (see Figure 5, and Huettel and Gust, 1992 and Forster et al., 2003). Based on a

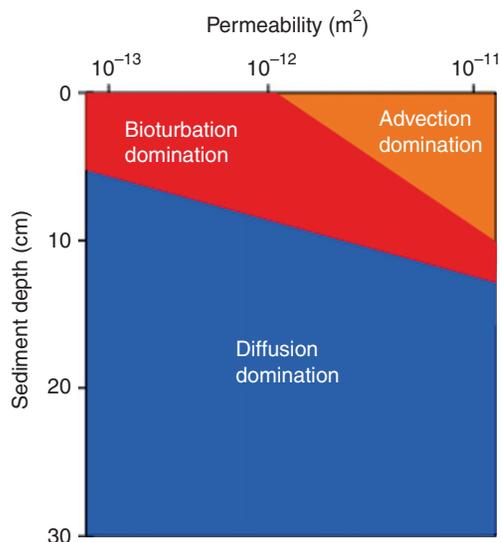


Figure 5 A schematic representation of the depth dependence of various pore-water transport processes (diffusion, bioturbation, and physical advection) as a function of sediment permeability. Note that there is some overlap in these three regions, such that diffusion and advection can also occur in the region where bioturbation occurs. Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton based on Huettel, M., and Webster, I.T., 2001. Porewater flow in permeable sediments. In: Boudreau, B.P., and Jørgensen, B.B. (Eds.), *The Benthic Boundary Layer*. Oxford University Press, Oxford, pp. 144–179.

log–log plot of measured permeability versus sediment grain size (data compiled in Burdige, 2006), this cutoff occurs at a median grain size of ~70–80 μm , that is, sediments that are larger than a very fine sand (also see Lerman, 1979; Bennett et al., 1990). Using a slightly different data set, Wilson et al. (2008) observed what appears to be distinct trend lines for these parameters for continental margin and coastal sediments. Here k values greater than $2 \times 10^{-12} \text{ m}^2$ occur for mean grain sizes greater than ~40 μm for coastal sediments and ~125 μm for continental margin sediments, values that span the grain size value estimated above. There is also some overlap in the regions illustrated in Figure 5, and many sandy sediments are also inhabited by benthic macrofauna, even at relatively high permeabilities (see below for details).

For typical bottom-water flows and surface structures, laboratory flume studies suggest that bottom waters can be forced several centimeters into the sediment, simultaneously drawing pore water from depths >~10 cm up to the sediment surface (Huettel et al., 1996). Field observations are generally consistent with these laboratory results (Marinelli et al., 1998; Rasheed et al., 2004; Reimers et al., 2004; Jahnke et al., 2005; Burdige et al., 2008). Changes in flow velocity (both magnitude and frequency) can have differing effects on oxygen uptake and the depth of oxygen penetration in permeable sediments, depending on the type of flow as well as the nature of the surface topography (Forster et al., 1996; Ziebis et al., 1996b; Berninger and Huettel, 1997; Precht et al., 2004).

In flume studies where the flow velocity was fixed (in a given experiment) but varied among different studies, oxygen penetration depth showed virtually no change with increasing flow velocity when the sediment surface was smooth (Forster

et al., 1996; Ziebis et al., 1996b). Such observations may be relevant to the effect of changing tidal flow velocities on advective pore-water exchange over tidal cycles, although this effect has not yet been examined *in situ*.

In contrast, flume studies in which short period (~1 s) water waves pass over a sediment surface rapidly lead to the formation of sand ripples which subsequently creates “an undulating oxic–anoxic boundary within the upper sediment layer, mirroring the topographical features of the sediment bed” (Precht et al., 2004). Here pore-water flow is also more complex, with oxygenated overlying water being forced into the sediments in the ripple troughs and deep anoxic pore water being upwelled to the surface under the ripple crests (e.g., Huettel et al., 1996). Similar effects also appear to impact processes such as denitrification (see Section 5.09.6) and the redox cycling of other solutes such as Fe^{2+} or Mn^{2+} (Huettel et al., 1998). Oxygenated bottom water that is advected into permeable sediments coming in contact with reduced pore waters should result in the types of linkages between oxic and anoxic organic matter remineralization and chemolithotrophic reactions associated with other mixed redox sediments (see Section 5.09.3).

Permeable sediments act as efficient sand filters because of these advective processes, analogous to those found in sewage treatment plants (Boudreau et al., 2001). Recent work has therefore shown that they are significantly more biogeochemically active than previously thought (also see Jahnke, 2005 for a summary). Rates of sediment oxygen uptake are greatly enhanced in permeable sediments due to increased oxygen input from bottom waters, coupled with the advective input of suspended organic particles (e.g., phytoplankton debris or bacteria) from the water column into the sediments, where they can subsequently undergo remineralization (Forster et al., 1996; Ziebis et al., 1996b; Huettel and Rusch, 2000; Rusch and Huettel, 2000).

Permeable sediments generally have very low organic carbon content, due, in part, to their nondepositional nature. However, the material that is input into the sediments appears to be relatively reactive, as compared to that found in many fine-grained depositional sediments (Boudreau et al., 2001). In part, this occurs because the input of reactive organic matter to the sediments is apparently not diluted by the accumulation of aged, and thus, less reactive, organic matter (Boudreau et al., 2001). Therefore, the low standing stock of organic carbon (TOC) in permeable sediments, and other sediment nutrients in general, may be controlled more by rapid turnover than by low input.

Finally, many permeable sediments occur in shallow waters, and recent estimates suggest that ~30% of the continental shelf seafloor receives sufficient light to support net primary production (Jahnke, 2005; Gattuso et al., 2006). Although estimates of benthic primary production in shallow water sands are subject to large uncertainties (Boudreau et al., 2001; Gattuso et al., 2006), in many cases, they appear to be comparable to rates of water-column primary productivity (Jahnke et al., 2000). Many permeable sediments are also inhabited by benthic macrofauna (Huettel and Gust, 1992; Ziebis et al., 1996a; D’Andrea et al., 2002; Meysman et al., 2005b). Their impact on biogeochemical processes in these sediments is several fold. First, the biogenic structures built by the macrofauna help create the near-seabed pressure gradients that drive advective pore-water exchange in these sediments. The activity of benthic

macrofauna in permeable sediments also adds an additional level of complexity to solute transport in these sediments (Meysman et al., 2006, 2007), which may result in synergistic effects that enhance remineralization and solute fluxes across the sediment–water interface in these settings (e.g., Volkenborn et al., 2007).

5.09.4.4 Bypass Zone Sediments

In one sense, these sediments may be thought of as being transitional between steady accumulating, bioturbated/bioirrigated silts and muds and high-permeability sands (Figure 3(a)). In these settings, physical energy (e.g., near bottom tidal current, and wind-wave action) is great enough to winnow fine-grained materials from the sediments (and advect this material out of the system as suspended sediments), but remains just above (or slightly below) critical levels that will cause net seabed erosion (e.g., Wright et al., 1997). These sediments often support active communities of bioturbating and bioirrigating macrofauna (Dellapenna et al., 1998; Schaffner et al., 2001), and organic matter remineralization processes in these sediments are strongly controlled by the mixed redox conditions that develop in the sediments as a result of this macrofaunal activity. Advective pore-water exchange is likely to occur in these sediments, given their grain size and, because they are bioturbated and bioirrigated, the presence of biogenic structures on the sediment surface that can contribute to near-seabed pressure gradients. These sediments may be nondepositional, but often have low rates of sediment accumulation as compared to other more typical estuarine settings. A well-studied sediment system acting as this type of a bypass zone is the bay stem plains in the lower Chesapeake Bay (Schaffner et al., 1987; Wright et al., 1987, 1997; Dellapenna et al., 1998; Schaffner et al., 2001).

As the physical energy in bypass sediments increases, the sediment will become increasingly inhospitable to macrofauna, and the sediments will move from one of little or no net deposition, to an erosional system. On the continental shelf, the processes that lead to highly mobile physically reworked sediments (Section 5.09.4.2) can also lead to erosional regions in which the surface sediments are scoured away and deeply buried materials are re-exposed (Kuehl et al., 1986; Sommerfield et al., 1995). This can then result in the non-steady-state release and re-oxidation of reduced metabolites such as CH₄, along with the oxic remineralization of organic carbon that had previously escaped remineralization and been buried in these sediments (Blair and Aller, 1995).

5.09.4.5 Macrophyte-Dominated Sediments

This group (also sometimes referred to as vegetated sediments) includes salt marshes, mangrove forests, and seagrass-dominated sediments. While the vegetations here include both emergent and submerged macrophytes, there is sufficient commonality among these sediment systems to consider them together.

Salt marshes are intertidal wetlands inhabited by salt tolerant grasses (nonwoody vascular plants), including species of *Spartina* (e.g., *S. alterniflora* and *S. patens*), *Juncus*, and *Salicornia*. They are common in low-energy estuarine and coastal settings in temperate, boreal, and arctic regions. In tropical and

subtropical settings, salt marshes are replaced by mangrove forests, which contain salt-tolerant trees, shrubs, and other plants. In contrast, seagrasses are submerged vascular plants (angiosperms) that are found in all estuarine and coastal areas except in Antarctica. Most seagrasses live in subtidal environments, with their depth distribution controlled by light limitations (Hemminga and Duarte, 2000); on average, they require ~11% or more of surface irradiance, which limits them to a water depth of ~40 m or shallower in very clear ocean waters. Seagrasses can live in muddy to sandy sediments, limited here by sediment stability or current velocities.

Macrophyte-dominated sediments are also often extensively bioturbated. In salt marshes and mangrove forests burrowing crabs tend to dominate (Alongi, 1998), while seagrass meadows generally support a broader range of benthic macrofaunal species (Hemminga and Duarte, 2000).

In intertidal salt marsh and mangrove sediments, tidal forcing can play an important role in regulating biogeochemical processes in the sediments, and ultimately solute fluxes across the sediment–water interface (Lacerda et al., 1999; Bouillon et al., 2007; Taillefert et al., 2007). The factors controlling this subsurface flow are complex, and, for example, rising and falling tides can induce both vertical as well as horizontal subsurface flow in these sediments based on factors such as marsh (or forest) topography and sedimentology (i.e., grain size), as well as the importance of fresh groundwater flow from upland sources (also see Mitsch and Gosselink, 2000; Tobias et al., 2001; Jahnke et al., 2003).

In terms of their interaction with the surrounding physical environment, the seagrass canopy dissipates the energy of local currents and promotes the deposition of organic detritus and fine-grained inorganic suspended material from the water column to the underlying sediments (Hemminga and Duarte, 2000; Koch et al., 2006). Salt marsh plants and mangrove trees have a similar effect on particulate deposition from the tidal or creek waters that flow through (or over) the marsh or forest (Mitsch and Gosselink, 2000; Kristensen et al., 2008).

Salt marsh, seagrass, and mangrove ecosystems are highly productive, and macrophyte-derived organic matter plays an important role in organic carbon remineralization in the underlying sediments (Holmer et al., 2001; Jones et al., 2003; Kaldy et al., 2006; Kristensen et al., 2008). At the same time, the external input of organic detritus (due to the processes described in the previous paragraph) represents a variable, but sometimes large, input of organic carbon to macrophyte sediments, that can then similarly contribute to sediment organic carbon remineralization (Papadimitriou et al., 2005; Bouillon and Boschker, 2006; Kaldy et al., 2006). Recent studies have re-examined organic carbon budgets in vegetated sediments (Chmura et al., 2003; Duarte et al., 2005b, 2010; Kristensen et al., 2008) and have suggested that organic carbon burial in these sediments is comparable in magnitude to estimates of organic carbon burial in nonvegetated, subaqueous deltaic and continental margin sediments (which have previously been suggested to be the primary sites of organic carbon burial in the oceans; Berner, 1989; Hedges and Keil, 1995). Salt marshes and mangrove forests may also represent an intertidal pump in which globally significant amounts of dissolved inorganic carbon (and to a lesser extent dissolved organic carbon, or, DOC) derived from the remineralization

of plant-derived organic matter are exported to the coastal ocean (Bouillon et al., 2008; Jahnke, 2009).

Salt marsh grasses, mangroves, and seagrasses all actively transport atmospheric or photosynthetically produced O_2 in the plants to their belowground tissues, which then results in either active or passive oxygen transport from the roots and rhizomes into the surrounding sediments (see reviews, and references therein, in Alongi, 1998; Canfield et al., 2005; Lovell, 2005; and Borum et al., 2006). The impact of this oxygen transport away from belowground plant tissues can be viewed in the context of the model for mixed (or oscillating) redox conditions in Section 5.09.3, and will also have impacts that are somewhat analogous to those which occur as a result of macrofaunal bioirrigation (also see Vale and Sundby, 1998). However, the contrast between oxidant (O_2) input from roots and rhizomes versus oxidant input (e.g., Mn and Fe oxides) that occurs by physical mixing (local and nonlocal bioturbation) can, under some circumstances, result in the predominance of differing types of redox cycling being linked to O_2 reduction (i.e., sulfur redox cycling in the latter case and iron redox cycling in the former case; e.g., Hines, 2006). These effects are not universal, though, depending on, for example, the iron content of the sediment or the presence of bioturbating macrofauna in a macrophyte sediment.

Many macrophytes live in fine-grained, high TOC sediments. Because sulfate reduction is often an important organic carbon remineralization process in these sediments, sulfide levels in the sediment pore waters are often high, and oxygen input by the plants into the surrounding rhizosphere is thought to protect the plant from sulfide and other phytotoxins such as reduced metals that are also commonly found in these anoxic sediments (Alongi, 1998; Lee and Dunton, 2000; Lovell, 2005; Fredericksen and Glud, 2006; Hines, 2006; Marbá et al., 2006; Miller et al., 2007). Many such plants also have a thin iron oxide coating (generally referred to as an iron plaque) that forms on the root surface as a result of the oxidation of Fe^{2+} produced in the surrounding anoxic sediments (St-Cyr et al., 1993; Sundby et al., 1998; Povidisa et al., 2009). Oxygen input in macrophyte sediments therefore plays an important role in not only metal but also sulfur, nitrogen, and carbon redox cycling (also see Burdige et al., 2010; Holmer et al., 1999; Ku et al., 1999; Kristensen et al., 2000; Sundby et al., 2003; Hu and Burdige, 2008; Hyun et al., 2009).

The region surrounding macrophyte roots and rhizomes may also be a region of enhanced microbial activity (see general reviews in Alongi, 1998; Duarte et al., 2005a; and Hines, 2006), again as is seen around macrofaunal burrows and tubes (Aller, 1988). In part, this may be due to the release of reactive DOM from the plant roots into the surrounding sediments, which supports both aerobic and anaerobic (sulfate reducing) remineralization in the sediments (Wetzel and Penhale, 1979; Moriarty et al., 1986; Ziegler and Benner, 1999; Hines, 2006; Kaldy et al., 2006; Kristensen and Alongi, 2006). More specifically, studies of salt marsh plants have shown that plant roots release both acetate and ethanol (Mendelsson et al., 1981; Hines et al., 1994; Hines, 2006), which are fermentation end products (presumably produced by anaerobic metabolism in the plants) and excellent substrates for both aerobic and sulfate-reducing bacteria.

Many aspects of the biogeochemistry of vegetated sediments are inherently time dependent due to the diel

variability in belowground input of photosynthetically produced O_2 , or temporal variability in the release of reactive DOC from roots (Fredericksen and Glud, 2006; Hebert et al., 2007; Miller et al., 2007). The factors that control the expression of this variability in, for example, pore-water sulfide profiles, are complex and in seagrass sediments may be a function of the seagrass density (Lee and Dunton, 2000). However, small-scale spatial variability may obscure temporal variability (Hebert et al., 2007), and developing appropriate sampling strategies that overcome these hurdles is an important consideration here (Morse et al., 2003).

For seagrasses living in more organic-poor carbonate sediments in tropical and subtropical regions, belowground O_2 input may also play an important role in P acquisition by the plants. In these setting, phosphorus is often a critical limiting nutrient due, in part, to the strong tendency of phosphate to adsorb to carbonate minerals. O_2 input by the plants into the sediments results in the dissolution of sedimentary carbonates as a result of CO_2 production due to sediment aerobic respiration (Burdige and Zimmerman, 2002), and this seagrass-mediated carbonate dissolution then liberates carbonate-bound phosphate (Jensen et al., 1998). This process also has important positive feedback characteristics since seagrass growth and the associated belowground O_2 input enhances sediment carbonate dissolution, which then further liberates phosphate from the sediments and promotes additional seagrass growth and carbonate dissolution (see Burdige et al., 2008 for further discussions).

5.09.4.6 Intertidal Mudflats and Sandflats

These sediments show a range of characteristics that have similarities to the sediment types discussed in the previous sections. As with salt marsh and mangrove sediments, tidal processes play an important role in the dynamics of these macrophyte-free intertidal sediments (Alongi, 1998). The fact that intertidal mudflats and sandflats are alternately exposed and submerged (versus permanently submerged subtidal sediments) also has an impact on the exchange of solutes and gases from these sediments (see Section 5.09.4).

High-energy sandy beaches show some commonality with subtidal high-permeability sediments (Section 5.09.4.3), and they are often discussed together (e.g., Boudreau et al., 2001; Huettel and Webster, 2001). In a similar fashion, intertidal mud banks are often discussed in the context of biogeochemical processes associated with physically reworked tropical mud belt sediments (e.g., Alongi, 1991; Aller et al., 2004b).

In contrast to these high-energy environments, tidal sandflats and intertidal mudflats are lower-energy environments that are usually actively bioturbated and/or bioirrigated, often-times by economically valuable organisms such as soft-shell or hard-shell clams (D'Andrea et al., 2002; Green et al., 2004; Hyun et al., 2009). As sediment grain size increases, pore-water advective exchange becomes increasingly important in these sediments. The surfaces of mudflats and sandflats are also generally covered by photosynthetic microalgal or macroalgal mats (e.g., Stephens et al., 2003; Sundback and McGlather, 2005). The presence of this microphytobenthos can often help stabilize the sediments against resuspension, by producing a mucilaginous biofilm (Miller et al., 1996; Decho, 2000).

5.09.5 Sediment Oxygen Consumption

In most estuarine and coastal sediments the large flux of reactive organic carbon to the sediments results in high potential rates of sediment O_2 consumption relative to O_2 transport into the sediments by processes such as molecular diffusion. Oxygen in the pore waters therefore generally goes to zero within a centimeter or less below the sediment–water interface, oftentimes in upper few millimeters (see summaries in [Burdige, 2006](#) and [Glud, 2008](#)). In contrast, nonlocal transport processes (e.g., bioirrigation or macrophyte root and rhizome oxygen input) can input oxygen into deeper portions of many estuarine and coastal sediments. Nevertheless, the tight coupling of O_2 input and consumption results in the near-zero to zero O_2 concentrations in the bulk of the pore waters, except in a region immediately adjacent to the particular nonlocal source ([Berg et al., 2003](#); [König et al., 2005](#); [Fredericksen and Glud, 2006](#); [Glud, 2008](#)).

Estimates of aerobic respiration as a percentage of total sediment organic carbon remineralization (R_{cox}) in estuarine and coastal sediments range from 0 to ~60% with an average of ~28% (see [Burdige, 2006](#) for a summary). Where macrofauna are present, their respiration (vs. microbial respiration) is ~15–20% of R_{cox} (for a review, see [Herman et al., 1999](#)). A direct comparison of these two percentages is equivocal given the way these results are presented in the literature, although they do suggest that when macrofauna are present, they could account for perhaps half of the total sediment aerobic respiration.

As discussed in Section 5.09.2.3, much of the oxygen uptake in estuarine and coastal sediments occurs at the expense of the oxidation of reduced sulfide, ammonium, Mn^{2+} , and Fe^{2+} ([Mackin and Swider, 1989](#); [Sampou and](#)

[Oviatt, 1991](#); [Rysgaard et al., 1998](#); [Berg et al., 2003](#); [Glud et al., 2003](#)). Where quantified, these re-oxidation reactions represent ~60–70% of the total sediment oxygen uptake (or TOU). The remaining oxygen uptake occurs by either macrofaunal or microbial respiration, since meiofaunal respiration is generally insignificant ([Middelburg et al., 2005](#)). [Canfield et al. \(2005\)](#) estimated that macrofaunal respiration accounts for ~5–30% of TOU. This estimate of macrofaunal respiration as a percentage of TOU does not appear to be inconsistent with the discussion above of macrofaunal respiration as a percentage of R_{cox} although a direct comparison of these results is not possible.

Oxygen consumption during the oxidation of these reduced solutes then results in low concentrations of these solutes near the sediment–water interface due to their oxidative removal (see [Figure 6](#) and, e.g., [Burdige, 1993](#) and [Martin, 2009](#)). It impacts benthic fluxes of these solutes to the overlying water column and also has a larger-scale effect on sediment trace metal cycling (see Section 5.09.10 for details). The Mn and Fe oxides produced by such reactions are also important since the mixing of the oxides into deeper portions of the sediments can drive a number of other biogeochemically important processes (see Sections 5.09.2.3).

5.09.6 Organotrophic Denitrification, Anammox and Anoxic Nitrification

Previous estimates ([Burdige, 2006](#)) suggest that organotrophic denitrification accounts for ~10–20% of R_{cox} in estuarine and coastal sediments. These estimates have generally been based on diagenetic models applied to pore-water nitrate profiles,

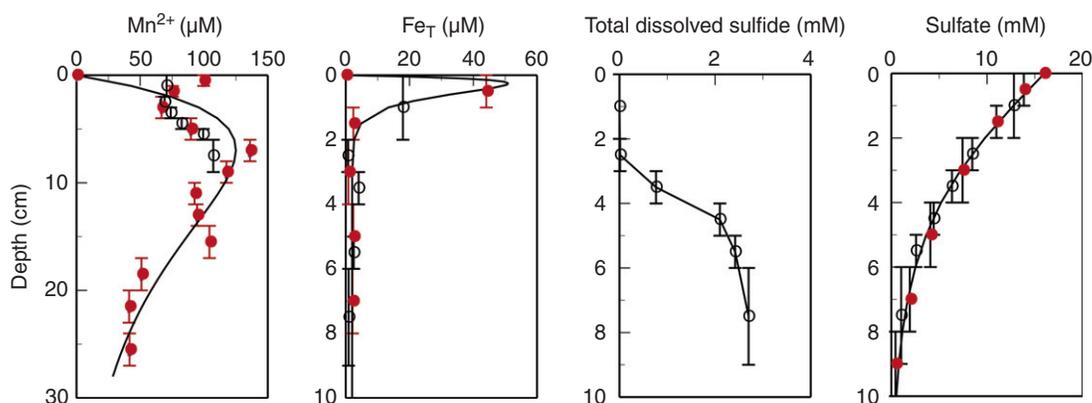


Figure 6 Pore-water profiles (collected 10/94) for dissolved Mn^{2+} , total dissolved Fe ($\approx [Fe^{2+}]$), total dissolved sulfide and sulfate at a site in the mesohaline region of Chesapeake Bay. Note that the manganese profile has an expanded depth scale as compared to the other three profiles. The curves through the data are meant to better illustrate the trends in the data; they are not model fits and are not meant to imply any functional relationships. Given the importance of sulfate reduction in these sediments (see sulfate profile and data in [Marvin-DiPasquale and Capone, 1998](#)), Mn and Fe reduction here is likely coupled to sulfide oxidation, although this has not been definitively demonstrated (also see related discussions in [Burdige, 1993](#)). The accumulation of iron in the pore waters is caused by a balance between production from the reduction of iron oxides, and consumption during manganese reduction (see reaction 9 in [Table 2](#)) and precipitation of iron sulfides. Although sulfate reduction starts essentially at the sediment–water interface, sulfide does not accumulate in the pore waters until all the reactive iron oxides have been reduced, as evidenced here by the draw down of all iron in the pore waters. Finally, note that removal of Mn^{2+} from the pore waters occurs at deeper sediment depths (>10 cm) than does Fe removal, presumably due to the requirement of higher pore-water sulfide and/or alkalinity levels (found deeper in the pore waters) for the precipitation of the more soluble Mn carbonate and/or sulfide phases ([Holdren et al., 1975](#); [Suess, 1979](#); [Aller, 1980b](#); [Middelburg et al., 1987](#)). Redrawn from [Skrabal, S.A., Donat, J.R., and Burdige, D.J., 2000](#). Pore water distributions of dissolved copper and copper-complexing ligands in estuarine and coastal marine sediments. *Geochimica et Cosmochimica Acta* 64, 1843–1857.

sediment incubations (often using ^{15}N -tracers), and benthic lander determinations of sediment nitrate uptake or N_2 gas efflux. However, recent studies have shown that nitrate loss or N_2 production in sediments does not exclusively occur by organotrophic denitrification (as illustrated in Table 1), but can also occur by processes such as anammox (ammonium oxidation by nitrite to produce N_2 gas), dissimilatory nitrate reduction to ammonium, or denitrification coupled to sulfide, Mn^{2+} and Fe^{2+} oxidation (see Table 2, Section 5.09.2.2.2, and the discussion in the next section). More work is therefore needed to elucidate carefully the different processes that impact nitrogen transformations in sediments, and to verify the role of organotrophic denitrification in sediment organic carbon remineralization (also see Chapter 5.08).

Recent studies in permeable sediments have also provided evidence for the occurrence of aerobic denitrification, that is, N_2 production in the presence of up to $\sim 100 \mu\text{M O}_2$ (Rao et al., 2007; Gao et al., 2009). While this type of denitrification has been observed in pure culture laboratory studies with a broad range of bacteria (also see Zehr and Ward, 2002; Rao et al., 2008), studies of denitrification in other more muddy marine sediments and oxygen-deficient water-column environments are consistent with the conventional view of denitrification as an anaerobic processes that does not occur until dissolved oxygen is essentially completely zero (less than $\sim 2\text{--}4 \mu\text{M}$; Brandes et al., 2007). Although the exact mechanism(s) by which aerobic denitrification in permeable sediments occurs is not well understood, one possible explanation is that organisms capable of carrying out this process have adapted to the varying redox conditions associated with the advective flow and exchange of anoxic pore water and oxic bottom water that occurs in permeable sediments (see Gao et al. (2009), and references cited therein). An alternate explanation is that the process actually occurs under anoxic conditions through closely coupled nitrification/denitrification in microenvironments isolated from the bulk pore waters (Jenkins and Kemp, 1984; Brandes and Devol, 1995; Rao et al., 2008). In this sense, this latter explanation shows some similarities to a process referred to oxygen-limited autotrophic nitrification–denitrification, or OLAND (Brandes et al., 2007). At the present time, the

evidence favoring any of these mechanisms over the others is equivocal.

Interest in denitrification in sediments stems, in part, from the fact that it represents the major removal process for fixed nitrogen in the oceans (Devol, 2008). Global-scale model calculations (Middelburg et al., 1996b) indicated that much of this removal ($\sim 60\%$) occurs in continental slope sediments (defined here as sediments in water depths $>150 \text{ m}$), with the remaining removal occurring primarily in shallower continental shelf sediments (also see Burdige, 2006). However until recently, the overwhelming majority of studies of sedimentary denitrification has been carried out in relatively fine-grained, muddy sediments, and these results largely formed the database used in the Middelburg et al. (1996b) calculations.

Estimates of denitrification rates in permeable sands are shown in Table 3, along with the model estimates from Middelburg et al. (1996b). At first glance, it would appear that estimates of denitrification in permeable sediments are slightly lower than the Middelburg et al. (1996b) model estimates. However, this conclusion must be tempered by the observation that when the occurrence of advective processes in permeable sediments is not incorporated into the experimental design, estimates of rates of biogeochemical processes in permeable sediments may be inaccurate and not representative of the true *in situ* rate (Huettel and Gust, 1992; Jahnke et al., 2000; Reimers et al., 2001; Berg and Huettel, 2009). Similarly, given the complexity of advective flow in permeable sediments, rate measurements (or model estimates) that do incorporate the occurrence of this flow may be difficult to interpret, or scale up, to obtain a larger-scale understanding of the rates of biogeochemical processes in permeable sediments (e.g., Cardenas et al., 2008).

However since sandy continental shelf sediments comprise $\sim 70\%$ of all continental shelves globally, if denitrification rates in high-permeability, sandy sediments are less than those in muddy sediments at similar water depths, then previous global estimates of marine sediment denitrification (Middelburg et al., 1996b) may have overestimated the magnitude of this loss term. Such considerations have implications regarding questions of whether or not the oceanic nitrogen budget is in

Table 3 Denitrification rates in continental shelf sediments

Site/methodology	Advection ^a	Denitrification rate ($\text{mmol m}^{-2} \text{ day}^{-1}$)
<i>Permeable sediments</i>		
Static core incubation, South Atlantic Bight (Vance-Harris and Ingall, 2005)	No	0.02
Benthic flux chamber incubation, mid-Atlantic Bight (Laurson and Seitzinger, 2002)	No	1.7
Static core incubation (stirred overlying water), North Sea (Lohse et al., 1996)	No	0.28
Benthic flux chamber incubations, Washington (USA) shelf (Devol, 1991; Devol and Christensen, 1993)	No	$\sim 2.3\text{--}3.2$
Flow-through sand columns, South Atlantic Bight (Rao et al., 2007)	Yes	0.25–1.46
Core incubations using continuous advection chambers ^b , Gulf of Mexico (Gihring et al., 2010)	No	0.13
	Yes	0.26–0.87
Numerical simulations with continental shelf parameters using coupled hydrodynamic and sediment biogeochemical models (Cardenas et al., 2008)	Yes	<0.24 to ~ 0.72
Data-driven, model estimate for North Atlantic continental shelf sediments (Seitzinger and Giblin, 1996)	N/A	0.69
Middelburg et al. (1996b) model estimate for continental margin sediments	No	$\sim 1.0\text{--}1.7$

^a This column indicates whether pore-water advective processes were incorporated into the experimental (or modeling) techniques used here to determine denitrification rates.

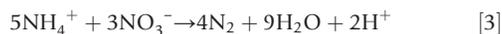
^b By varying the stirring rate in these chambers, one can go from diffusion-controlled chambers with no pore-water advection across the sediment–water interface, to chambers with varying amounts of pore-water advection (also see Huettel and Rusch, 2000, for details).

steady state with regard to input and removal terms (see Cardenas et al., 2008 for details), and will require further study.

Denitrification (in general) accounts for the removal of up to ~50% of the reactive nitrogen input to estuarine sediments (see compilation in Burdige, 2006). In whole estuary N budgets, denitrification, which largely occurs in the sediments (Boynton and Kemp, 2008), represents 2–3% to up to ~75% of the total nitrogen input to the estuary, and is a strong function of the water residence time in the estuary (Nixon et al., 1996). In shallow estuarine systems (i.e., those with significant benthic primary production), factors associated with this primary production may also control the rates of sedimentary denitrification (Joye and Anderson, 2008). This topic is discussed in greater detail in Chapters 5.07 and 5.08.

5.09.6.1 Anammox

In recent years, it has been shown that denitrification can be combined with the oxidation of substrates other than organic matter (i.e., see reactions 1–4 in Table 2), and one such reaction that has been of particular interest in recent years is the anammox reaction (reaction 1 in Table 2). Strictly speaking, this reaction involves ammonium oxidation at the expense of nitrite (rather than nitrate) reduction. However, in nature, nitrite is generally observed at much lower concentrations than nitrate, and is often a transient intermediate in oxidative and reductive processes in the nitrogen cycle (e.g., nitrification and denitrification; Hulth et al., 2005). Furthermore, because nitrate is readily reduced to nitrite in environments where anammox occurs (Dalsgaard et al., 2005), the biogeochemical significance of anammox is often considered from the perspective of nitrate reduction coupled to ammonium oxidation, or



In fact, early evidence for the occurrence of anammox was based on thermodynamic calculations and field observations that suggested the occurrence of this specific reaction (for this historical perspective, see Dalsgaard et al., 2005; Hulth et al., 2005; and Devol, 2008).

Anammox is expected to occur in O₂-deficient sedimentary environments similar to those in which organotrophic denitrification occurs. However, anammox is presumably carried out by autotrophic organisms (who fix carbon using the energy gained from reaction 3), whereas organotrophic denitrifiers are heterotrophs. This difference is not well discussed in literature in terms of the relative importance of the two processes (although do see discussions in Ward et al., 2009), and it may be important in terms of the overall controls on the occurrence of these two N removal processes. Anammox also requires a source of both nitrite and ammonium, and this too may play a role in regulating the occurrence of this process in sediments (see below for details).

Rates of anammox have been determined in a range of estuarine, coastal, and continental margin sediments, from the intertidal down to water depths of ~700 m (see Dalsgaard et al., 2005 for a review). As a percentage of overall N₂ production in sediments, the importance of anammox increases with increasing water depth (Dalsgaard et al., 2005), from less than ~5% in intertidal sediments to ~60–70% in Danish continental

margin sediments of the Skagerrak (700 m water depth). In this data set, this trend is largely controlled by a strong decrease in the rate of organotrophic denitrification (roughly 2 orders of magnitude) with water depth. Absolute anammox rates are perhaps higher at shallower depths, although the overall magnitude of change in the observed rates is one order of magnitude or less.

More specifically though, rates of organotrophic denitrification in sediments are positively correlated with somewhat interconnected parameters such as sediment organic matter reactivity or reductant availability (Thamdrup and Dalsgaard, 2002; Trimmer et al., 2003; Dalsgaard et al., 2005; Engström et al., 2005). In contrast, the anammox rate shows no such behavior (Dalsgaard et al., 2005; Engström et al., 2005). This could then explain the observed trend of an increase in the relative importance of anammox with increasing water depth since, for example, sediment organic matter remineralization rates show a significant inverse correlation with water-column depth (Dalsgaard et al., 2005; Burdige, 2006). Ultimately, however, nitrite availability may play a key role in regulating anammox activity in sediments (e.g., Hulth et al., 2005), although how this occurs is not well understood. Finally, the issue of sediment stability (as discussed, for example, in the next section regarding anoxic nitrification) may be important in regulating anammox activity in sediments (Dalsgaard et al., 2005; Hulth et al., 2005), although again this suggestion is not well tested.

In estuarine settings, the relative importance of anammox to total N₂ production generally decreases with increasing salinity (Trimmer et al., 2003; Rich et al., 2008; Koop-Jakobsen and Giblin, 2009), although, consistent with the discussion above, in all of these studies anammox was ~10% or less of total N₂ production in estuarine sediments, except in tidal freshwater sediments in the upper Chesapeake Bay where this value was ~20% (Rich et al., 2008). It is unknown at the present time whether the observed trend in relative anammox production rates with salinity is the result of a direct salt effect on microbial processes affecting nitrogen cycling, or is the result of an indirect effect that simply covaries with salinity.

5.09.6.2 Anoxic Nitrification

The anammox reaction represents one of a number of alternate pathways for anoxic ammonium oxidation in nature. Other such reactions that have generated interest in recent years include anoxic nitrification (reaction 5 in Table 2) as well as Mn reduction coupled to oxidative N₂ production (reaction 6 in Table 2). A wide range of seemingly contradictory observations are reported in the literature for and against the occurrence of these reactions and/or biological involvement in these reactions (see recent discussions in Hulth et al., 2005 and Bartlett et al., 2008). For anoxic nitrification, Bartlett et al. (2008) have attempted to reconcile these observations by suggesting that the reaction is strongly dependent on sediment stability (defined in a very broad sense to include physical processes such as flood events or sediment slumping, sediment mixing by bioturbation, as well as perturbations to the sediments that occur during experimental setup in manipulative studies examining anoxic nitrification). Future work will be needed to test this suggestion and thus better understand the

role (and significance) of these processes in Mn and N dynamics in marine sediments.

5.09.6.3 Nitrogen Loss from Sediments: Closing Thoughts

The identification of a number of new nitrogen reactions has indicated that oceanic and sedimentary nitrogen cycling is more complex than previously thought (e.g., Hulth et al., 2005). Interest in nitrogen cycling in estuarine and coastal sediments stems, in part, from this fact, and the fact that these sediments represent the major sites for the removal of fixed nitrogen in the oceans. Historically, this removal has been thought to occur primarily by N_2 production associated with anaerobic organotrophic denitrification (Devol, 2008). However in this regard, we know very little about the qualitative and quantitative significance of aerobic denitrification, anammox, and other pathways for nitrogen removal with more direct linkages to the Mn and Fe redox cycling (e.g., see Table 2), and more work here is clearly needed (also see similar discussions in Hulth et al., 2005 and Chapter 5.08). These new linkages of N cycling to Fe and Mn redox cycling further suggest that suboxic sediments such as physically reworked deltaic shelf sediments (e.g., the Amazon shelf; see Section 5.09.4.2) may be more important sites for nitrogen cycling (and perhaps fixed nitrogen loss) than previously thought (e.g., Hulth et al., 2005).

5.09.7 Iron and Manganese Reduction

Unlike the other respiratory processes discussed here, organotrophic manganese and iron reduction use solid, rather than dissolved, electron acceptors. (Note that here metal oxide reduction coupled to organic carbon remineralization will be referred to as organotrophic metal oxide reduction, to differentiate it clearly from abiotic (or microbial) reduction coupled to the oxidation of other chemical species (e.g., sulfide).) The most reactive forms (with respect to abiotic or microbial reductive dissolution) are generally poorly crystalline, amorphous oxides, or oxyhydroxides (Burdige et al., 1992; Thamdrup, 2000), referred to here, in a general sense, as metal (or Fe or Mn) oxides. In sediments these oxides are often found as coatings on inorganic or biogenic particles, such as clays or siliceous tests (for a more detailed discussion of the mineralogy of these oxide phases, see Burns and Burns, 1981; Cornell and Schwertmann, 1996; and Post, 1999). Microbes can also reduce other forms of oxidized manganese and iron, including more crystalline oxide phases, as well as structural Fe(III) in clay minerals such as smectite (e.g., Burdige et al., 1992; Roden and Zachara, 1996; Kostka et al., 2002a; Dong et al., 2003). More detailed discussions of the mechanisms of microbial Fe and Mn reduction and the organisms involved can be found elsewhere (Nealson and Saffarini, 1994; Lovley, 2000).

An important aspect of Fe and Mn biogeochemistry is that these elements undergo redox transformations at Earth surface conditions, which change their solubility. Reduced forms can, under some conditions, be soluble, while oxidized forms (solid oxides or oxyhydroxides) are highly insoluble. The occurrence of iron and manganese reduction in sediments is often consistent with the concept of biogeochemical zonation discussed earlier. However Mn and Fe oxides can also be reduced by

inorganic compounds such as sulfide, and a number of organic acids and ligands; furthermore, Fe^{2+} itself can reduce manganese oxides (Burdige and Nealson, 1986; Myers and Nealson, 1988b; Yao and Millero, 1993; Stone et al., 1994; Sunda and Kieber, 1994; Yao and Millero, 1996). In particular, since sulfate reduction is an important process in estuarine and coastal sediments, upward fluxes of sulfide from deeper sediments can lead to Fe^{2+} and Mn^{2+} production in more shallow regions of the sediments through sulfide mediated metal oxide reduction (i.e., not directly coupled to bacterial respiration), despite the fact that organotrophic metal oxide reduction might be predicted to occur there. The same is also likely true in the upper portion of the sulfate reducing zone of such sediments, particularly when sulfate reduction begins essentially at the sediment–water interface (e.g., see Figure 6 and relevant discussions in Thamdrup, 2000). Not only does this confound, at times, the ability to estimate rates of organotrophic Fe and Mn reduction in sediments (Kostka et al., 2002c), but these interactions between the Mn and Fe redox cycles and the sulfur cycle likely play a role in regulating the relative importance of organotrophic Fe and Mn reduction in overall sediment organic carbon remineralization.

Compared to other organic matter remineralization processes, far fewer studies have directly examined rates of organotrophic metal oxide reduction in sediments. There are a number of reasons for this (Thamdrup, 2000; Thamdrup and Canfield, 2000), including the fact that during sediment incubations the production of chemical reductants of these oxides (e.g., sulfide production by bacterial sulfate reduction) can make it difficult to distinguish between microbial (organotrophic) Mn and Fe reduction and abiotic, chemical reduction. Rates of organotrophic Mn and Fe reduction can also be obtained by modeling pore-water profiles (Berg et al., 2003), and, somewhat more indirectly by subtracting the rates of other remineralization processes (e.g., sulfate reduction or aerobic respiration) from estimates of the rate of total sediment carbon oxidation (Canfield et al., 1993a, 1993b; Kristensen et al., 2000; Thamdrup, 2000; Jensen et al., 2003; Hyun et al., 2009).

Where rates of metal oxide reduction have been examined in the context of total organic carbon remineralization in estuarine and coastal sediments (Figure 7), we see that the relative rates range from 0% to almost 100%, with a large number of sites having relative rates of ~20–50%. Although not explicitly shown here, under almost all circumstances Fe reduction, rather than Mn reduction, is the predominant organotrophic metal oxide reduction process (see below for details). Canfield et al. (2005) similarly suggested (using much of the same data shown here) that where rates of iron reduction have been directly determined, iron reduction is, on average, 17% of total sediment organic carbon remineralization and 26% of anaerobic organic carbon remineralization. In past studies, the failure to explicitly account for organotrophic metal oxide reduction potentially leads to an overestimate of the importance of aerobic respiration relative to sulfate reduction (Jensen et al., 2003).

The results in Figure 7 also show that there does not appear to be any consistent trend in the relative rates of organotrophic metal reduction with water-column depth, beyond the fact that the process becomes insignificant in sediments in water depths greater than ~1000–2000 m. In these deep-water sediments,

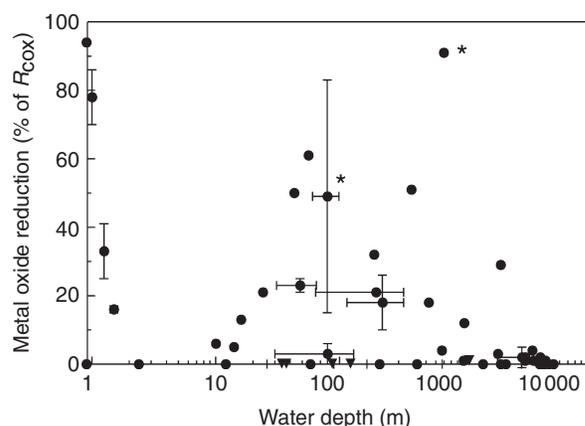


Figure 7 The relative rate of organotrophic Fe and Mn reduction (as compared to total sediment organic carbon oxidation or R_{COX}) vs. water depth. At all sites except those where the data points are annotated with ‘*’ (and where Mn reduction dominates) Fe reduction is the predominant (and almost the exclusive) organotrophic metal oxide reduction process. Low bottom-water oxygen sites are indicated by red triangles. Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton where references to most of the original data can be found. New data shown here are from Rysgaard, S., Thamdrup, B., Risgaard-Petersen, N., Fossing, H., Berg, P., Christensen, P.B., Dalsgaard, T., 1998. Seasonal carbon and nutrient mineralization in a high-Arctic coastal marine sediment, Young Sound, Northeast Greenland. *Marine Ecology Progress Series* 175, 261–276; Kristensen, E., Andersen, F.Ø., Holmboe, N., Holmer, M., Thongtham, N., 2000. Carbon and nitrogen mineralization in sediments of the Bangrong mangrove area, Phuket, Thailand. *Aquatic Microbial Ecology* 22, 199–213; Thamdrup, B., 2000. Bacterial manganese and iron reduction in aquatic sediments. *Advances in Microbial Ecology* 16, 41–83; Thamdrup, B., Canfield, D.E., 2000. Benthic respiration in aquatic sediments. In: Sala, O.E., Jackson, R.B., Mooney, H.A., Howarth, R.A. (Eds.), *Methods in Ecosystem Science*. Springer, New York, NY, pp. 86–102; Kostka, J.E., Gribsholt, B., Petrie, E., Dalton, D., Skelton, H., Kristensen, E., 2002b. The rates and pathways of carbon oxidation in bioturbated saltmarsh sediments. *Limnology and Oceanography* 47, 230–240; Kostka, J.E., Roychoudhury, A., Van Cappellen, P., 2002c. Rates and controls of anaerobic microbial respiration across spatial and temporal gradients in saltmarsh sediments. *Biogeochemistry* 60, 49–76; Berg, P., Rysgaard, S., Thamdrup, B., 2003. Dynamic modeling of early diagenesis and nutrient cycling. A case study in an Arctic marine sediment. *American Journal of Science* 303, 905–955; Glud, R.N., Gundersen, J.K., Røy, H., Jørgensen, B.B., 2003. Seasonal dynamics of benthic O_2 uptake in a semienclosed bay: importance of diffusion and faunal activity. *Limnology and Oceanography* 48, 1265–1276; Jensen, M.M., Thamdrup, B., Rysgaard, S., Holmer, M., Fossing, H., 2003. Rates and regulation of microbial iron reduction in sediments of the Baltic–North Sea transition. *Biogeochemistry* 65, 295–317.

sediment O_2 uptake keeps up with the low organic carbon flux to the sediments and aerobic respiration dominates sediment organic matter remineralization (Emerson et al., 1985; Burdige, 2006).

Despite the fact that organotrophic Mn reduction is generally not a significant organic carbon remineralization process in most marine sediments, Mn redox cycling is often significant in estuarine and coastal (and other continental margin) sediments, and can play an important role as an electron shuttle in the sediments (see Section 5.09.2.3, and Burdige and Neelson, 1986; Canfield et al., 1993b; and Aller, 1994b). For example, in Long Island Sound sediments, re-oxidation of

Mn^{2+} annually accounts for ~40% of the sediment oxygen uptake, while sulfate reduction is the dominant organic matter remineralization process (Aller, 1994b). The proposed coupling of such redox reactions in these sediments is illustrated in Figure 1(b).

In examining metal oxide reduction rates in sediments (regardless of whether or not the process is microbially catalyzed), it has been noted that high rates of metal oxide reduction require internal processes that continually replenish the reactive metal oxides, since the needed supply of oxides greatly exceeds their input by sedimentation (Burdige, 1993; Canfield et al., 1993b; Thamdrup, 2000). This implies that there must be significant internal redox cycling between the reduced and oxidized forms of these metals, through processes described in Sections 5.09.2.3 and 5.09.3, to sustain high rates of metal oxide reduction. The initial oxides that form in sediments from Fe^{2+} and Mn^{2+} oxidation are amorphous, poorly crystalline phases (Burdige, 1993), which given time will slowly transform into more stable crystalline forms. This rapid redox cycling therefore maintains sediment metal oxides in their most reactive form, which may act as a positive feedback on organotrophic metal oxide reduction (Thamdrup, 2000).

The specific transport processes associated with this redox cycling vary among different sediments. Internal Mn and Fe redox cycling can be driven by relatively slow processes such as molecular diffusion and sediment burial (e.g., Burdige and Gieskes, 1983), although an examination of the sites summarized in Figure 7 suggests that these processes do not significantly contribute to the high relative rates of metal reduction shown in this figure. In many sediments (particularly fine-grained subtidal sediments in estuaries and on the continental shelf), bioturbation or bioirrigation play an important role in this redox cycling. They may provide the needed oxidant (e.g., O_2) input for the re-oxidation of reduced metals, and bioturbation also transports particulate oxides that are diagenetically produced in surface sediments to deeper depths where they are then consumed by microbial or chemical metal oxide reduction (Sundby and Silverberg, 1985; Aller, 1990; Canfield et al., 1993b; Aller, 2001; Berg et al., 2003). In intertidal (e.g., salt marsh) sediments, the activities of fiddler crabs and similar benthic organisms can play an analogous role in this redox cycling (e.g., Kostka et al., 2002b), while in vegetated subtidal and intertidal sediments (e.g., salt marshes, mangrove forests, seagrass beds) the input of photosynthetically produced O_2 also is important (Holmer et al., 1999; Kristensen et al., 2000; Hyun et al., 2009).

Oxygen input by pore-water advective exchange in permeable sediments (Section 5.1.2.1) can also promote the redox cycling of Mn and Fe, as well as other redox-sensitive trace metals. Such Mn and Fe redox cycling has been demonstrated in laboratory flume studies with natural permeable sands (Huettel et al., 1998), although the mechanism(s) and biogeochemical significance of this metal redox cycling have to date not been examined *in situ*.

Physical reworking of mobile tropical muds and deltaic sediments (Section 5.09.4.2) has similarly been shown to mediate Fe (and to a lesser extent Mn) redox cycling. The frequency and intensity of physical reworking lead to non-steady-state conditions in the sediments (Mackin et al., 1988) and the continual re-oxidation of reduced Fe or Mn (or S) that is produced in the sediments. Thus, in comparison to sediments

in low-energy environments which have comparable rates of net sediment accumulation and organic carbon remineralization (see Section 5.09.4.1), these reworked sediments are, roughly speaking, poised at a redox state such that in a net sense iron reduction, rather than sulfate reduction, dominates organic matter remineralization (e.g., Aller et al., 1986).

The term net is used here, since it has not been definitively demonstrated that the observed iron reduction in these sediments is indeed directly coupled to organic carbon remineralization. Rather it may involve a coupling with sulfur redox cycling in which bacterial sulfate reduction is actually the predominant respiratory process in the sediments, which is coupled to iron reduction through sulfide oxidation (Aller et al., 1986; Madrid et al., 2001). However, calculations presented by Aller (2004) suggest that if the biogeochemical zonation inferred by Table 1 occurs in physically reworked sediments not in vertical sense (as it is normally considered), but in a temporal sense (i.e., during the non-steady-state diagenesis of the sediments as a whole after a resuspension/reoxidation event), then the availability of oxygen, nitrate, and reactive Fe and Mn oxides is such that sulfate reduction should not occur in these sediments in less than ~1 year. Therefore, because the occurrence of physical reworking has a frequency of less than $\sim 1 \text{ yr}^{-1}$ (e.g., McKee et al., 2004), the sediments should be poised at suboxic conditions with no net (and minimal gross) sulfate reduction.

As noted earlier (Section 5.09.4.2), this type of physical reworking of sediments and its associated metal redox cycling are not restricted to continental shelf mobile muds, and can also occur in certain high-energy regions of estuaries, such as the estuarine turbidity maximum (Dellapenna et al., 1998; Abril et al., 1999; Schaffner et al., 2001; Galler and Allison, 2008). Studies of the estuarine turbidity maximum in the Gironde estuary (between salinity 0.15 and 6) clearly demonstrate that fluid muds in this region are sites for intense metal cycling (Robert et al., 2004). However, studies have been unable to differentiate whether the observed Mn and Fe reduction occurs through organotrophic metal oxide reduction, or, as discussed above, through a coupling with sulfate reduction and sulfide oxidation (Audry et al., 2006; Audry et al., 2007a, 2007b; also see Section 5.09.10).

Organotrophic iron reduction shows some dependence on the concentration of reactive Fe(III) oxides (Thamdrup, 2000; Gribsholt et al., 2003; Jensen et al., 2003), and the importance of organotrophic iron reduction (relative to total anaerobic remineralization) generally begins to significantly decline when the concentration of highly reactive Fe(III) drops below $\sim 30\text{--}40 \mu\text{mol} \cdot \text{cm}^{-3}$ (Figure 8). Since anaerobic remineralization generally dominates organic carbon remineralization in the largely estuarine and coastal sediments shown in this figure (Section 5.09.5), these observations further point to the importance of organotrophic iron reduction in shallow water sediments. It can also be seen in Figure 8 that there is a fair bit of scatter around the curve here. In part, this may be the results of some of the inherent difficulties (and large uncertainties) in determining rates of organotrophic metal oxide reduction (Thamdrup, 2000; Thamdrup and Canfield, 2000). However, these results may also point to the possibility that high rates of internal Fe redox cycling can stimulate high rates of organotrophic iron reduction in a manner that is not simply

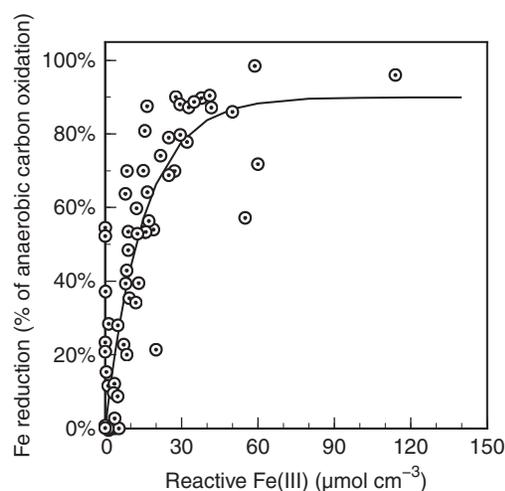


Figure 8 The relative rate of organotrophic Fe reduction (as compared to anaerobic sediment organic carbon oxidation) in marine and estuarine sediments vs. the concentration of reactive Fe(III) oxides in the sediments. The empirical best fit curve through the data is $\% \text{FeR} = 90 \cdot (1 - e^{-0.069 \cdot \text{Fe(III)}})$; see Jensen et al., 2003 for a very similar best-fit curve obtained with a subset of these results). Reactive Fe is defined here as the amount of Fe in oxides that is available for reductive dissolution by sulfide or organotrophic metal oxide reduction. Many of the analytical schemes used to examine iron speciation in sediments refer to this as 'poorly crystalline' or 'highly reactive' Fe(III). From Kristensen, E., Andersen, F.Ø., Holmboe, N., Holmer, M., Thongtham, N., 2000. Carbon and nitrogen mineralization in sediments of the Bangrong mangrove area, Phuket, Thailand. *Aquatic Microbial Ecology* 22, 199–213; Thamdrup, B., 2000. Bacterial manganese and iron reduction in aquatic sediments. *Advances in Microbial Ecology* 16, 41–83; Gribsholt, B., Kostka, J.E., Kristensen, E., 2003. Impact of fiddler crabs and plant roots on sediment biogeochemistry in a Georgia saltmarsh. *Marine Ecology Progress Series* 259, 237–251; Jensen, M.M., Thamdrup, B., Rysgaard, S., Holmer, M., Fossing, H., 2003. Rates and regulation of microbial iron reduction in sediments of the Baltic–North Sea transition. *Biogeochemistry* 65, 295–317; and Hyun, J.-H., Mok, J.-S., Cho, H.-Y., Kim, S.-H., Lee, K., Kostka, J., 2009. Rapid organic matter mineralization coupled to iron cycling in intertidal mud flats of the Han River estuary, Yellow Sea. *Biogeochemistry* 92, 231–245.

dependent on the sediment concentration (pool size) of reactive Fe(III).

Assuming that a threshold Mn concentration comparable to that seen in Figure 8 also holds for organotrophic manganese reduction (Thamdrup et al., 2000), it suggests that the low concentration of manganese in most estuarine and continental margin sediments (Table 4) may limit organotrophic manganese reduction, at the expense of either sulfate reduction or organotrophic iron reduction. Such a situation is also expected to have a negative feedback on organotrophic manganese reduction, since the end products of these other metabolic processes (sulfide and Fe^{2+}) rapidly reduce manganese oxides (Figure 6). Differences in the rates of reduced metal re-oxidation ($\text{Fe}^{2+} > \text{Mn}^{2+}$ at natural pH values) and in the solubility of reduced metal phases such as sulfides or carbonates ($\text{Fe(II)} < \text{Mn(II)}$) may play some role here by allowing many sediments to better retain reduced Fe versus Mn during metal redox cycling (e.g., see benthic flux chamber results in Balzer, 1982 and Sundby et al., 1986). Therefore, factors that enhance the retention of Mn in the sediments (a relatively deep oxygen penetration depth as in the Skaggerak sediments) or lead to

Table 4 Representative values of Fe and Mn in differing marine sediments

Location	Concentration ^a	
	($\mu\text{mol gdw}^{-1}$)	($\mu\text{mol cm}^{-3}$)
<i>Reactive Fe^b</i>		
Mesohaline Chesapeake Bay ^c	150–200	~20–50
Continental margin sediments ^d	~50–200	~25–100
N. American temperate nearshore and continental margin sediments ^e	~100–200	~25–100
<i>Selected sites where Fe reduction appears to be a major component of sediment organic carbon remineralization</i>		
Gulf of Papua ^f	390–450	~240–270
Amazon continental shelf ^g	~280	~80–200
Georgia (US) salt marsh sediments ^h		100–125
Baltic-North Sea transition sediments ⁱ		25–40
Intertidal mangrove sediments, Thailand ^j	~15–30	~9–16
<i>Reactive Mn^b</i>		
Mesohaline Chesapeake Bay ^k	~5–30	~1–16
Nearshore muddy sediments ^l	<15	<8
<i>Sites where Mn reduction appears to be a major component of sediment organic carbon remineralization</i>		
Panama Basin (3890 m water depth) ^m	180–730	70–290
Skaggerak (Danish continental margin sediments; 695 m water depth) ⁿ		~100–150
Oxic Black Sea sediments (surface sediments; 62–100 m water depth) ^o		~20–120

^a Concentrations reported in the literature as $\mu\text{mol gdw}^{-1}$ (or wt.%) were converted to $\mu\text{mol cm}^{-3}$ (total volume of wet sediment) for ease of comparison among the entire compilation of data presented here. This conversion is very sensitive to the assumed porosity of the sediment (ϕ) since the calculation depends on the term $(1-\phi)$. Thus, for example, a range in assumed porosities of 0.8–0.9 (~11% difference) results in a factor of two difference in concentrations expressed per cm^3 of total sediment (for further details, see [Burdige, 2006](#)).

^b Reactive Fe or Mn is defined here as the amount of Fe and Mn in oxides that is available for reductive dissolution by sulfide or organotrophic metal oxide reduction. For iron, many of the analytical schemes used to examine iron speciation in sediments refer to this as poorly crystalline or highly reactive Fe(III) oxides.

^c From [Cornwell and Sampou \(1995\)](#). Porosity was assumed to range from 0.9 to 0.95.

^d From results in [Canfield et al. \(1992\)](#) and [Raiswell and Canfield \(1998\)](#). These workers report a range of 1–4 wt.% total Fe in these sediments, and based on their extraction techniques they estimate that 25–28% of the total iron is highly reactive iron. Porosity was assumed to be 0.8.

^e From a summary presented in ([Aller et al., 2004a](#)). Porosity was assumed to range from 0.8 to 0.9.

^f From [Aller et al. \(2004a\)](#). Porosity was assumed to be 0.75.

^g From [Aller and Blair \(1996\)](#). Based on a porosity range of 0.72–0.9, using % water data in [Aller and Aller \(1986\)](#).

^h From [Kostka et al. \(2002b\)](#).

ⁱ From [Jensen et al. \(2003\)](#).

^j From [Kristensen et al. \(2000\)](#).

^k From [Holdren et al. \(1975\)](#). Porosity was assumed to range from 0.9 to 0.95.

^l From [Chester \(2000\)](#). Since this is the total Mn content of the sediment, this is an upper limit of the Mn that is found in reactive oxides. Porosity was assumed to be 0.8.

^m From [Aller \(1990\)](#). Porosity was assumed to be 0.85. For comparison, these concentrations are 1–4 wt% Mn.

ⁿ From [Canfield et al. \(1993b\)](#) and [Canfield \(1993\)](#).

^o From [Thamdrup et al. \(2000\)](#).

elevated Mn input to sediments (hydrothermal inputs to Panama Basin sediments) appear to be important for organotrophic manganese reduction to be a significant remineralization process. However, why extraordinarily high concentrations of sedimentary manganese oxides are required for organotrophic Mn reduction to be quantitatively significant is not well understood (see [Thamdrup, 2000](#) for further discussions).

To the best of my knowledge, there have been no studies that have specifically addressed the importance of organotrophic metal oxide reduction as a function of salinity in an estuary. Organotrophic iron reduction is important in freshwater wetlands ([Roden and Wetzel, 1996](#)), and inhibits the occurrence of methanogenesis (also see [Lovley and Phillips, 1987](#)), consistent with the biogeochemical zonation and anaerobic food chain models discussed earlier. Historically, the distribution of remineralization processes in estuarine sediments has been examined in terms of the relative roles of sulfate reduction versus methanogenesis (e.g., [Martens and Goldhaber, 1978](#)), based on sulfate availability in an estuary

as a function of salinity, and the competition between sulfate reducers and methanogens for key carbon substrates (also see [Capone and Kiene, 1988](#)). However, organotrophic iron reduction is both thermodynamically ([Table 1](#)) and kinetically ([Section 5.09.2.1.1](#)) favored over sulfate reduction and methanogenesis. Thus, the relative importance of organotrophic iron reduction should not be directly affected by the increasing importance of sulfate reduction and the decreasing importance of methanogenesis as one moves down an estuary. The relative importance of organotrophic iron reduction may be indirectly affected by other factors that vary through an estuary, such as the intensity of iron redox cycling in the sediments (to supply the needed reactive oxides), as well as competition between iron reduction mediated by sulfide oxidation versus organotrophic iron reduction. Based on the discussions above, these factors themselves may be related to, for example, changes in the quality and quantity of estuarine organic matter, changes in the intensity and types (e.g., bioturbation versus bioirrigation) of benthic macrofaunal processes, as well as changes in the

importance of sulfate reduction in estuarine sediments. More work is needed to examine critically these suggestions.

Finally, Mn and Fe redox cycling in general, regardless of the exact mechanisms by which it occurs, plays an important role in the biogeochemical cycles of other elements (e.g., phosphorus and other trace metals) in estuarine and coastal sediments and water columns. This will be discussed in Section 5.09.11 (also see Ruttenberg, 2003 and Chapter 5.06).

5.09.8 Sulfate Reduction and Sulfide Mineral Formation

Sulfate reduction plays an important role in organic matter remineralization in estuarine and coastal sediments, generally accounting for ~50% (to up to ~100%) of R_{cox} (Canfield et al., 2005; Burdige, 2006). When compared to other anaerobic remineralization processes, the large concentration of sulfate in seawater (~28 mM) versus that of other oxidants such as nitrate or oxygen plays a role. However, as one moves into the low-salinity reaches of an estuary, this general observation can break down (see the end of this section for details).

Low relative rates of sulfate reduction can also be observed in estuarine and coastal sediments, suggesting that a number of factors regulate its occurrence in these environments. For example, discussions in Section 5.09.7 have shown that organotrophic iron reduction can be a major component of anaerobic remineralization in many coastal sediments. Similarly, the occurrence of sulfate reduction requires a

relatively large flux of reactive organic matter to the sediments, as compared to the input of oxidants such as O_2 or nitrate. Thus nearshore sediments with low carbon inputs are likely to be sites where sulfate reduction is of minor importance.

The sulfur cycle in estuarine and coastal sediments (and continental margin sediments in general) is also of interest and importance for other reasons. These regions represent the dominant sites of sulfur removal from the modern oceans due to burial here of pyrite (FeS_2) or diagenetically produced organic sulfur (Vairavamurthy et al., 1995; Berner and Berner, 1996; Goldhaber, 2003). Both of these are products of sulfate reduction (Figure 9). Long-term changes (>100 million years) in this burial rate are linked to changes in the global redox state of the Earth's surface, that is, this plays a role in controlling atmospheric oxygen levels on these long timescales (Berner, 1999; Hedges, 2002; Berner, 2004). This topic is beyond the scope of this article, although the interested reader is urged to look at the references cited here for further details. Finally, in estuarine and coastal sediments, the cycling of trace metals (many of which may be found at relatively high levels as a result of anthropogenic inputs) is strongly linked to sulfur redox cycling (uptake in sulfide phases such as pyrite, release during pyrite oxidation). The topic is discussed in Section 5.09.10.

The conceptual model in Figure 9 that is used to describe sulfur cycling in recent marine sediments includes many processes that have been discussed previously, including bacterial sulfate reduction and sulfide oxidation. One set of processes that have not been discussed are sulfur disproportionation

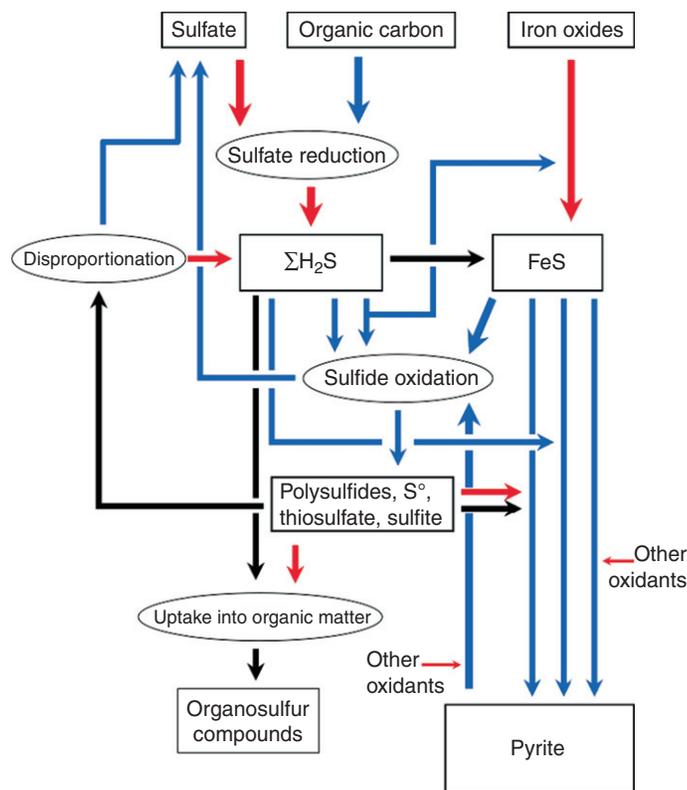


Figure 9 A schematic representation of the sediment sulfur cycle. Note that red arrows indicate reductive processes, blue arrows indicate oxidative process, and black arrows indicate no redox transformation. Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton.

reactions involving elemental sulfur, thiosulfate, and sulfite. These reactions are the inorganic equivalent of organic fermentation reactions (see Section 5.09.2.1.1) and result in the production of reduced sulfide and oxidized sulfate from these intermediate oxidation state sulfur species (Jørgensen and Bak, 1991). For example, thiosulfate disproportionation can be written as



In addition, analogous reactions can be written for S^0 and sulfite disproportionation. An important aspect of sulfur disproportionation is that it results in significant sulfur isotope fractionation. In particular, the sulfide that is produced by this disproportionation can be depleted in ^{34}S by $\sim 3\text{--}28\%$ relative to the starting intermediate oxidation state sulfur compound (Canfield and Thamdrup, 1994; Habicht et al., 1998; Habicht and Canfield, 2001). The significance of this is discussed below.

In examining Figure 9 we start with bacterial sulfate reduction, which produces dissolved sulfide as one of its end products. In nearshore sediments with TOC contents of $\sim 1\text{--}3\%$, sulfate reduction occurs over the upper tens of centimeters to several meters of sediment. Depending on whether sulfate or reactive organic carbon is limiting, sulfate concentrations either decrease to zero, oftentimes in an exponential-like fashion (see Figures 6 and 10), implying sulfate limitations, or reach some asymptotic nonzero concentration at depth, implying limitations by reactive organic carbon. The dissolved sulfide produced by bacterial sulfate reduction in sediments has several possible fates: reaction with iron oxides or Fe^{2+} to form FeS (see below), incorporation into sediment organic matter (formation of organo-sulfur compounds), reaction with FeS to form pyrite, and oxidation to form S^0 or other more oxidized sulfur species, up to, and including, sulfate.

The reaction of sulfide with iron oxides is an important process in sediments and plays a key role in explaining why

sulfide does not accumulate in pore waters until some depth below that where sulfate reduction (sulfide production) begins to occur (Figure 6). In such regions of the sediment, reactive iron oxides (Section 5.09.7), if present, are rapidly reduced by dissolved sulfide, effectively removing sulfide from the pore waters. Once these reactive oxides are exhausted, and Fe^{2+} in the pore waters precipitates out as FeS, more refractory forms of oxidized iron (e.g., more crystalline oxides, magnetite, and iron in silicates) are less efficient at removing (i.e., reacting with) sulfide. As a result, sulfide then begins to accumulate in the pore waters (Canfield et al., 1992; Raiswell and Canfield, 1998).

5.09.8.1 Pyrite Formation in Sediments

In sediments where sulfate reduction occurs, pyrite (FeS_2) is the dominant form of solid-phase sulfur. Pyrite has a range of crystal morphologies, although in marine sediments only a limited number are known to occur, with single euhedra and framboids generally dominating (Canfield and Raiswell, 1991b; Goldhaber, 2003; Rickard and Luther, 2007).

Other sulfide minerals found in marine sediments include amorphous-FeS and mackinawite (FeS_{1-x} , $x \leq \sim 0.1$). Both are commonly referred to in the literature as FeS. Another metastable sulfide phase is greigite (Fe_3S_4), the sulfur analog to magnetite (Fe_3O_4). All of these phases are soluble in nonoxidizing mineral acids such as HCl and are often referred to as acid volatile sulfide (AVS). Pyrite is not soluble in HCl and requires more stringent (i.e., oxidizing or reducing) conditions to be solubilized. These differences in solution chemistry have led to the development of selective leaching techniques, which at least operationally allow one to separately quantify AVS and pyrite in marine sediments (Canfield et al., 1986; Cornwell and Morse, 1987; Morse et al., 1987).

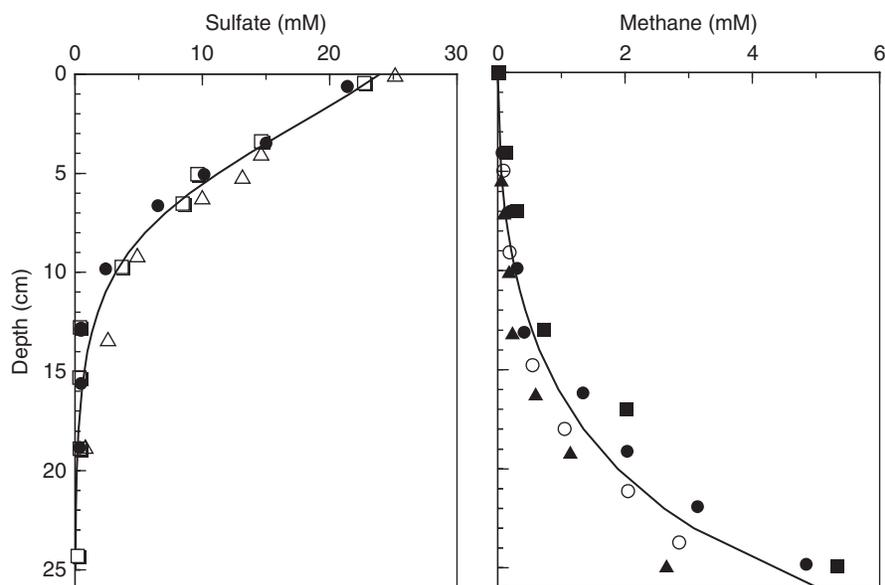


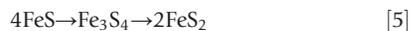
Figure 10 Pore-water sulfate and methane depth profiles from sediments in Saanich Inlet, British Columbia. From Devol, A.H., Anderson, J.J., Kuivala, K., Murray, J.W., 1984. A model for coupled sulfate reduction and methane oxidation in the sediments of Saanich Inlet. *Geochimica et Cosmochimica Acta* 48, 933–1004.

The black color that is common in many organic-rich coastal sediments is due to the presence of these sulfide phases. AVSs are metastable phases that will eventually transform into pyrite, the thermodynamically stable sulfide phase under early diagenetic conditions (e.g., Rickard and Luther, 2007). Another form of sulfur found in marine sediments is solid elemental S⁰, which forms during sulfide oxidation, and also plays an important role in pyrite formation.

Because FeS is metastable, once it is produced it is either re-oxidized (see below) or transformed into pyrite. The oxidation of FeS in sediments, along with dissolved sulfide and pyrite, can occur either chemically or microbially, using oxidants such as O₂, nitrate or metal oxides (see Section 5.09.2.2). In mixed redox sediments, these processes are mediated by a whole host of transport processes (e.g., bioturbation, bioirrigation, or macrophyte O₂ input; e.g., see Section 5.09.3); in their absence (e.g., Section 5.09.4.1) these oxidation reactions may occur as a result of the downward diffusion of oxygen or nitrate into the sulfidic sediments. The occurrence of these reactions plays a role in the extent to which sulfides produced by bacterial sulfate reduction are retained in the sediments, that is, buried as reduced sulfur. At the same time though, because the disulfide in pyrite (FeS₂) is more oxidized than its initial source, for example, sulfide in either dissolved sulfide or FeS, these oxidative processes also play a role in pyrite formation, and hence have an opposite effect on sulfur burial in sediments.

Experimental studies examining pyrite formation suggest three possible mechanisms for pyrite formation in marine sediments. In all three cases, FeS is the initial precursor for pyrite formation, because of the ease with which it forms by the reaction of dissolved sulfide with either Fe²⁺ or iron oxides, and because direct precipitation of pyrite from solution appears to be kinetically inhibited (Schoonen and Barnes, 1991). A detailed discussion of these mechanisms can be found in recent reviews (Goldhaber, 2003; Rickard and Luther, 2007).

One mechanism for pyrite formation involves the addition of the zero-valent sulfur in dissolved polysulfides (S_x²⁻) to FeS by a dissolution/precipitation reaction (Luther et al., 1991; Rickard et al., 1995). A second mechanism can be thought of as pyrite formation through iron loss (coupled to FeS oxidation), as opposed to sulfur addition, through a greigite intermediate,

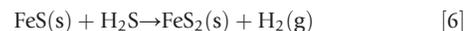


(Sweeney and Kaplan, 1973; Schoonen and Barnes, 1991; Wilkin and Barnes, 1996; Morse and Wang, 1997; Benning et al., 2000). A number of possible oxidizing agents, in addition to zero-valent forms of sulfur, may play a role in this type of pyrite formation. These include other sulfur species with intermediate oxidation states (e.g., thiosulfate) as well as O₂ itself. The factors controlling the occurrence of these two possible modes of pyrite formation are not well understood (see discussions in Schoonen and Barnes, 1991; Wang and Morse, 1996; and Goldhaber, 2003).

Given the potential oxidants required in these two modes of pyrite formation, their occurrence is consistent with the fact that much of the pyrite that forms in marine sediments does so close to the sediment–water interface, where rates of sulfate reduction are usually the highest and the availability of reactive iron is likely to be the greatest, that is, in association with mixed redox conditions in these surface sediments (Chanton et al.,

1987; Canfield et al., 1992; Goldhaber, 2003). Evidence in support of these oxidative processes and their role in pyrite formation comes, in part, from a wide range of sulfur isotope studies in the laboratory and in the field (Canfield and Thamdrup, 1994; Habicht and Canfield, 1997; Habicht et al., 1998; Habicht and Canfield, 2001; Sørensen and Canfield, 2004).

Pyrite formation also occurs deeper in sediments, where dissolved sulfide levels are high (Figure 6) and the oxidants discussed above (i.e., O₂, intermediate oxidation state sulfur species, or reactive Fe(III) oxides) are likely to be in very low concentrations or nonexistent. Here a third mechanism of pyrite formation may be



where H₂S now serves as the oxidizing agent of FeS, and reduced hydrogen gas is produced as an end product (Rickard, 1997). Although this reaction has a negative ΔG° (Wilkin and Barnes, 1996), experimental evidence in support and against its occurrence has been presented (Rickard et al., 1995; Wilkin and Barnes, 1996; Rickard, 1997; Benning et al., 2000). It is interesting to note, however, that H₂ is an excellent substrate for both sulfate reducers and methanogens, and is generally found at nM levels in anoxic marine sediments (Hoehler et al., 1998). Therefore in the region of the sediments where reaction (6; Table 2) is likely to be most important, the low hydrogen levels observed there could enhance the thermodynamic driving force for the occurrence of this reaction.

5.09.8.2 Pyrite Burial and Sulfur Burial Efficiency

Much of the pyrite found in marine sediments appears to form as a result of the interaction between oxidative, or mixed redox, processes and bacterial sulfate reduction. The occurrence of these same processes also leads to only a small fraction of the total sulfide produced by sulfate reduction eventually being buried as pyrite. Expressed another way, sulfur (≈pyrite) burial at depth is generally much smaller than the integrated gross rate of sulfate reduction; the ratio of the two is thus defined as the sulfur burial efficiency. Historically, oxygen has been assumed to be the predominant oxidant of pyrite (Morse, 1991). However, recent studies have also shown that other substances, such as nitrate, manganese, and iron oxides, may oxidize pyrite anaerobically by both biotic and abiotic processes (Luther and Church, 1992; Luther et al., 1992; Schippers and Jørgensen, 2002). As is also the case for anaerobic FeS oxidation (see Section 5.09.2.2), evidence to date regarding chemical versus microbial mediation of anaerobic pyrite oxidation is equivocal.

In most sediments sulfur burial efficiency is generally less than ~10–20% (Jørgensen, 1982b; Berner and Westrich, 1985; Chanton et al., 1987; Canfield, 1989; Swider and Mackin, 1989), although there are examples of sediments with much higher burial efficiencies (e.g., in Cape Lookout Bight sediments sulfur burial efficiency is 77%). Sediments with such high sulfur burial efficiencies are often sites with high sedimentation rates, high rates of sulfate reduction, and are also generally not extensively bioturbated or bioirrigated (Canfield, 1994; Goldhaber, 2003; also see Section 5.09.4.1). A high sulfur burial efficiency can also occur at low rates of sulfate reduction if large amounts of reactive iron are present in

the sediments (Marvin-DiPasquale and Capone, 1998). This observation points to the fact that the availability of sulfate, reactive iron, and metabolizable organic matter are all important parameters that control sulfur burial efficiency, and that of these, the availability of these last two quantities appears to be most critical. A detailed discussion of this topic is beyond the scope of this article, although any of the references cited above provide a good discussion of the topic (also see Berner, 1970; Morse and Berner, 1995).

In estuarine sediments, sulfate availability has the potential to limit sulfate reduction as one moves upstream into the low salinity reaches of an estuary. However, in actuality this is often not the case. Sulfate-reducing bacteria (both in lab and field studies) have a high affinity (low half saturation constant or K_m) for sulfate (Boudreau and Westrich, 1984; Ingvorsen and Jørgensen, 1984; Roden and Tuttle, 1993), suggesting that sulfate reduction will be limited by sulfate availability only at concentrations below ~2–3 mM, which will roughly occur at $S \approx 2.5$ –4. Nevertheless, as one moves into the very low salinity upper reaches of an estuary, the importance of sulfate reduction decreases, with a concomitant increase in the importance of methane production (Kelley et al., 1990; Middelburg et al., 1996a). This point is discussed in more detail in the next section.

In contrast, other factors such as organic carbon availability and reactivity do appear to play a role in regulating sulfate reduction in estuarine and coastal sediments (Westrich and Berner, 1984; Berner and Westrich, 1985; Marvin-DiPasquale and Capone, 1998). In sediments with a low sulfur burial efficiency, the effective recycling of sulfate in these sediments further minimizes the possibility of sulfate limitations on sulfate reduction. As discussed in Section 5.09.2.3 and illustrated in Figure 1(a), here sulfate largely serves as an electron shuttle for transporting oxidation equivalents into the sediments that ultimately are used to remineralize sedimentary organic carbon. At the same time though, in extremely organic-rich sediments sulfate reduction can become sulfate limited at depths where sulfate concentrations go to zero and methanogenesis begins to occur (Reeburgh, 1969; Martens and Berner, 1977; Devol et al., 1984; Martens and Klump, 1984; Martens et al., 1998). The depth in the sediments at which this occurs plays an important role in regulating methane gas loss from these sediments (see the next section for details).

5.09.9 Methanogenesis, Methane Oxidation, and Methane Fluxes to the Atmosphere

Upon complete sulfate depletion in sediments, methanogenesis occurs below the zone of sulfate reduction, consistent with the concepts of biogeochemical zonation discussed in Section 5.09.2.1. Given the high concentration of sulfate in seawater, the occurrence of methanogenesis in shallow marine sediments requires a relatively large flux of reactive organic matter to the sediments. As a result, methanogenesis is generally responsible for a small amount of sediment carbon remineralization. Globally, organic carbon remineralization by methanogenesis in sediments is ~12% that of organic carbon remineralization by sulfate reduction (Henrichs and Reeburgh, 1987), although in some sediments methanogenesis can be more important. For example, in Cape Lookout Bight sediments, organic carbon

remineralization by methanogenesis is ~43% that of remineralization by sulfate reduction (Martens and Klump, 1984).

In estuaries, the salinity decrease that occurs as one moves up the estuary also decreases the estuarine sulfate concentration. With this, the necessary carbon flux to the sediments required to achieve complete sulfate depletion also decreases. Thus as one moves into the very low salinity upper reaches of an estuary, there is an increase in the importance of methanogenesis to total sediment organic carbon remineralization (e.g., Kelley et al., 1990; Middelburg et al., 1996a).

In many marine sediments, much of the methane produced during methanogenesis is oxidized anaerobically, apparently using sulfate as the electron acceptor. This reaction, termed anaerobic oxidation of methane (AOM), can be written as



which is thermodynamically favored under typical *in situ* conditions ($\Delta G = -25 \text{ kJ mol}^{-1}$; Martens and Berner, 1977). While geochemical evidence since the 1970s has been consistent with the occurrence of AOM (Reeburgh, 1982; Alperin and Reeburgh, 1985), a complete understanding of the microbial processes involved in AOM remained elusive for a number of years (for a discussion of this history, see Canfield et al., 2005). However, it now appears that AOM is mediated by a consortium of sulfate-reducing bacteria and methanogens, through a process that has been termed ‘reverse methanogenesis’ (Hoehler et al., 1994; Boetius et al., 2000; Orphan et al., 2001; Strous and Jetten, 2004; Alperin and Hoehler, 2009).

In marine and estuarine sediments, AOM occurs in the transition zone between sulfate reduction and methanogenesis, as sulfate concentrations approach zero, and it often leads to characteristic concave-up methane pore-water profiles (see Figure 10; Martens and Berner, 1977; Reeburgh, 1982; Devol et al., 1984; Alperin and Reeburgh, 1985; Iversen and Jørgensen, 1985). In these situations, AOM serves as a quantitative sink for virtually all of the methane that is produced in the sediments (Henrichs and Reeburgh, 1987; Reeburgh, 2007). The process therefore significantly limits the global importance of the oceans as a source of methane to the atmosphere.

Methane produced in sediments that escapes oxidation by sulfate can also be oxidized aerobically by methanotrophic bacteria (Hanson and Hanson, 1996), and in low salinity or tidal freshwater systems this process can similarly play an important role in regulating the methane flux from these sediments. A microbial consortium capable of anaerobic methane oxidation at the expense of denitrification has also been described (Raghoebarsing et al., 2006). Like AOM coupled to sulfate reduction this reaction is thermodynamically favored, although virtually nothing is known about the biogeochemical significance of this process.

Although sediment systems are, for the most part, very efficient, at recycling methane that is produced at depth, methane can escape sediments by gas bubble ebullition, transport mediated by macrophytes, or upward diffusion across the sediment–water interface. Given the importance of methane as a greenhouse gas, an understanding of the factors controlling methane fluxes to the atmosphere is important for both quantifying these fluxes along with improving our understanding of how these gas fluxes may respond to climate change (Whiting and Chanton, 2001; Middelburg et al., 2002; also see Chapter 5.04).

Diffusion can play an important role in methane loss from sediments in conjunction with either of the other two transport processes discussed here (Chanton et al., 1989; Kelley et al., 1990). However, in strictly diffusive systems (i.e., those without plants or gas ebullition), there appears to be a fairly efficient coupling between methane production and oxidation in the sediments, with small net methane losses from the sediments (Martens et al., 1998). This is controlled largely by the interplay between the microbial and physical processes occurring in such sediments (also see Chanton and Dacey, 1991).

In sediments where large pore-water methane concentrations build up, gas bubble can form in the sediments when the sum of the partial pressures of all dissolved gases exceeds the local hydrostatic pressure (Chanton and Whiting, 1995). This often, but not always, occurs when the sediment pore waters become saturated with respect to methane. Not only do these bubbles cause what is referred to as acoustic turbidity (Wever et al., 1998), but the bubbles can rise through the sediments (ebullition), resulting in a flux of gaseous methane from the sediments. In the process of gas bubble formation, growth, and ebullition, the bubbles strip other dissolved gases out of the pore waters, including ^{222}Rn (which can be used as a tracer for bubble formation), CO_2 , N_2 , and H_2S and other reduced sulfur gases (Chanton and Whiting, 1995). In subtidal sediments, methane gas ebullition forms cylindrical bubble tubes that lead to enhanced rates of sediment–water exchange through the creation of additional sediment surface area for benthic exchange (Martens et al., 1980). Gas ebullition from methanogenic sediments is of importance beyond its effect on sediment–water exchange because it transports methane, and possibly other reduced gases produced in anoxic sediments, directly to the atmosphere, bypassing their possible oxidation in the sediments or water column (Kipput and Martens, 1982; Martens and Chanton, 1989; see Chapter 5.04).

Gas ebullition is common in many tidal freshwater and wetland soils and sediments, as well as in some subtidal coastal sediments, such as Cape Lookout Bight and Long Island Sound (Martens and Berner, 1977; Kipput and Martens, 1982; Chanton et al., 1989; Chanton and Dacey, 1991; Albert et al., 1998; Martens et al., 1998). In many of these environments, gas ebullition occurs seasonally, during warmer months when there are higher rates of sediment organic carbon remineralization, and concomitantly higher inventories of gas in the sediments (Chanton et al., 1989). More specifically, bubble ebullition appears to be driven by a decrease in the local hydrostatic pressure associated with low tides (Martens and Klump, 1980; Chanton et al., 1989). However, a more detailed explanation of the linkages here has not yet been presented (see recent discussions in Algar and Boudreau, 2009). Gas ebullition from sediments can also be triggered by discrete wind events or physical disturbance of the sediments (Chanton and Whiting, 1995).

In vegetated sediments, the presence of plants can impact methane fluxes from the sediments in that the plants serve as conduits for methane exchange with the atmosphere, using many of the same mechanisms that allow them to transport O_2 into the sediments (see Section 5.09.4.5 and Chanton and Dacey, 1991). Plant O_2 input also allows for the occurrence of belowground aerobic methane oxidation, while belowground organic carbon production and root exudation by

the plants can stimulate methanogenesis (again see related discussions in Section 5.09.4.5). Many of these same processes can similarly stimulate iron redox cycling in freshwater-vegetated wetland sediments (Roden and Wetzel, 1996; van der Nat and Middelburg, 1998), and the resulting stimulation of organotrophic iron reduction then inhibits methanogenesis in the sediments (Section 5.09.7) and lowers the methane flux from these sediments. In general, the positive factors (plant gas exchange and stimulated belowground production) appear to more important than the negative factors (belowground methane oxidation, the inhibition of methanogenesis by iron redox cycling), since methane fluxes often show a positive correlation with plant biomass or photosynthetic activity (Chanton and Whiting, 1995). However, as Roden and Wetzel (1996) also noted, the impact of these different controlling factors (and the relevant times scales of operation) may vary among different types of wetland sediments.

5.09.10 Trace Metal Cycling

The geochemistry of many trace metals and trace elements in estuarine and coastal marine sediments is strongly influenced by many of the processes discussed throughout this article. In particular, the redox cycling of iron and manganese oxides is of importance here, as is the redox cycling of iron sulfide minerals (e.g., FeS or pyrite).

Linkages between Fe and Mn redox cycling and trace metal cycling exist in part because Fe and Mn oxides and iron sulfides are enriched in a wide range of trace metals (e.g., Cu, Ni, Zn, Cd, Mo, and Co). The processes that lead to these enrichments vary, and include simple adsorption, direct incorporation of these metals into crystal structures, and coprecipitation, for example, of trace metal sulfides in conjunction with iron sulfides (Balistrieri and Murray, 1986; Morse and Luther, 1999; Glasby, 2000; Li, 2000). Furthermore, many Mn and Fe oxides occur either as coatings on other particles or as fine-grained amorphous solids, and therefore tend to have large specific surface areas. Thus for surface processes such as adsorption, small amounts of these oxides can play an important role in controlling the geochemical cycling of trace metals.

For many of the trace elements discussed here, their association with Mn and Fe oxides can lead to these elements undergoing indirect (or passive) redox cycling in association with Mn and Fe redox cycling (Elderfield et al., 1981b; Salwan and Murray, 1983; Westerlund et al., 1986; Shaw et al., 1990; Shimmield and Pedersen, 1990; Audry et al., 2006; and others). Here, changes in redox conditions do not generally change the oxidation state or speciation of these trace elements, nor directly affect their solubility.

In contrast, there are other trace elements (e.g., V, Re, U) that do have multiple oxidation states and different solubilities associated with their different redox states. In general, the oxidized forms are soluble in seawater while the reduced forms are not. Furthermore, the more active redox cycling of these elements in sediments shows some broad similarities to that seen for sediment Mn and Fe redox cycling, that is, the redox transformations occur when O_2 concentrations equal zero, at redox potentials consistent with suboxic or anoxic conditions (Shaw et al., 1990; Morford and Emerson, 1999;

McManus et al., 2006; Morford et al., 2009). Sediment profiles of these redox-sensitive metals have the potential to be used as tracers (across a range of timescales) of past changes in sediment redox conditions due to variations in either bottomwater oxygen concentration or the organic carbon flux to the sediments (Calvert and Pedersen, 1993; Adelson et al., 2001; Crusius and Thomson, 2003; McManus et al., 2006).

The uptake of trace metals into AVS and pyrite also plays an important role in their cycling in estuarine and coastal sediments given the importance of sulfate reduction and sulfide production in these sediments (as compared to, e.g., freshwater or deep-sea sediments). Examining the uptake of an operationally defined reactive metal fraction into pyrite has been done by examining what is termed the degree of trace metal pyritization, or DTMP (Huerta-Diaz and Morse, 1992), a parameter defined in the same manner as the degree of pyritization (DOP) is for iron. DOP is defined as

$$\text{DOP} = \frac{\text{pyrite-Fe}}{\text{pyrite-Fe} + \text{'reactive'-Fe}} \quad [8]$$

where reactive-Fe is iron that is soluble in HCl (i.e., pyrite is not soluble in HCl), and it is likely to include iron in phases whose reactivity toward sulfide ranges from hours to perhaps $\sim 10^4$ – 10^5 years (Raiswell and Canfield, 1998; Goldhaber, 2003). DTMP is defined in an analogous sense based on the concentration of metals co-extracted with the reactive-Fe and pyrite-Fe fractions.

Comparisons of DTMP and DOP in a large number of sediments (also see recently Scholz and Neumann, 2007) have proved to be useful in terms of understanding the degree to which various metals are incorporated into pyrite relative to the formation of pyrite itself (Figure 11). Such studies have observed the following general pattern of DTMP values for these metals:

$$\text{Hg} > \text{As} = \text{Mo} > \text{Cu} = \text{Fe} > \text{Co} > \text{Ni} \gg \text{Mn} > \text{Zn} > \text{Cr} \\ = \text{Pb} > \text{Cd} \quad [9]$$

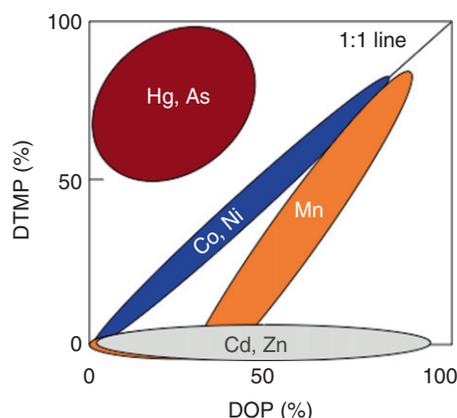


Figure 11 A schematic representation of DTMP (degree of trace metal pyritization) vs. DOP (degree of pyritization) for selected trace metal (see the text for further details). Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton based on results presented in Huerta-Diaz, M.A., Morse, J.W., 1992. Pyritization of trace metals in anoxic marine sediments. *Geochimica et Cosmochimica Acta* 56, 2681–2702 and Morse, J.W., Luther, G.W., III, 1999. Chemical influences on trace metal–sulfide interaction in anoxic sediments. *Geochimica et Cosmochimica Acta* 63, 3373–3378.

While sulfidic sediments can be an important sink for all of these trace metals (see discussions below), DTMP values indicate whether this uptake occurs in metal (Me) monosulfide phases (MeS) versus pyrite phases, or phases that are operationally extracted with pyrite. This has some impact on the stability of these metals in anoxic or mixed redox sediments (see discussions at the end of this section for further details).

Morse and Luther (1999) have examined the thermodynamic and kinetic controls on the observed trends in eqn [9] using the rate of water exchange for soluble water–metal complexes as a first-order proxy for the relative reactivity of a metal to form a MeS phase. This approach explains many, but not all, of the observations in eqn [8] and in Figure 11. For elements such as As and Mo, which show high DTMP values that are almost independent of DOP, they are first reduced by sulfide (i.e., As^{5+} to As^{3+} and Mo^{6+} to Mo^{4+}) before forming sulfide phases. They then undergo a more complex set of redox reactions than the simple substitution reactions discussed above, and these reactions appear to favor strongly their co-precipitation with pyrite. High DTMP values for Hg may be a function of the more complicated Hg solution chemistry that appears to favor Hg incorporation into pyrite. At the same time, because HgS is extremely insoluble in HCl (Cooper and Morse, 1998b), it will also operationally be extracted with the pyrite fraction.

Near the sediment–water interface in subtidal sediments with oxic bottom waters, trace metal dynamics are largely controlled by processes such as regeneration from biogenic (organic matter) carrier phases, uptake into (or in association with) diagenetically produced Mn and Fe oxides, and release from (or in association with) the reductive dissolution of Mn and Fe oxides (see discussions, and summaries, most recently in Burdige, 2006 and Martin, 2009). In many cases, this may lead to the release (benthic flux) of dissolved metals from sediments, which can play an important role in affecting dissolved metal concentrations in shallow water coastal ecosystems (Westerlund et al., 1986; Skrabal et al., 1997; Colbert et al., 2001; Warnken et al., 2001; Caetano et al., 2007; Point et al., 2007 and references therein). At the high anthropogenic metal levels that are often be found in some nearshore sediments, benthic metal fluxes may play some role in controlling the toxicity and bioavailability of these metals to water-column organisms (Riedel et al., 1997; Shine et al., 1998). This observation is in contrast to that observed in open ocean settings, where the availability of certain trace metals can limit phytoplankton growth (Morel et al., 2003).

The processes discussed above can also be examined in the broader context of a conceptual model of trace metal and trace element cycling in continental margin sediments (including estuarine and coastal sediments) that is shown in Figure 12. The figure is presented in a generic sense and thus different aspects of the processes shown here may be more or less important for a specific trace metal. In addition, in many cases the reactions of interest are actually redox reactions directly between Mn and Fe oxides and iron sulfides, which can be mediated by macrofaunal activity under mixed redox conditions (see Section 5.09.2.2).

Since most of the reactions in this figure are dissolution/precipitation processes, the cycling of these metals generally goes through a dissolved phase. Furthermore, as trace metals move between oxide and sulfide phases during sediment redox cycling (or are regenerated from organic carrier phases), the

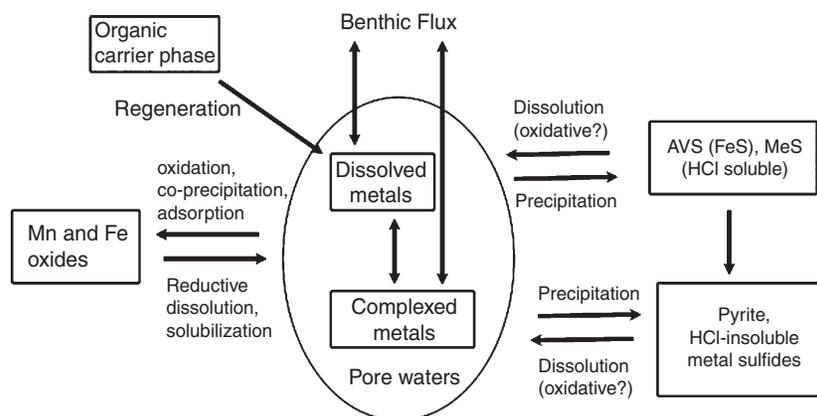


Figure 12 A conceptual model for trace metal cycling in coastal and nearshore sediments, presented in terms of the major sediment carrier phases of these metals (e.g., oxides and sulfides). Although not explicitly shown here, some of the relevant redox reactions these sulfides and oxides undergo involve both as reactants (e.g., see reaction 7 in Table 2). Modified from Burdige, D.J., 2006. *Geochemistry of Marine Sediments*. Princeton University Press, Princeton.

release from one phase may be slower than uptake by the other phase, or the release and uptake processes may be separated from one another within the sediment column. Under these conditions, metals can accumulate in sediment pore waters. Such considerations will then also play a role in regulating the magnitude and direction of benthic fluxes of trace metals from sediments. Metals in sediments can also be returned to the water column by sediment resuspension (Saulnier and Mucci, 2000; Kalnejais et al., 2007). However, the bioavailability of particle-bound metals to water-column organisms likely depends on the release into solution (e.g., desorption, solubilization, dissolution) of the metals from the solid phase (Chen and Mayer, 1999).

Organic complexation of trace metals is also likely to occur in pore waters (Elderfield, 1981; Skrabal et al., 2000; Skrabal et al., 2006). This complexation might be expected to be of greatest importance in anoxic sediments where sulfate reduction occurs, due to the high DOC levels generally observed in such sediments (Burdige, 2002). The potential importance of this metal complexation in pore waters has been discussed in terms of its impact on metal benthic fluxes (also see Skrabal et al., 1997), although it also appears to play a role in the solubilization and precipitation of metals in sediments (Luther et al., 1992).

Bottom-water oxygen concentration, carbon rain rate, and benthic macrofaunal activity all play important roles in regulating benthic trace metal fluxes, in part, because of their impact on iron, manganese, and sulfur redox cycling in sediments (see references discussed below and Sundby et al., 1986; Shaw et al., 1990; Aller, 1994b; and Riedel et al., 1997). In particular, factors such as these control the sediment oxygen penetration depth (e.g., Glud, 2008), and the relationship between the timescale of transport through this oxic surface layer, versus the timescale of either oxidative removal (for Mn and Fe) or uptake onto freshly formed oxides (for the other trace metals) will then determine the extent to which metals regenerated at depth are retained in the sediments, or released as a benthic flux. Because Fe oxidation is much faster than that of Mn (Section 5.09.2.1), such processes are more likely to lead to Mn versus Fe benthic fluxes (e.g., Balzer, 1982). This would also suggest that there could be some divergence in the

behavior of trace elements more strongly associated with Fe versus Mn oxides.

Remobilization of metals near the sediment surface can also lead to the downward diffusive flux of regenerated metals into the deeper, anoxic sediments (Figure 6; also see, e.g., Cu profiles in Skrabal et al., 2000). Here the uptake of some of these metals into sulfide phases (as outlined above) or sometimes carbonate phases (mostly Mn; see Holdren et al., 1975; Suess, 1979; Aller, 1980b; Middelburg et al., 1987) will be important. In the absence of bioturbation, these sulfides will not be re-oxidized and will simply be buried in the sediments.

The relative balance of the diagenetic processes discussed above can also, under some circumstances, lead to sediments taking up certain metals from the water column. For example, Colbert et al., 2001 demonstrated with benthic flux measurements that coastal and continental margin sediments go from being a source of Cd to the water column to being a sink for water-column Cd with increasing rates of sediment sulfate reduction. The sediment uptake of Cd at high sulfate reduction rates appears to be related to the precipitation of the highly insoluble CdS in the sediments. At low rates of sulfate reduction, other oxidative processes apparently contribute to the net release of dissolved Cd from the sediments. Earlier studies by Elderfield et al. (1981a, 1981b) similarly suggested that anoxic sediments could be sinks for both Cd and Ni (which also forms a highly insoluble sulfide), based on both pore-water profiles and measured benthic fluxes.

The occurrence of bioturbation and/or bioirrigation, and the resulting mixed redox conditions, has a more complex effect on sediment trace metal cycling and benthic fluxes. Metals that are sequestered as sulfides may be mixed upward into surficial portions of the sediments, where they can be re-oxidized by a number of dissolved and solid oxidants, for example, O₂, nitrate, and manganese and iron oxide. Since this oxidation liberates, at least in a transient sense, metals into the pore waters, their potential flux out of the sediments may be enhanced. The diffusive openness of bioirrigated sediments (Section 5.09.4.1) also provides a means of enhancing the transport of dissolved oxidants into the sediments and, as a result, allows metals that are remobilized/solubilized by oxidative processes a greater likelihood of escaping the sediments as

a benthic flux (e.g., Emerson et al., 1984). Consistent with these suggestions, in coastal sediments the magnitude of benthic fluxes of metals such as Cd, Cu, Zn, and Ni (and in some cases also the direction of the flux) is strongly affected by the occurrence of these oxidative processes (Westerlund et al., 1986; Gobeil et al., 1987; Riedel et al., 1997; Skrabal et al., 1997; Shine et al., 1998; Colbert et al., 2001). Of equal importance is the fact that metal sulfide production at depth in sediments does not necessarily imply permanent burial of metals.

However, O₂ input through the burrow walls of irrigating macrofauna, and macrophyte roots as well, results in localized precipitation of Mn and Fe iron oxides in regions immediately adjacent to these subsurface O₂ sources (Aller and Yingst, 1978; Aller, 1988; St-Cyr et al., 1993; Sundby et al., 1998; Vale and Sundby, 1998). Thus, in a similar fashion to oxides which form in nonirrigated sediments near the sediment–water interface and may act as a barrier for benthic fluxes of trace metals out of the sediments (i.e., see the discussion above and compare Figures 2(a) and 2(b)), the same may be true here for trace metal loss in association with macrofaunal burrow irrigation (Berg et al., 2003; Meile et al., 2005). (Recall based on previous discussions that in the context of these figures, metal oxide precipitation is likely to occur in (or near) the regions marked O₂ and NO₃⁻.)

Metals that are remobilized and solubilized at depth in association with the reduction of manganese and iron oxides show somewhat differing behaviors under mixed redox conditions. For Mn, for example, it has been observed that while mixed redox conditions promote greater internal redox cycling of manganese (e.g., Figure 1(b)), benthic Mn fluxes do not appear to be greatly enhanced (Sundby et al., 1986; Aller, 1990, 1994b; Aller and Aller, 1998).

Low dissolved oxygen in bottom waters and/or increased carbon fluxes to the sediments will enhance benthic Mn fluxes along with the fluxes of other metals (e.g., Co) that are associated with both Mn and Fe oxides (Sundby et al., 1986). Seasonal studies of benthic Mn fluxes also show that benthic Mn fluxes increase with increasing temperature (Aller and Benninger, 1981; Elderfield et al., 1981a; Hunt, 1983). However, identifying the causes of such seasonal trends is hampered by the fact that changes in temperature, bottom-water oxygen, organic carbon input to the sediments, and sediment O₂ penetration depth often co-occur, although not always by direct causality (see discussion in Aller, 1994b). In a related fashion, studies of iron fluxes from California continental margin sediments suggest that these fluxes are only significant for sediments with shallow oxygen penetration depths, that is, less than ~20 mm, and/or those underlying low bottom-water O₂ concentrations of less than ~20 μM (McManus et al., 1997).

Deposit feeding organisms living in sediments are also capable of solubilizing metals such as Cu, Cd, and Pb from contaminated sediments during their passage through macrofaunal digestive systems (Mayer et al., 1996; Chen and Mayer, 1998). This process is mediated by soluble proteins in the animal's digestive fluids, and thus a large fraction of these solubilized metals are also complexed. This process increases the bioavailability of the metals to the deposit feeding organism itself, and can therefore lead to metal accumulation in the

organism; at the same time, it may also lead to the release of these metals into the pore waters.

Seasonal variations of redox conditions in coastal sediments affect the sediment cycling and benthic fluxes of many other trace metals in addition to Mn (e.g., Hines et al., 1984; Aller, 1994b; Shine et al., 1998). The results of Cooper and Morse (1998a) further suggest that for metals which form highly insoluble sulfides (e.g., Cu and Zn in their study), both the amounts and seasonal changes in the sediment AVS content play an important role in regulating seasonal sediment metal cycling. Based on comparative studies of two sites in Chesapeake Bay, they suggest that if sediment Fe in AVS is less than ~20% of HCl-soluble Fe, then seasonal changes in AVS content can affect the cycling of these other metals. In contrast, when Fe in AVS is greater than ~20% of the reactive Fe, there appears to be enough sulfide available in the sediments to trap effectively these metals and buffer temporal changes in metal dynamics.

Such factors may also play a role in explaining metal toxicity to organisms living in coastal sediments. For metals that show a low DTMP, and which form highly insoluble monosulfides (e.g., Cd, Ni, Zn, Pb, and Cu), the molar ratio of the acid (HCl)-extractable metal to AVS is strongly correlated with sediment metal toxicity (see DiToro, 2001 and references therein). When this ratio is less than 1, the excess AVS in the sediment apparently titrates all of the available metal, such that no free metal is available to sediment infauna. In contrast, as this ratio increases, sulfide availability limits metal uptake as a sulfide precipitate and thus makes metals more available to organisms.

Although pyrite is the ultimate burial phase for most sulfur in estuarine and coastal sediments, the low sulfur burial efficiency (Section 5.09.8.2) implies that both pyrite and AVS undergo extensive cycling in surface sediments. While AVS appears to be more reactive than pyrite with respect to oxidation (Morse, 1991), pyrite oxidation does occur on early diagenetic timescales (again see Section 5.09.8.2). Laboratory studies by Morse (1994) have shown that pyrite oxidation releases significant amounts of metals such as As, Cu, Hg, and Mo, all of which generally show high values of DTMP. More importantly, the percentage loss of these metals from the pyrite fraction is similar to or greater than the percentage loss of Fe during pyrite oxidation. Thus, pyrite oxidation, driven by sediment resuspension or *in situ* sediment redox processes, also has the potential to increase the bioavailability of pyritized metals.

5.09.11 Concluding Remarks

A variety of physical and biological forcing functions act on estuarine and coastal sediments across a broad range of time and space scales, and can have a profound effect on the processes associated directly or indirectly with the remineralization of sedimentary organic carbon. These interactions exert a strong influence on the cycling of biogeochemically reactive elements, and result in linkages between and within elemental cycles (e.g., between the Mn and N cycle, or simply with the N cycle itself) that are far more complex than previously envisioned. There is still much to be learned here, and many important questions await answers. The author's hope is that this chapter accurately presents the current state of knowledge and sets the stage for this future work.

There has also been the increased recognition that biogeochemical processes in estuaries and the coastal ocean (and their underlying sediments) can have large-scale impacts on global ocean processes. Thus, studies of these processes have implications not only in terms of the internal dynamics and elemental budgets of estuarine and coastal sediments, but also on benthic–pelagic coupling, and perhaps global oceanic cycles and budgets of biogeochemically active elements. Again, future studies in this area will better address these topics as well.

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