

# The biogeochemistry of manganese and iron reduction in marine sediments

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## ABSTRACT

Manganese and iron reduction in marine sediments are known to play important roles in the biogeochemical cycles of many elements, including carbon, sulfur, phosphorus and several trace elements. These reduction reactions affect these cycles on a variety of time scales, ranging from those as short as seasonal time scales (e.g., nutrient cycling in coastal ecosystems), to those as long as thousands to tens of thousands of years (e.g., glacial–interglacial transformations in deep sea sediments). In this review article I will briefly summarize the results of laboratory studies on the types of manganese and iron reduction that are known to occur in marine sediments, and then discuss the occurrence of these processes in different sedimentary environments. Particular efforts will be given to examining the rates and mechanisms of sedimentary manganese and iron reduction in relationship to other biogeochemical processes in sediments.

## INTRODUCTION

Manganese and iron reduction in marine sediments are known to play important roles in the biogeochemical cycles of many elements, including carbon, sulfur, phosphorus and several trace elements. For this reason considerable effort has been devoted to examining the rates and mechanisms of these reduction reactions in sediments. In this review article I will begin by first briefly summarizing the results of laboratory studies on the types of manganese and iron reduction that are known to occur in marine sediments. This will then be followed by a discussion of these processes in different sedimentary environments. The attempt here will be to examine the rates and mechanisms of sedimentary manganese and iron reduction in relationship to other biogeochemical processes. In recent years there have been several other review articles that have examined topics related to the subject of this review, including:

chemical aspects of reductive dissolution reactions (Stone and Morgan, 1987; Stumm and Sulzberger, 1992); microbial manganese and iron reduction (Ehrlich, 1987; Lovley, 1987, 1991; Ghiorse, 1988; Nealson and Myers, 1992); and manganese sediment geochemistry (Glasby, 1984; Schimmiel and Pedersen, 1990). Rather than simply duplicating or up-dating these articles, in this review article I will incorporate information from all of these different fields into a more unified examination of the current knowledge on manganese and iron reduction in sediments.

Manganese and iron reduction also occurs in stratified marine water columns such as the Saanich Inlet and the Black Sea (Emerson et al., 1982), in the low oxygen waters of some open ocean environments (Landing and Bruland, 1987) and in the water columns of many stratified lakes (Davison, 1985). Although there are many similarities between sedimentary manganese and iron reduction

and that which occurs in water column environments, this article will only discuss these processes in sediments.

#### THE CHEMISTRY AND MICROBIOLOGY OF MANGANESE AND IRON REDUCTION

##### *Definitions of iron and manganese reduction*

Under conditions of low Eh and pH, the reduced forms of manganese and iron (generally  $Mn^{2+}$  and  $Fe^{2+}$ ) are thermodynamically favored over their oxidized forms (generally  $Mn^{4+}$  and  $Fe^{3+}$ ), which are generally found in nature as solid oxides and oxyhydroxides (Stumm and Morgan, 1981). Manganese reduction will therefore be defined as the reduction of manganese oxides or oxyhydroxides to  $Mn^{2+}$ . Similarly, iron reduction will be defined as the reduction of oxidized iron minerals to  $Fe^{2+}$ .

Given the numerous problems in making and interpreting Eh measurements in natural environments such as sediments (Stumm and Morgan, 1981; Lindberg and Runnells, 1984), the presence/absence of oxygen is often taken as the "master" variable defining the environmental conditions favoring manga-

nese and iron reduction. While there are natural settings in which manganese and iron reduction occur in the presence of oxygen (Sunda et al., 1983; Hong and Kester, 1986) it is likely that the vast majority of manganese and iron reduction in sediments occurs under anoxic (or sub-oxic) conditions.

While the absence of oxygen generally appears to be required for the occurrence of sedimentary manganese and iron reduction, the factors ultimately controlling these processes are more complex. Understanding the factors controlling sedimentary manganese and iron reduction often involves determining: (1) the reductants involved in the reactions; (2) the processes by which these reductants are produced; and (3) the direct or indirect role of biota in mediating either the reduction of the oxides or the production of the chemical reductants. In general, manganese and iron reduction in sediments may be a strictly chemical (abiotic) process, or may be mediated by biota (primarily bacteria). Furthermore, there appear to be several different types of microbially-mediated metal oxide reduction. While many studies have indicated the ways that manganese and iron reduction *may* occur in sediments, there have been far fewer studies that have definitively



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demonstrated the exact mechanism(s) by which these processes actually occur in a given sediment.

*The chemistry of oxidized and reduced manganese and iron in sediments*

In the simplest sense, manganese oxides (or oxyhydroxides) in sediments are often referred to as  $\text{MnO}_x$ , although other cations are also incorporated into the crystal lattices of these materials.  $\text{MnO}_x$  is a non-stoichiometric formula since  $x$  is greater than one and generally less than two. This therefore implies that the "average" oxidation state of manganese in these materials is between two and four. Whether this is caused solely by mixtures of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  in the solid, or also involves the occurrence of  $\text{Mn}^{3+}$  has been the subject of some debate.  $\text{Mn}^{3+}$  is generally thought to be thermodynamically unstable relative to disproportionation to  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  (Morgan, 1967), although studies have shown that  $\text{Mn}^{3+}$  is indeed found in certain manganese oxides (Glausinger et al., 1979; Murray et al., 1985).

The mineralogy of manganese oxides in sediments can also vary. These oxides are generally thought to be amorphous materials, and are often found as coatings on inorganic (e.g., clays) or biogenic (e.g., siliceous tests) sedimentary particles. They are also usually found in close association with sedimentary iron oxides. Attempts to identify sedimentary manganese oxides is difficult, in part because the small crystal size and lack of long-range ordering within the crystal structure often precludes analysis by conventional X-ray diffraction techniques. Studies using techniques such as transmission and scanning electron microscopy, electron diffraction and X-ray photoelectron spectroscopy have, however, proven useful in further describing the crystal chemistry and mineralogy of sedimentary manganese and iron oxides (Burns and Burns, 1979, 1981; Glausinger et al., 1979; Murray, 1979; Murray et al., 1985).

Burns and Burns (1979, 1981) suggest that the predominant manganese oxides found in sediments include: todorokite,  $(\text{Ca}, \text{Na}, \text{K})(\text{Mg}, \text{Mn}^{2+})\text{Mn}_5\text{O}_{12} \cdot x\text{H}_2\text{O}$ ; vernadite (also known as  $\delta\text{-MnO}_2$ ),  $\text{MnO}_2 \cdot n\text{H}_2\text{O} \cdot m(\text{R}_2\text{O}, \text{RO}, \text{R}_2\text{O}_3)$ , where  $R = \text{Na}, \text{Ca}, \text{Co}, \text{Fe}, \text{Mn}$ ; and birnessite,  $(\text{Na}, \text{Ca}, \text{K})(\text{Mg}, \text{Mn}^{2+})\text{Mn}_6\text{O}_{14} \cdot 5\text{H}_2\text{O}$ . However the results of laboratory studies of manganese oxidation (Hem and Lind, 1983; Murray et al., 1985) also suggest that other manganese oxides (e.g., hausmannite,  $\text{Mn}_3\text{O}_4$ , or feitknechtite,  $\beta\text{-MnOOH}$ ) should exist in sediments. Burns and Burns (1979, 1981) and Schimmiel and Pedersen (1990) further discuss the implications of these laboratory studies in terms of manganese oxide mineralogy in sediments.

The end-product of manganese reduction is generally been thought to be  $\text{Mn}^{2+}$ , although soluble  $\text{Mn}^{3+}$  may also be produced (Ehrlich, 1987). Evidence from the chemical literature suggests that  $\text{Mn}^{3+}$ -organic complexes should be stable or metastable under a range of anoxic and oxic conditions (e.g., see a recent review in Luther et al., 1993), and the possible occurrence of dissolved  $\text{Mn}^{3+}$ -complexes in anoxic waters of the mid-Chesapeake Bay has recently been discussed (Luther et al., 1993). However, whether such  $\text{Mn}^{3+}$ -complexes occur in sediment pore waters and if so, whether they are produced by oxidative or reductive processes are both questions that will clearly require further study. The  $\text{Mn}^{2+}$  produced during sedimentary manganese reduction is generally found dissolved in pore waters as either a "free" ion or more likely an organically-complexed ion (Elderfield, 1981). However in anoxic sediments where manganese concentrations and carbonate alkalinity reach sufficiently high levels, some of this divalent manganese may precipitate out of the pore waters as a pure or mixed carbonate phase (Holdren et al., 1975; Grill, 1978; Suess, 1979; Aller, 1980; Pedersen and Price, 1982; Thomson et al., 1986; Middelburg et al., 1987). Schimmiel and Pedersen (1990) further discuss the factors controlling man-

ganese solubility under these conditions.

Iron oxide mineral phases that have been identified in sediments include goethite ( $\alpha$ -FeOOH), ferrihydrite ( $5 \text{ Fe}_2\text{O}_3 \cdot 9 \text{ H}_2\text{O}$ ), akageneite ( $\beta$ -FeOOH), and lepidocrocite ( $\gamma$ -FeOOH) (Burns and Burns, 1977, 1981; Murray, 1979). As with the identification of manganese oxides in sediments, similar problems also exist in the identification of sedimentary iron oxides. Another iron oxide mineral found in both marine and freshwater sediments is magnetite ( $\text{Fe}_3\text{O}_4$ ), a magnetic phase containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In sediments, magnetite is often a detrital component derived from the weathering of continental rocks or submarine (hydrothermal) volcanism (Murray, 1979). However authigenic magnetite can also be produced both in the presence and absence of oxygen (Blakemore, 1975; Bell et al., 1987; Karlin et al., 1987; Bazylinski, 1990; Lovley, 1990), and under some conditions anaerobic magnetite production may be the result of microbial iron reduction (Lovley, 1990). At the same time, magnetite can itself undergo reductive dissolution in the presence of sulfide (Canfield and Berner, 1987).

The more common end-product of iron reduction is, however,  $\text{Fe}^{2+}$ . In contrast to  $\text{Mn}^{2+}$  though, ferrous iron is far less soluble and forms insoluble phases such as: siderite,  $\text{FeCO}_3$ ; pyrite,  $\text{FeS}_2$ ; iron monosulfides,  $\text{FeS}$ ; and vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (Emerson and Widmer, 1978; Martens et al., 1978; Suess, 1979; Berner, 1980, 1984; Postma, 1982). These differences in the solubility of reduced iron and manganese can, in some circumstances, lead to significant differences in the diagenetic cycling of these elements across redox boundaries (Burdige and Nealson, 1986).

Finally, it should be noted that both manganese and iron oxides are known to take up a variety of transition elements and heavy metals (e.g., As, Cu, Ni, Zn, Co, Mo and Pb), either by adsorption to the oxide surface or by direct incorporation into the crystal structure (Murray, 1975; Burns and Burns, 1981;

Millward and Moore, 1982; Balistrieri and Murray, 1986). Iron and manganese redox cycling in sediments then also leads to associated diagenetic cycles of these other elements (e.g., Jenne, 1968; Turekian, 1977), since the reduction/dissolution and oxidation/precipitation of these metal oxides also causes the cycling of these transition elements and heavy metals between sedimentary pore waters and solid phases (see *Coastal and estuarine sediments* for further details).

#### *Chemical (abiotic) manganese and iron reduction*

A wide range of organic and inorganic compounds are able to chemically reduce manganese and iron oxides. These possible reductants include: sulfide (Kessick and Thomson, 1974; Pyzik and Sommer, 1981; Burdige and Nealson, 1986); nitrite (Bartlett, 1981);  $\text{Fe}^{2+}$  (for manganese oxides) (Postma, 1985; Myers and Nealson, 1988b; Burdige et al., 1992); organic acids such as pyruvate and oxalate (Stone, 1987a) and certain aromatic compounds (Stone, 1987b; LaKind and Stone, 1989; Stone and Ulrich, 1989). The reduction of iron oxides by sulfide has important implications in the formation of sedimentary pyrite and plays an important role in the global sulfur cycle (e.g., Berner, 1982, 1984; Garrels and Lerman, 1984). However, this subject is beyond the scope of this review, and the reader is therefore urged to examine the references cited here for further details on this topic.

While the compounds discussed above may chemically reduce manganese and iron oxides, their occurrence in natural settings is often a result of biological activity. As such, understanding the importance of these abiotic reduction processes in sediments also involves determining the mechanisms by which these reductants are produced, and the role biota play in this production.

#### *Microbial manganese and iron reduction*

The processes by which microorganisms couple the reduction of manganese or iron

oxides to the oxidation of organic compounds (or  $H_2$ ) are often referred to as dissimilatory (or heterotrophic) iron or manganese reduction. There have been several recent review articles on this subject (Ehrlich, 1987; Lovley, 1987, 1991; Ghiorse, 1988; Nealson and Myers, 1992), and these processes will therefore only be briefly summarized here.

Dissimilatory manganese and iron reduction appear to be strictly anaerobic processes, although many manganese and iron reducing organisms are facultative anaerobes (i.e., in the presence of oxygen many use  $O_2$  as an electron acceptor). The manganese and iron reducing bacteria that have been examined in pure culture generally use only a limited number of relatively simple compounds as their energy source (e.g., hydrogen, lactate, acetate or formate), although an iron reducing organism has also been observed to oxidize a wide range of aromatic organic compounds (Lovley, 1991). Microbial manganese and iron reduction coupled to organic matter oxidation also appears to require direct contact of the bacteria with the oxide surface (Tugel et al., 1986; Arnold et al., 1988; Ghiorse, 1988; Myers and Nealson, 1988a). Finally, lab studies have shown that the rates of microbial manganese and iron reduction are a function of the mineralogy or specific surface area of the oxides undergoing reductive dissolution (Lovley and Phillips, 1987b, 1988; Burdige et al., 1992), with amorphous oxides generally showing greater reactivity than more highly crystalline forms. However, the results of Burdige et al. (1992) suggest that differences in the rates of microbial manganese reduction with different oxides are also a function of the absolute rate of the process itself.

Recent studies have also suggested the existence of another type of direct microbial manganese reduction, in which microorganisms appear to be able to couple the reduction of manganese oxides to the oxidation of sulfide to sulfate (Aller and Rude, 1988). This process is distinctly different from abi-

otic manganese reduction coupled to sulfide oxidation, in that elemental sulfur ( $S^0$ ) appears to be the predominant end-product of the abiotic reaction (Burdige and Nealson, 1986). This type of microbially-mediated manganese reduction is apparently catalyzed by chemolithotrophic bacteria (i.e., organisms that use the energy of this reaction for autotrophic  $CO_2$  fixation, or chemosynthesis), although the organisms responsible for this process have not yet been identified. Furthermore, iron oxides are apparently not used by these organisms in an analogous reaction with sulfide (Aller and Rude, 1988). This process may be important in certain sediments where physical or biological mixing of the sediments brings solid phase sulfides into contact with manganese oxides (Aller and Rude, 1988; King, 1990; Canfield et al., 1993), and will be discussed below in greater detail.

The types of microbial manganese and iron reduction described above may be considered "direct" microbial reduction, in that the organisms appear to directly (and presumably enzymatically) catalyze the reduction processes. There are, however, other types of "indirect" microbial manganese and iron reduction in which the reaction occurs as a result of perhaps localized acid production, or production of reduced compounds (e.g., sulfide,  $Fe^{2+}$  and certain organic acids) which then react with the oxides. Under these conditions for example, sulfate reducing bacteria could then be considered indirect manganese and iron reducing bacteria.

#### GENERAL ASPECTS OF SEDIMENTARY MANGANESE AND IRON REDUCTION

Early studies of manganese redox cycling in sediments led to the observation that manganese is reduced from the +4 to the +2 oxidation states when sedimentary conditions change from "oxidizing" to "reducing" with depth (Murray and Irvine, 1895; Wangersky, 1962; Lynn and Bonatti, 1965; Li et al., 1969; Bonatti et al., 1971). The manganese oxides

involved in this process ultimately have external (e.g., river or aeolian) sources, although internal cycling of the oxides as a result of these redox changes also plays a role here (see below).

The depth of the manganese "redox" boundary in sediments is generally assumed to occur where oxygen concentrations in the pore waters go to near-zero levels, based in part on the examination of pore water manganese and oxygen profiles (Shaw et al., 1990; Reimers et al., 1992). Oxygen is therefore assumed to be the primary sedimentary oxidant of pore water manganese (Aller, 1990; Reimers et al., 1992). The  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox boundary generally occurs below the manganese redox boundary in many sediments (see below), and also often results in a brown to green color transition in non-sulfidic (e.g., pelagic) sediments (Lyle, 1983). This color change is reversible, and is apparently associated with the oxidation and reduction of iron in smectite clays, rather than the reductive dissolution of sedimentary iron oxides. Finally, at least in pelagic sediments, pore water iron profiles suggest that compounds other than  $\text{O}_2$  (i.e., manganese oxides and nitrate) are likely more important oxidants of  $\text{Fe}^{2+}$  during sedimentary iron redox cycling (see below).

With these redox changes in the sediments, the reduction of manganese and iron oxides leads to the production of their reduced, and generally more soluble, forms (see Fig. 1). As discussed in the previous section, the dissolved  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  produced by these reactions may precipitate out of the sediment pore waters as sulfide, carbonate or phosphate phases. However, these reduction reactions generally also lead to pore water gradients across the redox boundary of the reduced forms of these metals. The resulting upward diffusion of these ions then leads to their re-oxidation and the formation of new oxides. Subsequent burial and reduction of these authigenic oxides continues this redox cycle. For manganese, this internal redox cycling leads, under steady-

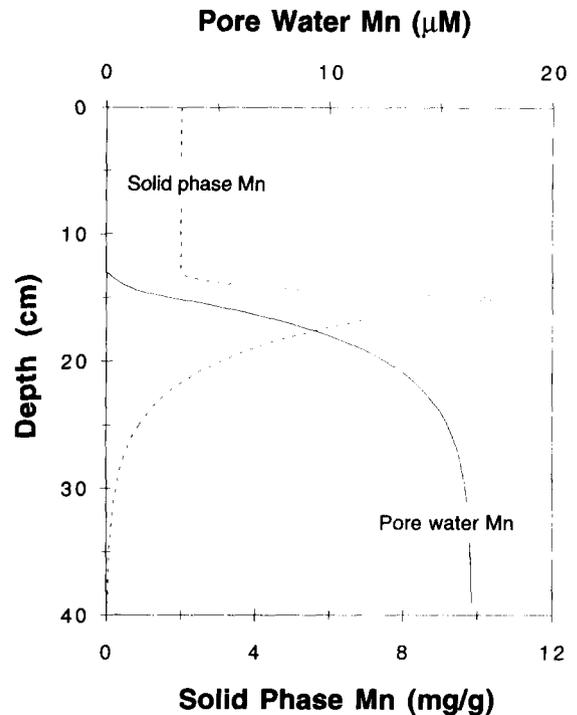


Fig. 1. Idealized steady-state pore water and solid phase manganese profiles resulting from the sedimentary redox cycling of manganese. The curves shown here were determined with the model equations presented in Burdige and Gieskes (1983). As discussed in the text, the depth of manganese redox boundary is found just below the depth of the peak in solid phase manganese (i.e., 13 cm).

state conditions and in the absence of significant bioturbation (Gratton et al., 1990; Rabouille and Gaillard, 1991) to a well-developed peak in solid phase manganese just above the redox boundary (see Fig. 1). This redox boundary moves upwards at a rate equal to the sedimentation rate, and therefore relative to the sediment-water interface the redox boundary and this manganese peak remain at a fixed depth in the sediments.

In addition to papers which have qualitatively described this redox cycling, several steady-state models have quantitatively examined manganese reduction and redox cycling in sediments (Michard, 1971; Holdren et al., 1975; Robbins and Callender, 1975; Burdige and Gieskes, 1983; Aller, 1990; Gratton et al., 1990; Rabouille and Gaillard, 1991). These models have examined this pro-

cess both in terms of the sediment manganese redox cycle discussed above, and in terms of the role of manganese reduction in sediment organic matter remineralization (see below). Similar models for iron reduction and sedimentary iron redox cycling have not been presented, although Bender and Heggie (1984) used a variation of the Burdige and Gieskes (1983) manganese model to estimate iron reduction rates in pelagic sediments (see below).

The remainder of this article will discuss manganese and iron reduction in pelagic, continental margin, estuarine, coastal and salt marsh sediments. The division of the following sections is based on this classification of sedimentary environments, and was used primarily for organizational purposes. It should be noted that in some cases these divisions are somewhat arbitrary, and that there is often a continuum among these sedimentary environments. Finally, although the primary focus of this article is manganese

and iron reduction in marine sediments, at the end of the article a brief discussion is also presented for comparative purposes on the occurrence of these processes in freshwater sediments.

### MANGANESE AND IRON REDUCTION IN PELAGIC SEDIMENTS

Broadly speaking, manganese and iron reduction in pelagic sediments has been examined in the context of: (1) their role in sedimentary organic matter oxidation (e.g., Froelich et al., 1979; Bender and Heggie, 1984); (2) their role in the formation of manganese nodules (e.g., Moore, 1981; Dymond et al., 1984); (3) their role in the formation of multiple, manganese rich layers in pelagic sediments (e.g., Berger et al., 1983; Finney et al., 1988) and (4) their occurrence during the diagenesis of deep-sea turbidites (e.g., Colley et al., 1984; Wilson et al., 1985).

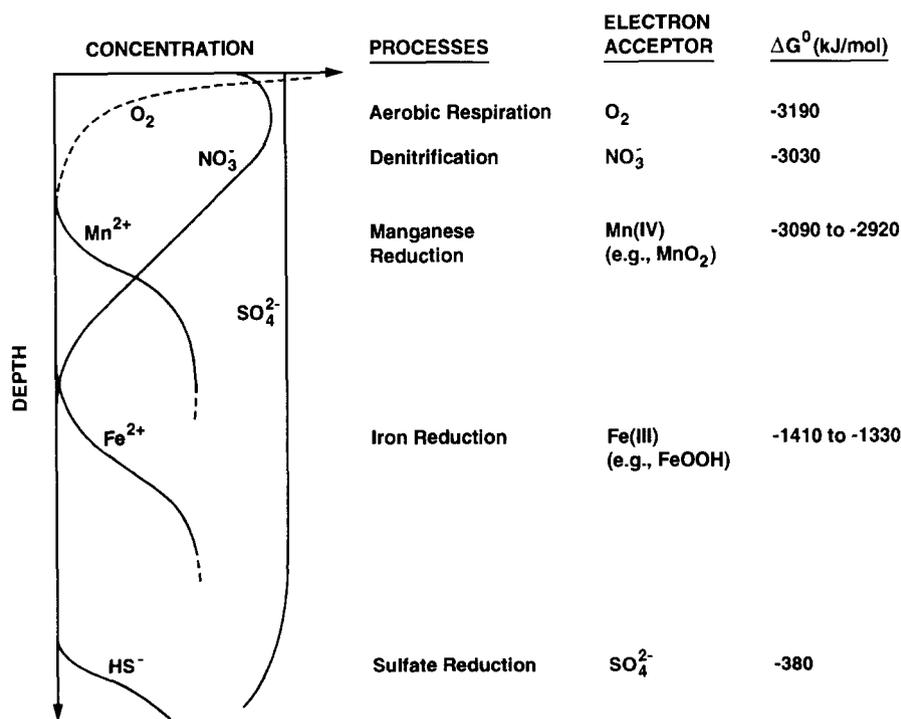


Fig. 2. Hypothetical pore water profiles predicted by the successive utilization of inorganic compounds as terminal electron acceptors in the decomposition of sedimentary organic matter (modified from Froelich et al., 1979). The ranges in  $\Delta G^{\circ}$  values for manganese and iron reduction are based on the choice of mineral phases presumed to be undergoing reductive dissolution.

*The role of manganese and iron reduction in the oxidation of sedimentary organic matter*

Studies in recent years have examined sedimentary manganese and iron reduction in a larger perspective than that discussed in the previous section, looking at these processes in the context of their role in the oxidation of sedimentary organic matter. In many sediments, there appears to be a well-developed sequence of electron acceptors used in the oxidation of sedimentary organic matter, with the "biogeochemical zonation" of these remineralization processes apparently controlled by the free energy yield for the oxidation of sedimentary organic matter by each electron acceptor (Claypool and Kaplan, 1974; Froelich et al., 1979). Under steady-state conditions this leads to a series of well-developed zones in the sediments where each process predominates, with regions in the sediments where the reduction of manganese and iron oxides should be coupled to the oxidation of organic matter (see Fig. 2). The depth scales over which these remineralization processes occur can vary among different sedimentary environments, and are controlled by factors such as the organic carbon rain rate to the sediment surface, the bottom water oxygen content, the sedimentation rate and the bioturbation rate (Froelich et al., 1979; Bender and Heggie, 1984; Emerson, 1985; Canfield, 1993). Deep-sea pore water profiles are often consistent with this biogeochemical zonation model (Froelich et al., 1979; Klinkhammer, 1980; Jahnke et al., 1982; Salwan and Murray, 1983; Bender and Heggie, 1984; Murray and Kuivala, 1990).

As processes coupled to the oxidation of organic matter, microbial manganese and iron reduction are less efficient than aerobic (oxic) respiration and more efficient than sulfate reduction (which is generally referred to as anoxic metabolism; see Fig. 2). Along with denitrification, manganese and iron reduction are referred to as "sub-oxic" remineralization processes (e.g., Froelich et al., 1979). Manganese reduction is generally con-

sidered to be less efficient than denitrification, although this is based on free energy calculations which assume that the manganese oxides undergoing reductive dissolution are well characterized, crystalline mineral phases. However, the free energy of formation of manganese (or iron) oxides varies not only among different oxide phases, but for a given phase also depends on the available surface area, differences in the average Mn oxidation state of the phase and variability in the degree of crystallinity of the phase (Murray, 1979; Hem et al., 1982). These factors should cause differences in the energetics and rates of microbial manganese and iron reduction with different oxides, as has been observed in lab studies of these processes (Lovley and Phillips, 1987b; Burdige et al., 1992).

These observations then suggest that there could be a certain degree of "overlap" both between the energetics of these sub-oxic processes, and their zonation in pelagic sediments. This appears to be more important for denitrification and manganese reduction, possibly because of similarities in the reported  $\Delta G^\circ$  values for these processes (see Fig. 2). Consistent with this suggestion, manganese reduction has been observed to occur before the complete reduction of pore water nitrate in several pelagic sediments (Klinkhammer, 1980; Lyle, 1983; Salwan and Murray, 1983; also see Fig. 3). These pore water data also sometimes suggest the possibility of overlap between the zones of manganese and iron reduction, although differences in the energetics of these processes do not strongly support this occurrence (see Fig. 2). Furthermore, ferrous iron is known to chemically reduce both nitrate (Buresh and Moraghan, 1976) and manganese oxides (see references in *Chemical (abiotic) manganese and iron reduction* and Fig. 4), and these reactions may contribute to the appearance of a more distinct boundary between the zone of iron reduction and the zones of the other sub-oxic processes.

The apparent upper boundary of the iron

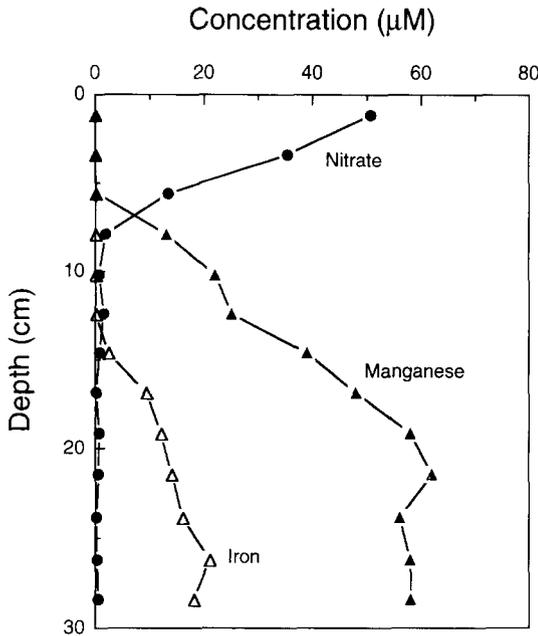


Fig. 3. Pore water concentrations of nitrate (dots), manganese (filled triangles), and iron (open triangles), all versus depth, in a core collected at MANOP site M (re-drawn from data presented in Klinkhammer et al., 1980). This site is in the eastern equatorial Pacific, 20–30 km east of the spreading axis of the East Pacific Rise, in a water depth of about 3100 m.

reduction zone (as inferred from the green-brown color transition in sediments) generally occurs below the manganese reduction zone and at the depth of complete nitrate removal from the pore waters (Lyle, 1983). Because of reactions between ferrous iron and manganese oxides and nitrate, any  $Fe^{2+}$  produced by iron reduction in the presence of manganese oxides or nitrate (i.e., in zones of manganese reduction and/or denitrification) should be re-oxidized back to iron(III) oxides, rather than accumulate in the pore waters. This may then explain the clearer separation of the apparent zone of iron reduction from the zones of either denitrification or manganese reduction, regardless of any actual overlap between these sub-oxic processes [also see Myers and Nealson (1988b) and Canfield (1993) for a further discussion of this phenomena]. The lack of a linear pore water iron profile through the zones of manganese reduction and denitrification provides further evidence in support

of these reactions between ferrous iron and manganese oxides and nitrate, and for the fact that the oxidant of the upwardly diffusing ferrous iron is likely not  $O_2$  but rather is either manganese oxides or nitrate (Klinkhammer, 1980; Sørensen, 1987; also see Fig. 4).

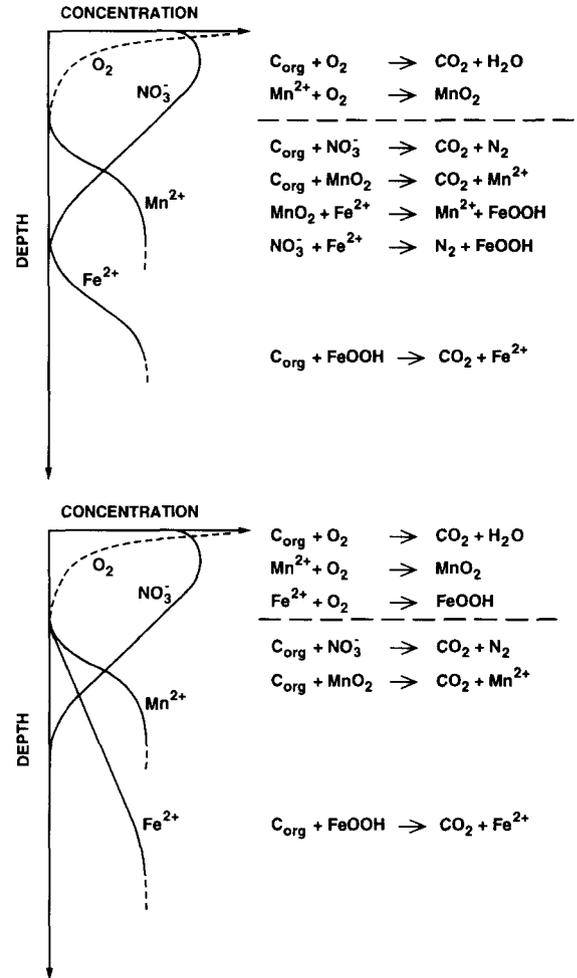


Fig. 4. A.(above) Pore water profiles in which the oxidation of iron in the pore waters is coupled to the reduction of either manganese oxides or nitrate (see equations to the right). Note that similar profiles are generally seen in many pelagic sediments (e.g., see Fig. 3). B.(below) Hypothetical pore water profiles that would exist if  $O_2$  was the primary oxidant of pore water iron (see equations to the right). Note that here it is assumed that iron oxidation is *not* coupled to either the reduction of manganese oxides or nitrate. Therefore iron must diffuse through the zones of manganese reduction and denitrification to a depth in the sediments where the upward iron flux reaches the downward oxygen flux.

Based on sediment concentrations, manganese and iron oxides should have a large capacity for oxidizing sedimentary organic matter (Reeburgh, 1983). However, evidence to date suggests that manganese and iron reduction are not quantitatively important in oxidizing organic matter in pelagic sediments. Bender and Heggie (1984) used pore water data from five pelagic sediments to estimate rates of sedimentary nitrate, manganese and iron reduction, and then used "Redfield"-type ratios to convert these rates to rates of organic carbon oxidation by each electron acceptor. Their results suggest that reactions involving all "secondary" oxidants (nitrate, manganese and iron oxides and sulfate) account for less than 10% of the total organic carbon oxidized in these sediments, with aerobic respiration accounting for the vast majority (> 90%) of the sedimentary organic matter remineralization. At the same time, it should also be noted that the occurrence of reactions such as iron oxidation coupled to either manganese or nitrate reduction complicates the use of calculated manganese, nitrate and iron reduction rates to estimate amounts of carbon oxidized by each sub-oxic process. However, this does not significantly affect their conclusion that sub-oxic processes do not account for a significant fraction of the observed organic carbon remineralization in the sediments they examined.

In contrast, Sayles and Curry (1988) presented pore water calculations which suggest that denitrification and manganese reduction account for up to ~ 40% of the total carbon oxidized in two deep-sea sediments with relatively shallow (~ 2–3 cm) surface oxic zones. In three other less reducing sites, with much thicker (> 20 cm) oxic surface zones, sub-oxic processes account for < 10% of the total carbon remineralized, a value similar to that observed by Bender and Heggie (1984). However when the results of both of these studies (Bender and Heggie, 1984; Sayles and Curry, 1988) are compared, one sees that there is not a simple relationship be-

tween reducing conditions in pelagic sediments and the importance of sub-oxic remineralization, because the sites studied by Bender and Heggie (1984) also had relatively shallow (~ 1–5 cm) surface oxic zones.

Bender and Heggie (1984) also presented a series of "theoretical" flux calculations which place general constraints on the importance of aerobic respiration, denitrification and manganese and iron reduction in the oxidation of organic matter in pelagic sediments. These calculations agree with their pore water results, again indicating the minor role that secondary oxidants should play in organic matter remineralization in pelagic sediments. Similar results were obtained by Rabouille and Gaillard (1991), using a steady-state diagenetic model for organic matter oxidation that includes aerobic respiration, denitrification and manganese reduction. Iron reduction was not included in their model, although its omission does not significantly affect this conclusion.

While manganese and iron reduction do not appear to be significant in the remineralization of organic matter in pelagic sediments, they may be important in other aspects of organic carbon dynamics in these sediments. In almost all marine sediments it is observed that some fraction of the organic carbon deposited to the sediment–water interface appears to escape remineralization. An understanding of the factors controlling this burial (or preservation) of sedimentary organic matter is important for several reasons, in part because this process represents the primary long-term repository for organic carbon in the global carbon cycle (Emerson and Hedges, 1988). Bender and Heggie (1984) showed that the amounts of organic matter remineralized by secondary oxidants (primarily nitrate, manganese oxides and sulfate) appear to be comparable to the amounts of organic matter preserved in the sediments. Based on this observation, they suggested that factors affecting organic carbon oxidation by secondary oxidants may thus play an important role in controlling the preserva-

tion of organic matter in pelagic sediments. A similar conclusion was also reached by Rabouille and Gaillard (1991) in their modeling study.

In contrast, Emerson and co-workers (Emerson, 1985; Emerson et al., 1985; Emerson and Hedges, 1988) have argued that since the vast majority of organic matter in pelagic sediments is oxidized by  $O_2$ , small changes in quantities affecting the rate of aerobic respiration (e.g., the organic carbon rain rate to the sediment surface or the bioturbation rate) ultimately control the preservation of sedimentary organic matter. Secondary oxidants are therefore presumed to play a minor role in both the remineralization and preservation of organic matter in pelagic sediments. Unfortunately, it is difficult at this time to evaluate these seemingly contradictory assertions, in part because of the above-discussed uncertainties in using pore water profiles to infer rates of manganese and iron reduction coupled to organic matter oxidation. In addition, recent studies have also demonstrated the important role that other factors may play in controlling the preservation of sedimentary organic matter. These include both the composition of the sedimentary organic matter itself (Westrich and Berner, 1984; Middelburg, 1989; Burdige, 1991), as well as the possible importance of oxygen (and processes associated with oxic conditions in sediments) in affecting the remineralization of certain types of organic compounds found in sediments (Henrichs and Reeburgh, 1987; Emerson and Hedges, 1988; Canfield, 1989b; Jahnke et al., 1989; Pedersen and Calvert, 1990; Henrichs, 1992; Lee, 1992). These observations therefore suggest that the factors controlling organic matter preservation in marine sediments are a function of both the organic matter itself as well as the specific remineralization processes associated with its oxidation. Future studies are clearly needed to resolve this complex problem.

Finally, it should be noted that while deep-sea pore water profiles are generally consistent with the biogeochemical zonation

model in Fig. 2, there have been no definitive studies to date that have demonstrated the occurrence of microbial manganese and iron reduction coupled to the oxidation of sedimentary organic matter where pore water data suggests that it is occurring. In addition, the discussion above further indicates that the use of pore water profiles to determine these biogeochemical zones is still somewhat tentative, due in part to an incomplete understanding of all the chemical and biological reactions affecting manganese and iron redox cycling in pelagic sediments (e.g., the importance of manganese or nitrate reduction coupled to ferrous iron oxidation versus organic matter oxidation). Studies in all of these areas are needed to resolve these uncertainties.

#### *The role of manganese and iron reduction in the formation of ferromanganese nodules*

Manganese reduction in pelagic and hemi-pelagic sediments may be involved in the formation of ferromanganese nodules, since under some circumstances manganese reduction in the sediments and the resulting upward diffusion of dissolved manganese across the sediment-water interface may be an important source of manganese to nodules (Calvert and Price, 1977; Grill, 1978; Moore et al., 1981; Dymond et al., 1984; Glasby, 1984). These processes may also play a role in the growth of freshwater manganese nodules (see the discussion below and in Dean et al., 1981).

In a detailed study of the geochemistry of manganese nodules at several contrasting sites in the Pacific, Dymond et al. (1984) referred to this process as the "sub-oxic diagenesis" nodule accretionary process. However in the sites they studied, this process appears to be involved in the formation of nodules only at a hemi-pelagic site which underlies productive waters in the eastern tropical Pacific (MANOP site H). Furthermore, while nodule composition data suggest the occurrence of this sub-oxic diagenetic

mechanism in the formation of nodules at this site, pore water data are apparently inconsistent with the possibility. This is the case because in these and other hemi-pelagic sediments, the "major" zone of manganese reduction is generally not sufficiently close to the sediment-water interface (e.g., see Fig. 3), and any manganese produced at depth does not likely escape oxidation and precipitation in the upper, oxic sediments (see also the discussion in MANGANESE AND IRON REDUCTION IN CONTINENTAL MARGIN SEDIMENTS). To reconcile these apparent contradictory observations Dymond et al. (1984) suggested that nodule accretion as a result of sub-oxic diagenesis is not a steady-state process, and that it occurs because of episodic high productivity events that lead to transient "zones" of manganese reduction in sediments near the sediment-water interface.

Sediment manganese oxidation state measurements (Kalhorn and Emerson, 1984; see

Fig. 5) and interfacial pore water manganese profiles (Heggie et al., 1986; see Fig. 6) provide additional evidence in support of the occurrence of manganese reduction in some "oxic" surficial sediments. These authors discuss the possible role that this type of manganese reduction may play in manganese nodule formation, and Kalhorn and Emerson (1984) used a simple box model to demonstrate that this rate of surficial sediment manganese reduction at MANOP site H is  $\sim 5$  times the manganese accumulation rate in nodules of this region. These authors also suggest several possible explanations for the occurrence of this manganese reduction in oxic surficial sediments, including: (1) manganese reduction in anoxic microenvironments within the sediments; (2) possible production of dissolved organic compounds capable of reducing manganese oxides in the presence of oxygen and (3) differences in the forms and reactivity of manganese oxides found at the sediment-water interface rela-

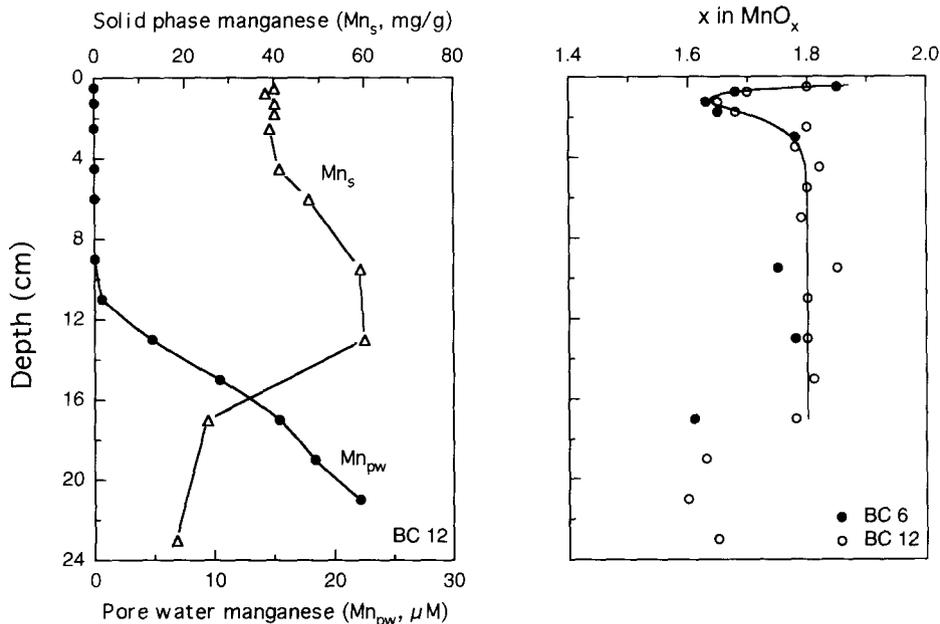


Fig. 5. Solid phase and pore water manganese concentrations (right), and the oxidation state of manganese in the solid phase ( $x$  in  $MnO_x$ ; left), all versus depth, in box cores collected at MANOP site H (re-drawn from data presented in Kalhorn and Emerson, 1984). Site H is in the eastern equatorial Pacific (water depth 2590 to 3420 m), about 900 km east of the East Pacific Rise in a sediment plain covered with manganese nodules. As discussed in the text, the minimum in the value of  $x$  at a depth of  $\sim 2$  cm is taken as an indication of the occurrence of manganese reduction in the otherwise "oxic" surface sediments. Note the "primary" zone of manganese reduction below a depth of  $\sim 12$ –14 cm.

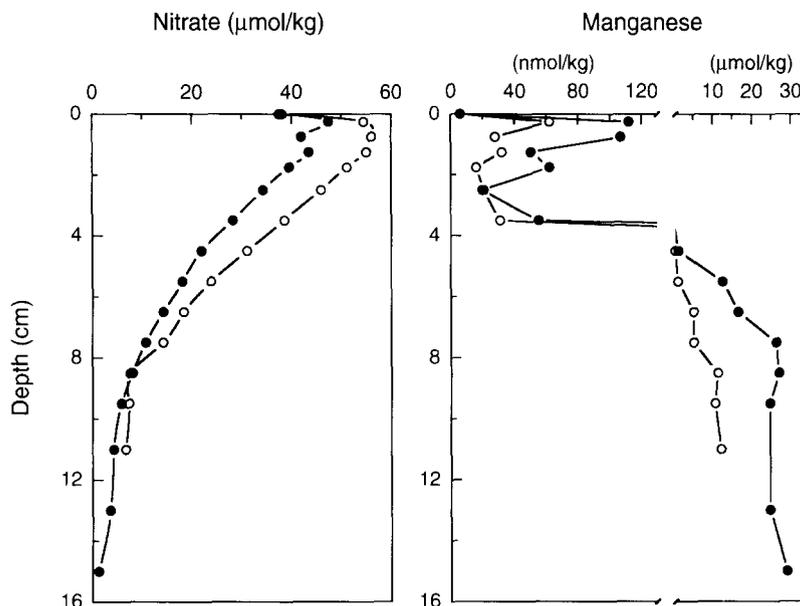


Fig. 6. Fine scale pore water profiles of manganese and nitrate, versus depth, in replicate cores collected at MANOP site M (re-drawn from data presented in Heggie et al., 1986). Note the scale break in the concentration axis of the manganese profile. The observed manganese production in the upper 1 cm of these sediments is in excess of that predicted from oxic organic matter remineralization and opaline silica dissolution, and is therefore assumed to come from the reduction of sedimentary manganese oxides (Heggie et al., 1986). As discussed in the text, this manganese reduction appears to differ from that which occurs in the "primary" zone of manganese reduction below ~5 cm. These profiles show the same general trends as those seen in previous studies at site M (see Klinkhammer et al., 1980, and Fig. 3), although better resolution near the sediment-water interface has been obtained here.

tive to those found deeper in the sediments (i.e., those which are produced during the deeper diagenetic recycling of manganese in the "main" zone of manganese reduction). While there is evidence in the literature consistent with each of these possibilities, none of them has been clearly shown to be responsible for the occurrence of manganese reduction in apparently oxic surficial sediments.

Related non-steady state phenomena may also play a role in the formation of alternating manganese and iron rich layers common in many marine and freshwater nodules (Sorem and Fewkes, 1977; Moore, 1981). In Oneida Lake, Moore et al. (1980) and Moore (1981) have shown that manganese nodules generally accrete a manganese-rich layer when exposed to oxygenated lake bottom waters. However, temporary burial of nodules by organic-rich sediment apparently leads to the development of anoxic conditions at the nodule surface and the selective

remobilization of manganese in this surface layer, since manganese reduction is thermodynamically favored over iron reduction (see Fig. 2; note that this anoxic sediment cover might result from the rapid sedimentation of phytoplankton debris after the "crash" of a bloom in the water column). These anoxic conditions then transform the nodule surface into one which is now enriched in iron, due to this selective manganese removal. The thickness of this "new" iron-rich layer, relative to the now deeper manganese-rich layer, depends on the time of nodule accretion under oxic conditions versus the time of burial under reducing condition. Removal of this anoxic sediment cover (e.g., by a storm event) allows for the accretion of new manganese rich material at the nodule surface, and the repetition of this process leads to the observed banding in these nodules. This mechanism may also play a role in the growth of deep-sea nodules, although deep-sea nodules

have not been examined in the context of such processes.

*The effects of Quaternary paleoceanographic changes on manganese reduction in pelagic sediments*

A common observation in many pelagic and hemi-pelagic sediments is the occurrence of multiple solid phase manganese peaks in the sediments (e.g., see Fig. 8). Such multiple manganese peaks are observed over a variety of depth and time scales, in some cases occurring as mm-scale laminae, rich in both manganese and iron (e.g., see the discussion in Wilson et al., 1986). However, multiple manganese rich layers of cm-scale thickness are also found in the upper meter to several meters of some pelagic and hemi-pelagic sediments, over time scales that go back not only to the most recent glacial–interglacial transition (i.e., the Glacial–Holocene boundary) but also cover much of the late Quaternary (Froelich et al., 1979; Gardner et al., 1982; Berger et al., 1983; Price and Froelich, 1987; Finney et al., 1988; Price, 1988; Dean et al., 1989; Mangini et al., 1990).

In the following discussion, the occurrence of these manganese peaks will be taken to be indicators of either the present-day location or the previous location(s) of the manganese redox boundary (see the discussion below and in GENERAL ASPECTS OF SEDIMENTARY MANGANESE AND IRON REDUCTION), based on the assumption that the predominant form of manganese in these peaks is manganese oxides. However, if some (or all) of this manganese actually exists as a carbonate (rather than an oxide) phase, these peaks would likely form some depth (on the order of several tens of cm) below the manganese redox boundary (Pedersen and Price, 1982; Burdige and Gieskes, 1983; Thomson et al., 1986; Schimmiel and Pedersen, 1990). This occurrence would obviously greatly affect the interpretations discussed below.

Under steady-state conditions the model

of Burdige and Gieskes (1983) predicts that only one manganese peak should be observed in sediments (e.g., see Fig. 1). Therefore, the existence of multiple manganese peaks has been attributed to the occurrence of non-steady state manganese redox cycling. In the simplest sense, these non-steady state conditions result from the net migration (relative to the sediment–water interface) of the manganese redox boundary, since under steady state conditions the redox boundary moves upwards at a rate equal to the sedimentation rate and therefore remains at a fixed depth in the sediments. Assuming that the manganese redox boundary occurs at the depth in the sediments where pore water oxygen goes to zero (see Fig. 2 and GENERAL ASPECTS OF SEDIMENTARY MANGANESE AND IRON REDUCTION), the depth of this boundary will increase with time (i.e., occur at a deeper depth) if, for example, bottom water oxygen concentrations increase, the flux of organic carbon to the sediments decreases, and/or the rate constant of sedimentary organic matter oxidation decreases (e.g., due to changes in the reactivity of this material). Similarly, the depth of this redox boundary will decrease if these parameters change in the opposite direction. It should also be noted here that changes in these parameters do not represent the only ways to cause shifts in the depth of the manganese redox boundary, and they are listed here simply as examples of possible ways the depth of this boundary can be shifted.

Evidence in support of such relationships between the depth of the manganese redox boundary in sediments and the parameters discussed above comes from several observations. The first are experimental and modelling results (Emerson, 1985; Emerson et al., 1985) that indicate the appropriate relationships between these parameters and the depth in pelagic sediments at which pore water oxygen concentrations go to zero. In addition, other studies have observed that the depth of the present-day manganese re-

dox boundary (as inferred from, e.g., manganese pore water profiles) is inversely correlated with the flux of organic carbon to the sediments (Lynn and Bonatti, 1965; Swinbanks and Shirayama, 1984; Finney et al., 1988).

A deepening redox boundary leads to a situation in which the downward progressing redox front “leaves” behind the manganese oxide peak at the old redox boundary. “New” manganese oxides are precipitated at the current redox boundary from the upward diffusion of the standing stock of pore water manganese in the deeper oxygen-depleted sediments. A distinct manganese peak will be seen to grow in at the new redox boundary if this redox downshift is relatively rapid and occurs a sufficient distance from the original redox boundary (see Fig. 7). Furthermore, when the old manganese peak is buried down to the new redox boundary, it then becomes involved in manganese redox cycling at this new boundary. However, the possibility also exists that some, or all, of this “old” peak may be buried through the new redox bound-

ary into the zone of manganese reduction, where it may then slowly dissolve and be reprecipitated at the new redox boundary (see the discussion below for further details).

In contrast, an upshift of the redox boundary may lead to the entrapment of the relict manganese peak in the new zone of manganese reduction (see Fig. 7). This peak will then either be preserved in the sediments, or undergo reductive dissolution and be re-precipitated at the new redox boundary. The extent to which either of these occurs is dependent on several factors which will be discussed below. Nevertheless, if the redox upshift occurs rapidly (relative to rates of manganese reduction and sediment accumulation) and the new redox boundary remains stable for a sufficient time period, a distinct manganese peak will be seen to grow in at the new redox boundary (see Fig. 7).

Since pore water manganese profiles respond more rapidly to changes in sediment redox conditions than do solid phase manganese profiles (Froelich et al., 1979; Pedersen et al., 1986; Price, 1988; Schimmield and

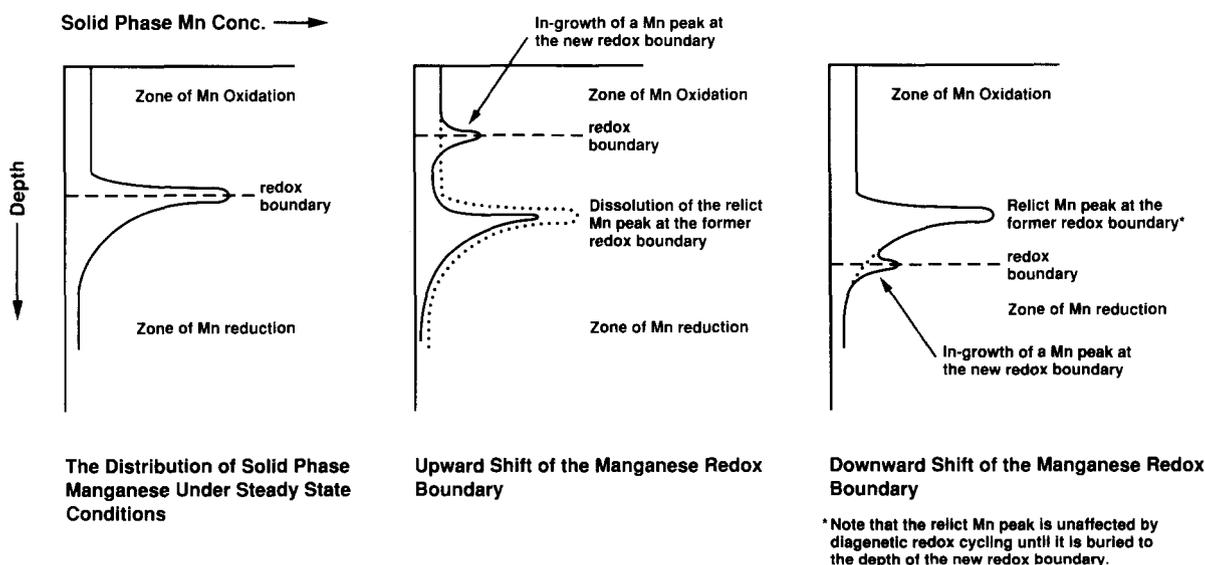


Fig. 7. The effects on solid phase manganese profiles due to changes in the depth of the redox boundary between the zones of manganese oxidation and reduction. The two figures to the right of the steady state profile represent sedimentary profiles that would be observed some time after the “instantaneous” (relative to the time scales of other sedimentary processes) upshift or downshift of the steady-state redox boundary. These changes in the depth of the manganese redox boundary are presented here in this fashion to more clearly illustrate the ways in which multiple manganese-rich layers can form in pelagic sediments.

Pedersen, 1990), pore waters quickly adjust to changes in the depth of the manganese redox boundary and begin precipitating a new solid phase manganese peak at the new redox boundary. Therefore in sediments containing multiple solid phase manganese peaks, the manganese pore water profile may be useful in distinguishing which of the manganese peaks is the active diagenetic feature associated with the current redox boundary. Relict peaks observed above the active redox boundary are indicative of a redox downshift, while relict peaks found below the current redox front likely result from a redox upshift. However, the possibility also exists that relict peaks found below the current redox boundary may be features associated with a redox downshift (e.g., see the discussion above). The interpretation of these peaks in the context of the redox history of a sediment and the controls on sedimentary redox conditions will be discussed below in greater detail.

Finally, if the movement of the redox

boundary occurs relatively slowly compared to the rate of sediment accumulation and/or the in situ rates of manganese oxidation and reduction, one should see a broad diffuse solid phase manganese peak whose one limit is the old redox boundary and whose other limit is the position of the current redox boundary. Again, pore water manganese profiles should be useful in elucidating the position of the current (active) redox boundary. Examples of what may be relatively rapid and slow redox upshifts can be seen in Fig. 8 for two cores from the equatorial Atlantic originally described by Froelich et al. (1979). In contrast, Pedersen et al. (1986) presented results from a core collected near the East Pacific Rise in which there appears to have been a  $\sim 10$  cm redox downshift which they suggested occurred within the past 1000 yr. However model calculations presented by Price (1988) indicate that this redox downshift may have occurred much more recently, perhaps within the past 10–20 yr.

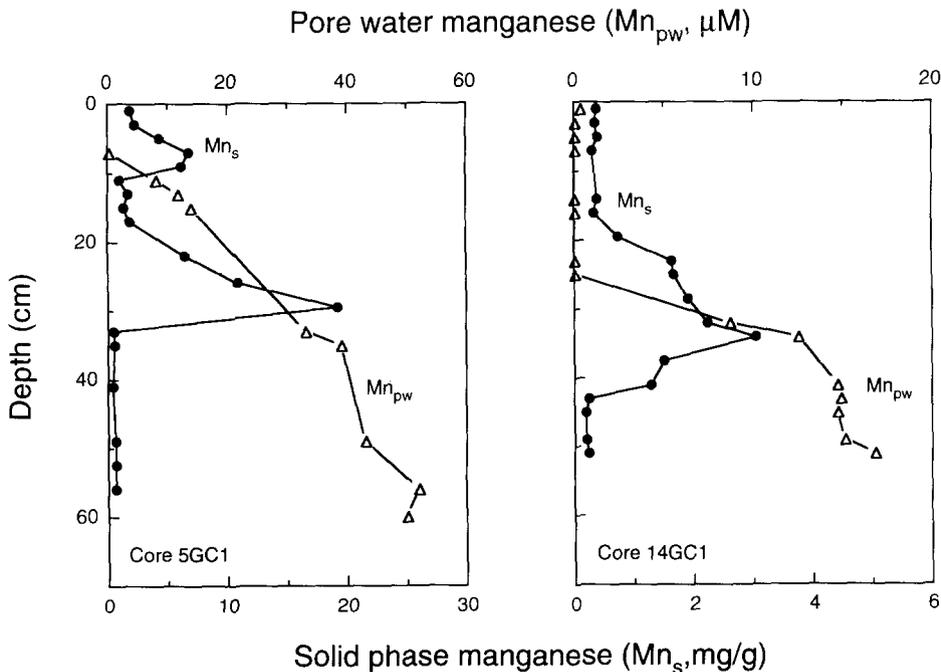


Fig. 8. Pore water (open triangle) and solid phase (dots) manganese, both versus depth, in cores collected in the eastern equatorial Atlantic (re-drawn from data in Froelich et al., 1979). Based on the discussion in the text (also see Fig. 7) it appears as if the rate of redox upshift was more rapid in core 5GC1 than in core 14GC1. However other phenomena may also possibly explain the observed differences between these two cores.

As discussed in the beginning of this section, multiple solid phase manganese peaks are observed in many pelagic and hemipelagic sediments (e.g., see Fig. 8). In discussing the processes leading to the formation of such layers in Glacial–Holocene sediments in the eastern equatorial Pacific, Berger et al. (1983) suggested that the upper layer (at 7–10 cm) is the active redox boundary while the deeper layer (near 30 cm and centered on the Glacial–Holocene boundary) is found at the relict redox boundary. They further proposed that this resulted from a decrease in ocean fertility (primary production) which occurred during the transition from Glacial to Holocene conditions (Pedersen, 1983). However, because such a decrease in primary productivity should have led to a decrease in carbon fluxes to the sediments, Price (1988) later recognized that such a decrease in ocean fertility at the beginning of the Holocene should have shifted the active redox boundary to deeper depths in the sediments (e.g., see the redox downshift scenario in Fig. 7 and the discussion in Thomson et al., 1984). The occurrence of the relict manganese peak below the current redox boundary as a result of a redox upshift further indicated to Price (1988) that if the scenario of Berger et al. (1983) was correct, then the present-day manganese profile could only have been obtained if this relict peak had also been buried through the current redox boundary.

Price (1988) also offered an alternate explanation for these observations. She suggested that a drop in ocean fertility during the early part of the Holocene indeed established a deeper redox boundary in these sediments, and resulted in the formation of the deeper manganese peak. The upper (or relict) pre-Holocene (i.e., Glacial) manganese peak was then buried to the early Holocene redox boundary, where it was incorporated into the manganese redox cycling occurring at this boundary. She then proposed that the formation of the second, surficial manganese peak (above the deep manganese peak) is a re-

sponse to a relatively recent, short-term increase in ocean fertility that occurred within the last few thousand years.

Evidence for such a recent redox upshift can be seen, for example, in core 5GC1 in the eastern equatorial Atlantic (Fig. 8) where the manganese pore water profile indicates that the upper manganese peak is found at the current redox boundary. Price (1988) also presented scaling calculations similar to those described in Froelich et al. (1979) which suggest that the in-growth of such an upper manganese peak after a redox upshift can occur in less than 5000 yr. Finally, cores showing such multiple manganese peaks occur predominantly in sediments underlying eastern equatorial upwelling systems in the Atlantic and Pacific Oceans (Price, 1988; Price and Froelich, 1987), and these authors have suggested that the formation of these multiple manganese peaks is related to relatively rapid, large-scale climate events such as the El Niño/Southern Oscillation (EN-SO). In support of this suggestion, they noted that changes in sedimentary organic carbon concentrations are generally associated with these multiple manganese layers, which they interpreted as indicators of variation in the organic carbon rain rate to these sediments over time.

In an attempt to further quantify the time scales over which such multiple manganese peaks form in these sediments, Price (1988) developed a non-steady state manganese diagenetic model based on the steady-state equations presented by Burdige and Gieskes (1983). In her model the depth of the manganese redox boundary is externally specified and allowed to vary with time. She also assumed (as was the formalism in Burdige and Gieskes, 1983) that the rate of manganese reduction is first order with respect to the amount of solid phase manganese present, and therefore that relict manganese peaks trapped in the manganese reduction zone undergo slow, continual reductive dissolution (e.g., see Fig. 7). While these assumptions have certain disadvantages (see below), her

model results lead to several interesting suggestions concerning the relationship between observed sediment manganese depth profiles and paleoceanographic conditions during the Holocene.

For a core in the eastern equatorial Pacific, calculations with the Price (1988) model indicate that alternating upshifts and downshifts of the manganese redox boundary over the past  $\sim 2000$  yr (caused perhaps by ENSO-type climate and primary productivity variations) can lead to a manganese distribution in the sediments that is consistent with the observed data (see Fig. 9). Furthermore, for core 5GC1 in the eastern equatorial Atlantic (see Fig. 8), her model calculations also show that the upper manganese peak in these sediments can form within approximately 2000 yr of a single redox upshift in

the sediments (see Fig. 10). One of the most interesting points to come from these calculations is that the required increase in carbon fluxes to the sediments (which then leads to such a redox upshift) need only have occurred within the last  $\sim 1500$ – $2000$  yr either as a single event (as in Fig. 10) or as an interrupted sequence (as in Fig. 9) to create the present-day sedimentary manganese distributions. From a paleoceanographic standpoint, this suggests that the present-day “normal” patterns of equatorial upwelling and carbon fluxes to the sediments of these regions are not typical of the entire Holocene, and that the early Holocene ocean was likely less productive and perhaps more reminiscent of what is now seen during presumably “atypical” ENSO conditions (Price, 1988).

Similar changes in the depth of the man-

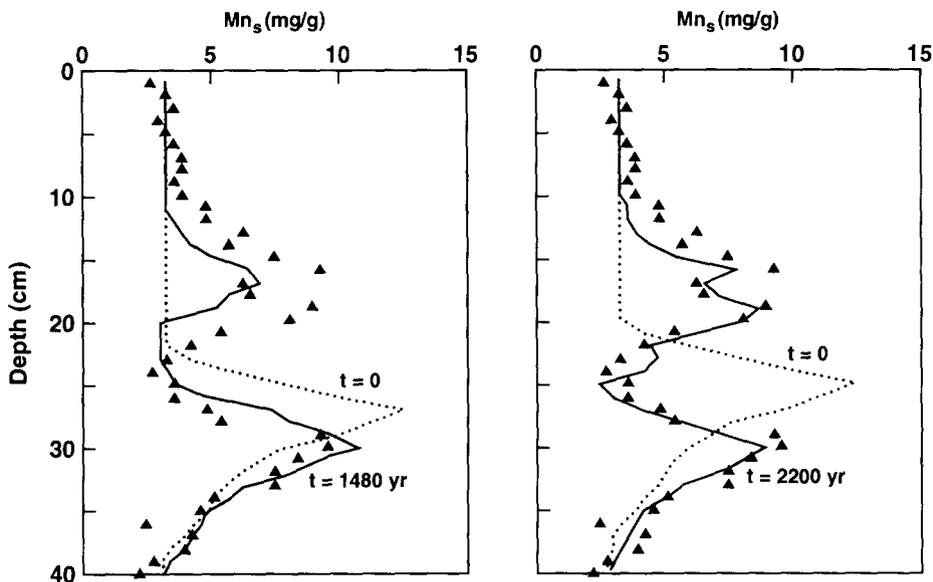


Fig. 9. The results of Price's (1988) non-steady state manganese model applied to data from a core (RC 52) in the eastern equatorial Pacific (data from P.N. Froelich, pers. commun. to B. Price; note that other data from this core are reported in Murray et al., 1984). The initial conditions used for each model run (i.e., the  $t = 0$  profiles) were determined as discussed in Price (1988) and are shown in each figure as a dotted line. The final profiles for the two model simulations are shown as solid lines, and the actual data are shown as triangles. A.(left) A model simulation in which the manganese redox boundary is alternately assigned to the depths of 16 cm and 27 cm using a time schedule for the occurrence of ENSO events derived with data from the Quelccayo ice cap in Peru. There are six “instantaneous” redox shifts in this time schedule over the 1480 yr simulation, with the time between redox shifts ranging from 120 to 350 yr. Price (1988) assumed that ENSO-dominated time periods (which are characterized by higher sea surface temperatures and reduced equatorial upwelling) are periods of lower carbon flux to the sediments. This then leads to more oxidizing conditions in the sediments, and therefore to a redox downshift. Conversely, ENSO-poor times are assumed to be dominated by a redox upshift in the sediments, due to increased upwelling and the resulting increase in carbon flux to the sediments. B.(right) A model simulation in which the manganese redox boundary is alternately assigned to the depths of 16 and 19 cm at 270 yr intervals over 2200 yr.

ganese redox boundary apparently also occurred several times earlier in the Quaternary. Gravity cores from hemi-pelagic sediments in the eastern equatorial Pacific (MANOP site H) exhibit several peaks in both solid phase manganese and organic carbon concentrations over the past  $\sim 400,000$  yr, and Finney et al. (1988) have suggested that they are caused by periodic changes in redox conditions that are similar to those described above for the most recent glacial–interglacial (i.e., the Glacial–Holocene) transition. To further examine these changes they developed a simple semi-quantitative model that used the organic carbon and manganese profiles to hindcast the depth of the manganese redox boundary over the age of the cores

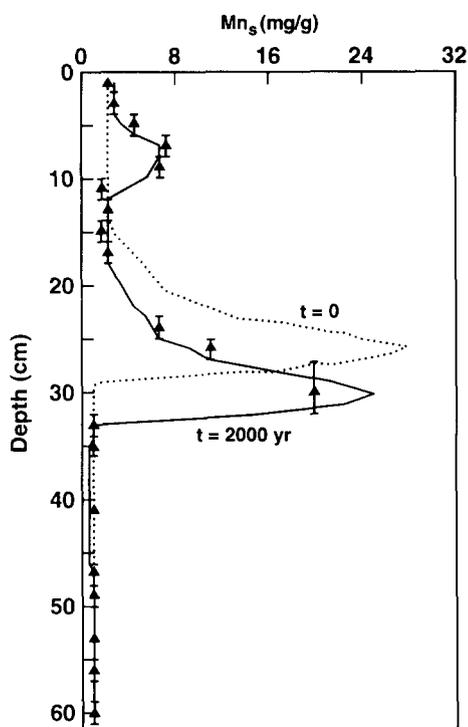


Fig. 10. The results of Price's (1988) non-steady state manganese model applied to data from core 5GC1 in the eastern equatorial Atlantic (see Fig. 8; data from Froelich et al., 1979). The initial condition used for this model run (i.e., the  $t = 0$  profile) was determined as discussed in Price (1988) and is shown as a dotted line. The final profile (shown as a solid line), results from a 2000 yr simulation following an instantaneous redox upshift from 26 to 7 cm.

(see Fig. 11). In contrast to the Price (1988) model, Finney et al. (1988) assumed that a relict manganese peak trapped in the manganese reduction zone by a redox upshift can become "permanently" buried in the sediments, since they suggest that little of this peak is remobilized once it is buried below the redox boundary. The roughly 100,000 yr periodicity seen in the depth of the manganese redox boundary at this site appears to be consistent with other paleoceanographic information on changes during the Quaternary of quantities (e.g., surface water productivity) which likely affect the depth of this redox boundary (Finney et al., 1988; Lyle et al., 1988).

The models of Price (1988) and Finney et al. (1988) have provided important insights into possible relations between manganese depth profiles in pelagic and hemi-pelagic sediments and Quaternary paleoceanographic changes that affect sedimentary organic matter remineralization and burial. However, as discussed above, there appear to be questions about several key assumptions made in these models, in part because of the ways that both models specify the depth of the manganese redox boundary and the kinetics of manganese reduction. This problem could be overcome by developing a more rigorous time-dependent diagenetic model (e.g., an expansion of the steady state model of Rabouille and Galliard, 1991) which, for example, would directly calculate the depth of the redox boundary with model-derived oxygen profiles (which would be determined using parameters such as the bottom water oxygen concentration and the organic carbon flux to the sediments). Such an approach would appear to be useful in further examining the conclusions of these studies.

#### *The occurrence of manganese and iron reduction during the diagenesis of deep-sea turbidites*

The deposition of organic-rich turbidites over more organic-poor pelagic sediments is

an additional non-steady-state system in which manganese and iron redox processes play important roles. Turbidites represent sediments transported by turbidity currents from the continental shelf down the continental slope and into the deep ocean basins (Open University, 1989). In general, turbidites contain levels of organic carbon that are elevated over those in most pelagic sediments, and the thicknesses of turbidite sequences range from tens of centimeters to several meters. Initial geochemical studies of these systems focussed on the effects of the deposition of a single turbidite in a pelagic sediment on organic matter remineralization and mobilization of redox-sensitive elements (Colley et al., 1984; Wilson et al., 1985, 1986; Wallace et al., 1988; Jahnke et al., 1989). However, later studies have also examined the geochemical consequences of repeated turbidite deposition in pelagic sediments (DeLange, 1986; Thomson et al., 1987; Buckley and Cranston, 1988; Dean et al., 1989; Thomson et al., 1989).

The deposition of an organic-rich turbidite over organic-poor pelagic sediments leads to a situation in which oxygen and nitrate diffuse downwards through the turbidite, oxi-

dizing organic carbon at a downward progressing redox front within the turbidite. This process has been described as one in which these oxidants “burn down” through the organic rich sediment, and hence this redox front has been described as a burn-down front (Wilson et al., 1985). In the context of the discussion in the third part of this section (and Fig. 7), these turbidite systems are similar to sediments in which there is a slow redox downshift. The current location of the burn-down front serves as a locus for subsurface aerobic respiration, iron and manganese oxidation, and denitrification, as can be seen in pore water, solid phase and denitrification depth profiles (Sørensen et al., 1984; Wilson et al., 1985, 1986; Wallace et al., 1988). The burn-down process also results in color change in the turbidite from green to brown (Lyle, 1983) and the remobilization of redox sensitive elements such as iron, manganese and uranium. The time scales over which this burn-down process occurs are related to quantities such as the thickness and initial organic carbon content of the turbidite, the pelagic sedimentation rate, and bottom water oxygen and nitrate concentrations (Colley et al., 1984; Wilson et

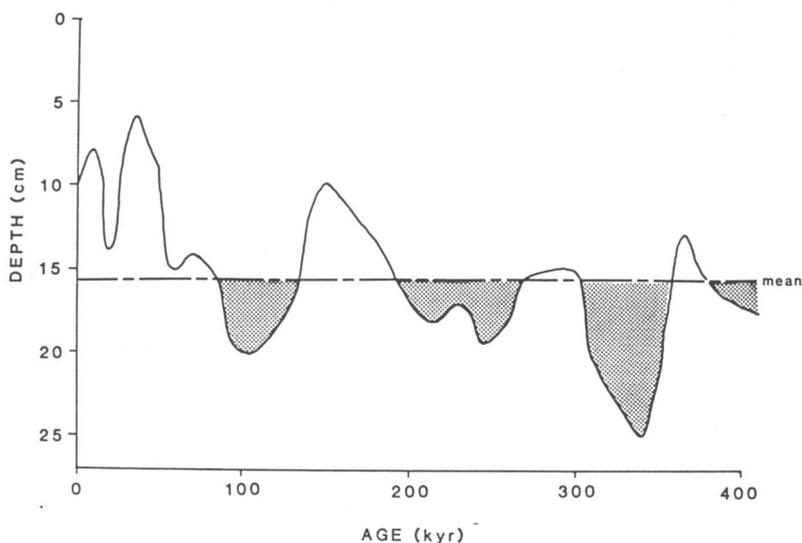


Fig. 11. Variations in the depth of the manganese redox boundary at MANOP site H over the past 400,000 yr, as determined using the model presented by Finney et al. (1988). Reprinted with permission from *Paleoceanography*, vol. 3, p.181, copyright 1988 by the American Geophysical Union.

al., 1985). However, model calculations suggest that burn-down fronts moves downward at rates comparable to pelagic sedimentation rates (Colley et al., 1984; Wilson et al., 1985, 1986).

In terms of manganese and iron redox chemistry, it is generally assumed that the turbidite represents a source of dissolved iron and manganese which is then oxidized at the downward progressing redox front. The ultimate source of this upwardly diffusing iron and manganese is generally assumed to be manganese and iron reduction occurring in the reduced turbidite sediments, although the exact mechanisms by which these reductions occur (i.e., what is the reductant), and its relationships to other geochemical processes in the turbidite sediments have not been well described. Several recent studies have examined these problems more directly, including a discussion of the possible role of ferrous iron reduction of manganese oxides in turbidite sediments (Thomson et al., 1987, 1989; Buckley and Cranston, 1988). This reaction is of some interest here because it appears to lead to secondary color changes in the turbidite sediments (referred to as diagenetic "haloes") beyond the brown-green color change seen at the burn-down front (see above). Understanding the formation of these diagenetic haloes appears to be of some use in interpreting the post-depositional history of interbedded pelagic and turbidite sediments, particularly those in which turbidite emplacement occurs on a time scale more rapid than that for the complete burn through (or oxidation) of the uppermost turbidite (Buckley and Cranston, 1988).

#### MANGANESE AND IRON REDUCTION IN CONTINENTAL MARGIN SEDIMENTS

The occurrence of manganese and iron reduction in continental margin sediments has been demonstrated with pore water profiles (Aller et al., 1986; Heggie et al., 1987b; Bender et al., 1989; Aller, 1990; Jahnke, 1990; Murray and Kuivala, 1990; Shaw et al., 1990;

Hines et al., 1991; Reimers et al., 1992). However, as with pelagic sediments, the mechanisms of these processes in margin sediments have not been clearly defined. Estimates of manganese and iron reduction rates in margin sediments (and their importance in sedimentary organic carbon oxidation) have also been made by modeling both pore water and solid phase sedimentary profiles (Heggie et al., 1987b; Bender et al., 1989; Aller, 1990; Reimers et al., 1992). While this modeling approach does not always yield an accurate estimate of the true rates of metal oxide reduction in sediments (see the discussion in previous section and in Canfield, 1993), the results of these calculations suggest that in the absence of significant physical or biological "mixing" (or particle transport) of sediments, manganese and iron reduction play minor roles in organic matter remineralization in continental margin sediments.

The reasons for this observation likely stem from differences in the ways that organic matter oxidants are transported in sediments. In the absence of sediment "mixing" processes (e.g., bioturbation), sedimentation is the dominant process by which manganese and iron oxides move downward in sediments, while diffusion in sediment pore waters is the dominant transport process of dissolved oxidants such as oxygen, nitrate and sulfate. As such, in most margin sediments the diffusion of these pore water oxidants appears to be sufficiently fast relative to sediment organic carbon fluxes and sedimentation of manganese and iron oxides. This then leads to a situation in which metal oxide reduction plays a minor role in overall organic carbon remineralization, with the predominant processes being aerobic respiration and denitrification (Bender et al., 1989; Reimers et al., 1992), and occasionally sulfate reduction (Christensen, 1989; Hines et al., 1991). It should also be noted that Bender and Heggie (1984) placed similar, and more quantitative, constraints on the relative roles of manganese and iron reduc-

tion in the remineralization of organic matter in pelagic sediments (see previous section).

In contrast, studies of Amazon continental shelf and the Panama basin sediments (Aller et al., 1986, 1991; Mackin et al., 1988; Aller, 1990) have indicated ways that sediment mixing processes can lead to situations in which manganese and iron reduction play more significant roles in sedimentary organic matter remineralization. In Panama Basin sediments, intense macrofaunal activity leads to extensive sediment mixing in the upper ~30 cm of sediment (Aller, 1990). Coupled with high manganese inputs to these sediments, due to their close proximity to hydrothermal sources of manganese on the East Pacific Rise, this leads to a situation in which manganese reduction appears to be responsible for all of the observed benthic carbon remineralization. At the same time, much of the oxygen flux into these sediments is directly utilized in the re-oxidation of reduced metabolites such as  $\text{Mn}^{2+}$  or  $\text{NH}_4^+$ , rather than in the oxidation of sedimentary organic mat-

ter [see Mackin and Swider (1989) and Aller (1993) for a further discussion of such phenomena in coastal marine sediments]. Since little of the  $\text{Mn}^{2+}$  produced in the sediments escapes as a benthic flux, oxygen actually serves as the ultimate oxidant for organic matter remineralization in these sediments. As a result, manganese oxides (and manganese redox cycling) therefore simply serve to shuttle electrons between  $\text{O}_2$  and organic matter in the sediments (see Fig. 12), in ways similar to those in which manganese redox cycling in coastal sediments may couple sulfide oxidation to  $\text{O}_2$  reduction (Burdige and Nealson, 1986; Aller, 1993; see also *Salt marsh sediments*).

This coupling of bioturbation, manganese redox cycling and organic matter remineralization in Panama Basin sediments increases the importance of anoxic decomposition in the sediments while at the same time decreasing the storage of reduced reaction products, and hence "diagenetic evidence" of anoxic pathways of organic matter decomposition (Aller, 1990). However, another way

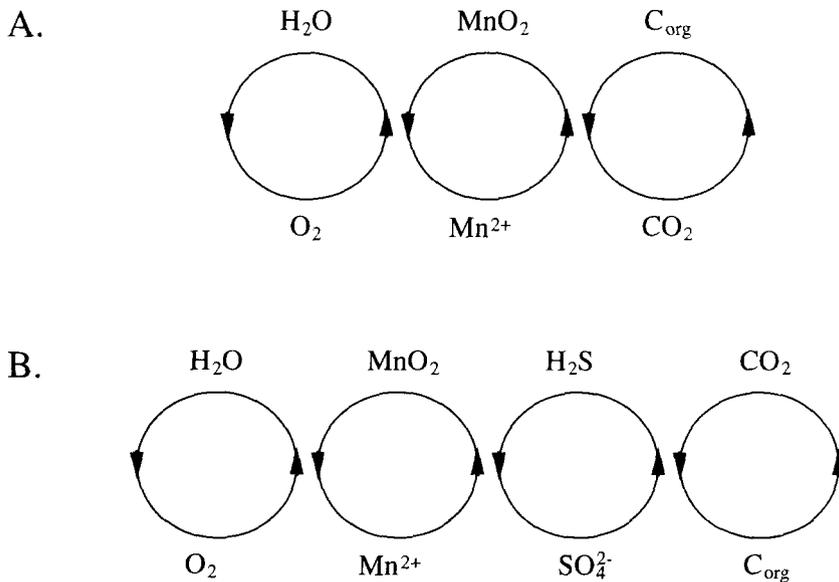


Fig. 12. Possible ways that manganese redox cycling can interact with the redox cycling of other elements in sediments (modified from Burdige and Nealson, 1986, and Aller, 1993). A. The coupling of manganese reduction to organic matter oxidation, and  $\text{Mn}^{2+}$  oxidation to  $\text{O}_2$  reduction (e.g., as in Panama Basin sediments; Aller, 1990). B. The coupling of manganese reduction to sulfide oxidation (produced by sulfate reduction coupled to organic matter oxidation), and  $\text{Mn}^{2+}$  oxidation to  $\text{O}_2$  reduction (e.g., as in Long Island Sound sediments; Aller, 1993).

that these interactions may affect sediment processes involves any potential effects associated with the preservation of sedimentary organic matter under anoxic conditions. Although in a *net* sense oxygen appears to be the ultimate oxidant of organic matter in these sediments, the specific mechanism by which organic matter is remineralized is apparently anoxic decomposition via manganese reduction (Fig. 12). Therefore, if there are factors that allow (or favor) the preservation of organic matter (or certain types of organic compounds) under anoxic conditions, then such preservation may be possible in these sediments, in spite of the net coupling of organic matter oxidation to  $O_2$  reduction.

In the sediments of the Amazon continental shelf, several factors lead to a situation in which iron reduction (and to a lesser extent manganese reduction) appears to be the predominant process by which sedimentary organic matter is remineralized (Aller et al., 1986, 1991; Mackin et al., 1988). These factors include: (1) relatively low reactive organic carbon concentrations; (2) relatively high solid phase iron concentrations and (3) intense physical mixing or reworking of the sediments.  $^{210}Pb$  profiles and non steady-state modeling of pore water profiles suggest that the upper 50 to ~ 150 cm of these sediments are mixed on roughly seasonal time scales, and this mixing apparently "recharges" sedimentary oxidants when reduced metabolic end-products (e.g.,  $Fe^{2+}$  or  $Mn^{2+}$ ) are exposed to oxygenated shelf bottom waters (Aller et al., 1986; Mackin et al., 1988). The timing of these processes and the chemical characteristics of the sediments therefore appear to "poise" these sediments at a point where iron reduction dominates organic matter remineralization.

At the same time, the exact mechanisms by which iron and manganese reduction are coupled to organic matter oxidation in these sediments are still unclear. Aller et al. (1986) suggested that metal oxide reduction could be directly coupled to sedimentary organic matter oxidation, or could be an indirect

result of bacterial sulfate reduction (i.e., sulfide production) followed by sulfide oxidation using iron and manganese oxides. However, the extent to which bacterial sulfate reduction can occur in the presence of "microbially-reducible" iron oxides is uncertain. Lovly and Phillips (1987a) suggested that the presence of these oxides should inhibit bacterial sulfate reduction, although Sørensen (1982) demonstrated the co-occurrence of bacterial sulfate reduction and iron reduction in coastal marine sediments. These latter results suggest that some of the observed iron reduction in Amazon shelf sediments could be related to a coupling of bacterial sulfate reduction, sulfide oxidation and iron reduction. However, net sulfate reduction appears to be of minimal importance in these sediments, based on sulfate pore water gradients and solid phase sulfur concentrations (Aller et al., 1986). Therefore, if iron and manganese reduction in these sediments are coupled to sulfate reduction and sulfide oxidation, then the complete oxidation of sulfide and other reduced sulfur intermediates (e.g.,  $S^0$ ,  $FeS$ ,  $FeS_2$ ) back to sulfate would have to occur under "almost complete anoxic (no free  $O_2$ )" conditions (Aller et al., 1986). While such sulfide oxidation reactions have been shown to occur with manganese oxides (Aller and Rude, 1988), similar reactions have not yet been demonstrated under surficial sediment conditions with iron oxides (e.g., see the discussion in Aller and Rude, 1988). Resolving these issues clearly has important implications on how iron and manganese reduction are coupled to the biogeochemical cycling of carbon and sulfur not only in Amazon shelf sediments, but in other sediments subject to similar types of physical mixing.

Finally, manganese and iron reduction in continental margin sediments may also play a role in affecting the oceanic water column distributions of these elements. In most pelagic and many continental margin sediments, the depth scales of the biogeochemical zones in Fig. 2 are such that very little (if any) of the manganese and iron produced by

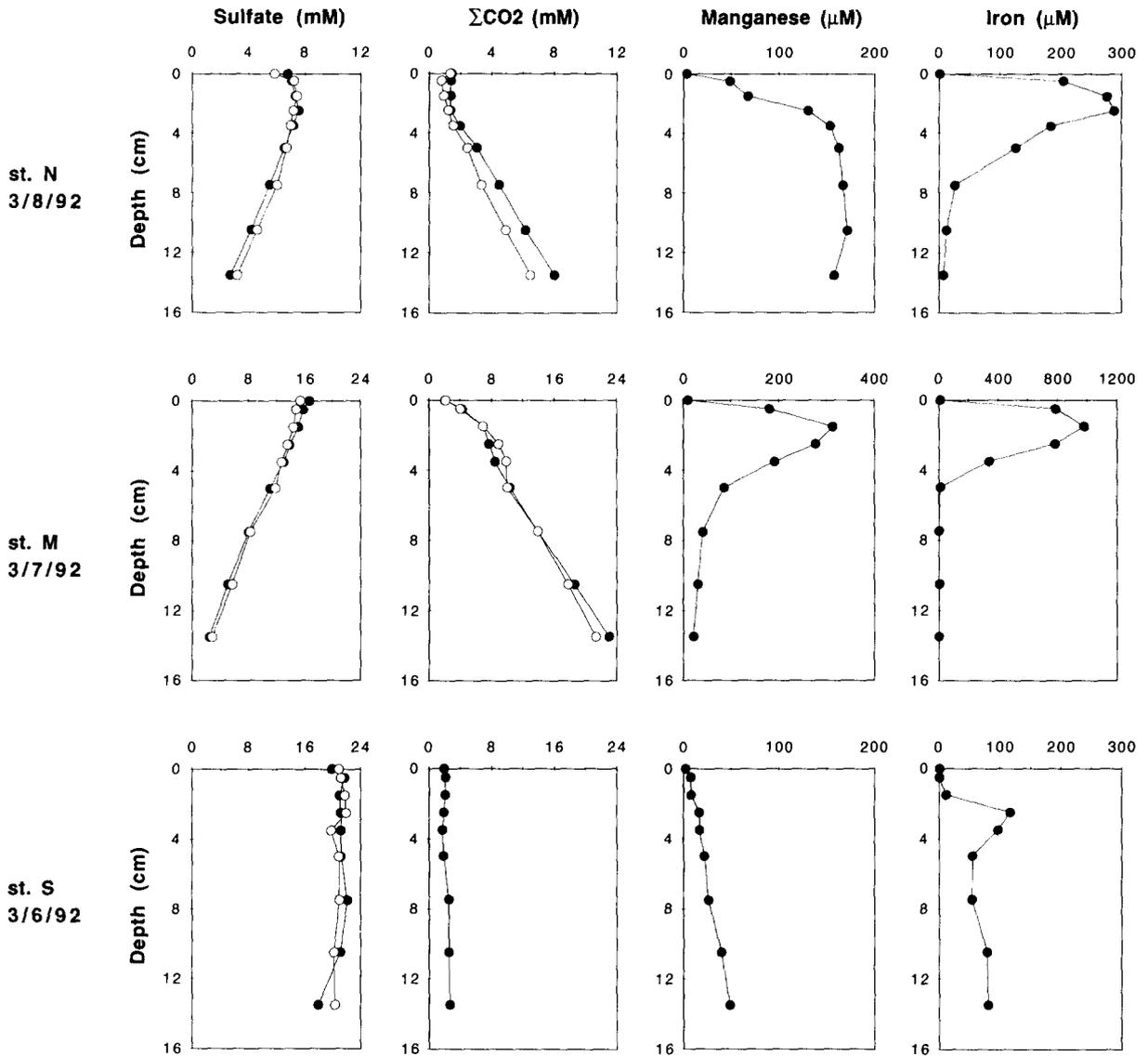


Fig. 13. Pore water profiles of: dissolved sulfate,  $\Sigma\text{CO}_2$  (total dissolved inorganic carbon), manganese and iron, all versus depth, at three sites in the Chesapeake Bay (Burdige, Homstead and Lustwerk, unpub. data). Site N is in the northern Bay and has relatively low bottom water salinities ( $\sim 3\text{--}10$  psu). These pore water profiles suggest a spatial separation between surficial zones of manganese and iron reduction and a deeper zone of sulfate reduction (below  $\sim 4$  cm). Site M is in the mesohaline portion of the Bay (bottom water salinities of  $\sim 10\text{--}20$  psu) where low oxygen or anoxic conditions generally occur in the summer months (Smith et al., 1992). The sediments at this site are highly reducing and sulfidic. These observations, along with measured rates of sedimentary sulfate reduction (Marvin and Capone, 1992) suggest that much of the manganese and iron reduction in these sediments may likely occur by sulfide oxidation. Site S is in the southern Bay (bottom water salinities of  $\sim 20\text{--}30$  psu) and has integrated annual rates of sulfate reduction that are half those of the mid-Bay region (Marvin and Capone, 1992). However these sediments are also inhabited by organisms that actively bioirrigate and mix the sediments. Evidence for this bioirrigation and sediment mixing is based on both visual observations of macrofauna in the sediments, and on the lack of significant sulfate and  $\Sigma\text{CO}_2$  pore water gradients in spite of measured rates of sedimentary sulfate reduction and  $\Sigma\text{CO}_2$  production (Marvin and Capone, 1992; Burdige, Homstead and Lustwerk, unpubl. data). Manganese and iron pore water profiles indicate the occurrence of metal oxide reduction in site S sediments, although the mechanisms by which these processes occur are unknown at the present time.

metal oxide reduction ultimately escapes the sediments. In general this occurs because the reduced forms of these metals either precipitate at depth as insoluble phases (e.g., manganese carbonates or iron sulfides), or are oxidized in the sediments upon upward diffusion. These solubility controls notwithstanding, the occurrence of an almost complete internal redox cycling of these metals is controlled by a balance between the thickness of the "oxidized" surficial zone, the downward fluxes of possible oxidants (e.g., O<sub>2</sub> diffusion), the upward fluxes of dissolved manganese and iron and the kinetics of manganese and iron oxidation.

The possibility does exist, however, that some fraction of the dissolved manganese and iron produced at depth during reductive dissolution may escape the sediments as a benthic flux. Using manganese as an example, this could occur in a situation in which the manganese redox boundary in the sediments is sufficiently close to the sediment-water interface as a result of, e.g., large organic carbon fluxes to the sediment or low bottom water oxygen concentrations. The "residence time" of the upwardly diffusing manganese in the surficial oxic sediments could then be sufficiently short, relative to the time scales (or rates) of manganese oxidation, and lead to a "leakage" of dissolved manganese through the oxic sediments to the overlying waters. Several authors have suggested that this situation may indeed occur in some continental margin sediments, and that the dissolved metals which leave the sediments as a benthic flux are then transported by cross-shelf mixing processes to the open ocean (Martin and Knauer, 1984; Heggie et al., 1987a; Landing and Bruland, 1987). These authors have further suggested that this process may play an important role in affecting open ocean water column distributions of manganese and perhaps iron.

Recent in situ benthic flux measurements in California continental margin sediments have indeed demonstrated the occurrence of manganese fluxes from these sediments

(Johnson et al., 1992). However, these authors also suggest that the sedimentary source of this dissolved manganese is not the reductive dissolution of manganese oxides, but rather is manganese remobilized near the sediment-water interface during the oxic (aerobic) remineralization of sedimentary organic matter and calcium carbonate dissolution. Furthermore, measured benthic manganese fluxes are largest from sediments in the shallowest (< 100 m) water depths, and decrease with water depth as one moves to sediments in water depths where the oxygen minimum zone in the water column impinges on the California continental shelf (600–1000 m). Such a distribution of benthic fluxes vs. water depth also appears to be inconsistent with previous suggestions for how margin sediments may act as sources of manganese to the open ocean (Martin and Knauer, 1984; Heggie et al., 1987a; Landing and Bruland, 1987). Clearly, further studies are required to determine if the observations of Johnson et al. (1992) are representative, in general, of other margin sediments. Such studies should also examine the possibility that the processes responsible for this Mn<sup>2+</sup> production near the sediment-water interface are similar to the types of "oxic" manganese reduction in pelagic sediments described by Kalhorn and Emerson (1984) and Heggie et al. (1986) (see *The role of manganese and iron reduction in the oxidation of sedimentary organic matter*, and Figs. 5 and 6).

#### MANGANESE AND IRON REDUCTION IN COASTAL, ESTUARINE, AND SALT MARSH SEDIMENTS

##### *Coastal and estuarine sediments*

Pore water profiles from coastal and estuarine sediments indicate the occurrence of manganese and iron reduction in these sediments (Holdren et al., 1975; Aller, 1980, 1993; Elderfield et al., 1981; Hines et al., 1984; Sundby and Silverberg, 1985; Sundby et al., 1986; Sørensen and Jørgensen, 1987; Can-

field, 1989a; Canfield et al., 1993 and others; also see Fig. 13). Furthermore, direct rate measurements verify the occurrence of these processes (Aller, 1980, 1993; Sørensen, 1982; Lovley and Phillips, 1987b; Aller and Mackin, 1989; Canfield, 1989a; Canfield et al., 1993; Lustwerk and Burdige, 1993). However, because sulfate reduction is generally the predominant pathway by which organic matter is oxidized in these sediments (Jørgensen, 1982; Martens and Klump, 1984; Henrichs and Reeburgh, 1987; Mackin and Swider, 1989), manganese and iron reduction are thought to play minor roles here in the oxidation of sedimentary organic carbon. At the same time though, the rates of all of these processes (e.g., sulfate, manganese and iron reduction as well as overall organic carbon remineralization) have generally not been simultaneously determined in any given sediment, precluding a definitive examination of the relative roles of these processes in overall carbon remineralization. A recent study by Canfield et al. (1993) is an exception, and in this study they observed that in certain Danish coastal sediments manganese and iron reduction can be significant processes (and in one place the only important process) by which organic matter is remineralized.

It also seems highly likely that mechanisms of manganese and iron reduction other than microbial reduction coupled to organic matter oxidation may be important in coastal and estuarine sediments. In general, pore water and rate profiles indicate that iron and manganese reduction is localized in a region quite close (i.e., within the upper few cm) to the sediment–water interface (e.g., see Fig. 13). Given typical dissolved sulfide and sulfate reduction rate profiles in such sediments, much of the manganese and iron reduction could then be mediated by abiotic chemical reactions involving dissolved sulfide (Pyzik and Sommer, 1981; Burdige, 1983; Burdige and Nealson, 1986). Manganese and iron pore water profiles also show a significant “overlap” in the zones of iron and manganese reduction, suggesting the possible im-

portance of manganese reduction via ferrous iron oxidation (Postma, 1985; Myers and Nealson, 1988b; Burdige et al., 1992). Finally, given the nature and intensity of macrofaunal activity in many of these sediments (e.g., bioturbation), oxic and anoxic processes often appear to “co-exist” in surficial sediments, since the activity of these organisms creates “a mosaic of biogeochemical microenvironments, rather than (the) vertically stratified distribution” of remineralization processes that is seen in Fig. 2 (Aller, 1982). These phenomena may then lead to a situation in which solid phase sulfides are brought into contact with manganese oxides, and under these circumstances manganese reduction may also be coupled to the oxidation of these sulfides by chemolithotrophic bacteria (Aller and Rude, 1988; King, 1990; Canfield et al., 1993).

As an example of how some of these processes may occur, a recent study of manganese cycling in Long Island Sound sediments has shown that the vast majority of the manganese reduction occurring in these sediments appears to result from sulfide oxidation, and that most of the  $Mn^{2+}$  produced by this process is internally re-oxidized by the oxygen flux into the sediments (Aller, 1993). Little  $Mn^{2+}$  escapes these sediments, much of the sediment oxygen uptake is accounted for by manganese oxidation, and overall, manganese redox cycling appears to couple sedimentary sulfide oxidation to  $O_2$  reduction (see Fig. 12; see also Burdige and Nealson, 1986). As discussed above, bioturbation plays a major role in driving these processes, in part by transporting manganese oxides and organic carbon into deeper, reduced (sulfidic) zones (Aller, 1993). Future studies in other estuarine and coastal sediments are needed to continue to resolve the role(s) of manganese (and iron) reduction in all of the redox cycles discussed above.

Because of the association of numerous trace elements (e.g., Mo, Cu, Zn, Co, As and the rare earth elements) with manganese and iron oxides (see *The chemistry of oxidized and*

*reduced manganese and iron in sediments*), sedimentary manganese and iron redox cycling may play important roles in the cycling of these elements in nearshore environments (Hines et al., 1984; Sundby et al., 1986; Westerlund et al., 1986; Sholkovitz and Elderfield, 1988). Given the close proximity of the zones of manganese and iron reduction to the sediment-water interface, these processes may then lead to benthic fluxes of these trace elements along with manganese and iron benthic fluxes (see also the previous section). Such benthic fluxes may affect the estuarine geochemistry and riverine fluxes of these elements (see references cited above and Hunt and Kelly, 1988). Similarly, many of these elements are found at elevated levels in coastal waters due to man's activities, and these concentrations may have deleterious (or "toxic") effects on coastal ecosystems. The cycling (and benthic fluxes) of these elements in conjunction with sedimentary manganese and iron reduction may therefore affect the extent to which coastal sediments represent "permanent" repositories for these elements.

Sedimentary iron redox cycling may also play an important role in the dynamics of phosphorus cycling in estuarine and coastal ecosystems. It is well documented that a significant fraction of the nutrients required for primary production in these ecosystems are supplied by the remineralization of sedimentary organic matter and their resulting benthic fluxes (Nixon, 1981; Klump and Martens, 1983). However, iron oxides strongly adsorb dissolved phosphate and remove it from sediment pore waters (e.g., Krom and Berner, 1980), and the existence of such oxides near the sediment-water interface can act as an effective trap for the upwardly diffusing phosphate produced by these remineralization reactions (Krom and Berner, 1981; Callender and Hammond, 1982; Sundby et al., 1986, 1992; Klump and Martens, 1987). In part, this leads to an increased sediment residence time for recycled phosphorus relative to recycled nitrogen or carbon (e.g., Klump and Martens, 1987), and in some ex-

treme cases the presence of these surficial iron oxides may also actually lead to a net *uptake* of phosphate by estuarine sediments (Boynton and Kemp, 1985; Garber, 1987; Burdige, 1989). This iron oxide "trapping" (or storage) of sedimentary phosphorus is not, however, always a permanent phenomena. The development of seasonal anoxia or low oxygen conditions in the bottom waters of estuarine and coastal environments such as, e.g., the mid-Chesapeake Bay (Smith et al., 1992) can cause the reduction of surficial sediment iron oxides and the release of phosphate stored "on" these oxides. This then leads temporarily to elevated phosphate fluxes from such sediments, above those predicted by pore water profiles and molecular diffusion (Cornwell and Boynton, in prep.).

It should also be noted that similar interactions between iron oxides and phosphate have been shown to occur in pelagic and hemi-pelagic sediments (Berner, 1973; Froelich et al., 1977; Morse and Cook, 1978; Filipek and Owen, 1981), and that phosphate adsorbed to these oxides may account for ~10% of the phosphorus ultimately buried in marine sediments (Froelich et al., 1982). As a result of these interactions, iron reduction in pelagic and hemi-pelagic sediments also leads to "excess" phosphate production in sediment pore waters above that predicted simply from phosphate liberation as a result of organic matter oxidation (e.g., Froelich et al., 1979). However, most of the phosphate produced in this fashion is likely retained within the sediments, given the depths at which iron reduction occurs in most pelagic and hemi-pelagic sediments (i.e., the majority of the upwardly diffusing phosphate produced during iron reduction is likely scavenged by iron oxides found in the upper, oxidized portions of the sediments). Iron reduction in these sediments therefore likely has minimal impacts on the marine phosphorus cycle.

#### *Salt marsh sediments*

Interest in iron reduction in salt marsh sediments stems in part from a recognition of

the importance of sulfur redox cycling in the overall biogeochemistry of salt marshes, and the apparent strong relationship between iron and sulfur redox cycling in these environments (Lord and Church, 1983; Giblin and Howarth, 1984; Howes et al., 1984; Cutter and Velinsky, 1988; Hines et al., 1989; Luther et al., 1991, 1992 and others). However, while iron redox cycling in salt marshes is generally assumed to be closely linked to sulfur redox cycling, Luther et al. (1992) recently presented a conceptual model which suggested that organic ligands as well as reduced sulfur compounds act as reductants of iron (III) minerals in salt marsh sediments. In their model iron reduction is presumed to be an abiotic chemical reaction, although they also suggested that bacteria and/or salt marsh plants likely produce the organic compounds that act as the reductants. Recent results also provide general support for this suggestion that the production of dissolved organic matter by salt marsh plants may play important roles in salt marsh biogeochemical processes. Based on the results of their studies, Hines et al. (1989, 1993) have suggested that the exudation of dissolved organic carbon (e.g., acetate) from the roots of salt marsh plants may account for a significant portion of the observed sulfate reduction in salt marshes during the active growing season of the plants.

In contrast to our knowledge about iron redox cycling in salt marsh sediments, much less is known of manganese redox cycling. In most salt marsh sediments total, solid phase manganese concentrations are generally much lower (up to two orders of magnitude) than those of total iron (Lord, 1980; Nixon, 1980; Luther et al., 1991), and this observation led Luther et al. (1991) to conclude that manganese redox cycling does not play an important role in iron and sulfur redox cycling in these environments. However pore water iron and manganese concentrations in salt marsh sediments are often more comparable in magnitude (Giblin and Howarth, 1984; Luther et al., 1991), suggesting the

possibility of a more dynamic manganese redox cycle in salt marsh sediments than that predicted by total solid phase concentrations alone. The conceptual model presented by Burdige and Nealson (1986) also indicated ways that manganese redox cycling could be as important as iron redox cycling in redox processes, in general, in salt marsh sediments. All of these observations suggest that more detailed work on manganese redox cycling in salt marsh sediments is needed to better resolve the role (and importance) of manganese reduction in these sediments.

#### MANGANESE AND IRON REDUCTION IN LAKE SEDIMENTS

Since many lakes undergo seasonal stratification, much of the manganese and iron redox cycling in lakes occurs in the water column, across the redox boundary which generally separates the epilimnion and the hypolimnion (e.g., Davison, 1985). However, in lakes that do not undergo such seasonal stratification, manganese and iron reduction often occurs in the sediments (Robbins and Callender, 1975; Dean et al., 1981; Davison, 1985; Sholkovitz, 1985; Cornwell, 1986; Cornwell and Kipphut, 1992; Aguillar and Nealson, 1993). As in other sedimentary systems, the mechanisms of manganese and iron reduction in lake sediments are poorly characterized. While many of the mechanisms of manganese and iron reduction observed in marine sediments likely also occur in lake sediments, the lack of significant sulfide production in most lacustrine systems (due to low sulfate concentrations) limits the importance of sulfide-mediated reduction. This then suggests that much of the metal oxide reduction in lake sediments could be coupled to organic matter oxidation, although future studies are clearly needed to verify this assumption. Manganese and iron reduction in lake sediments also appears to play important roles in the formation of lacustrine manganese nodules (e.g., Dean et al., 1981; Moore, 1981). Furthermore, as in coastal

sediments, iron redox cycling in lake sediments exerts a strong influence on the phosphorus dynamics of lake ecosystems (e.g., Emerson and Widmer, 1978; Cornwell, 1987).

## CONCLUSIONS

Manganese and iron reduction in marine sediments play important roles in the biogeochemical cycles of many elements. These reduction reactions affect these cycles on a variety of time scales, ranging from those as short as seasonal time scales (e.g., nutrient cycling in coastal ecosystems), to those as long as thousands to tens of thousands of years (e.g., glacial–interglacial transformations). In this review I have attempted to summarize the results of studies of these processes, indicate the relationships of manganese and iron reduction to other biogeochemical processes in sediments, and discuss what I believe are important areas of future research. In general, previous studies of manganese and iron reduction in sediments have taken two approaches. The first has involved studies aimed at describing the mechanisms of these processes, while the second has involved studies examining the geochemistry of these processes. Future work should emphasize the “inter-weaving” of these two approaches, thereby providing better information not only on the mechanisms of, and the controls on, sedimentary manganese and iron reduction, but also on how these reduction reactions are coupled to other sedimentary biogeochemical processes. Such information can then be used in developing more accurate and predictive models for systems in which sedimentary manganese and iron reduction occur.

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