

Mathematical models of diagenetic processes in marine sediments: iron and manganese redox cycling, and non-steady state diagenesis

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Introduction. An examination of many geochemical data sets demonstrates the importance of non-steady state (i.e., time-dependent) phenomena in affecting the early diagenesis of sediments. However, the vast majority of the models developed to study sediments generally assume steady-state conditions. While these models have had many successes in quantifying sediment processes, they also have certain limitations because of this steady-state assumption. An additional problem in many of these models are assumptions made regarding the kinetics of sediment biogeochemical reactions. For example, it is often assumed that the rate of organic matter decomposition is first order with respect to metabolizable organic carbon and independent of the electron acceptor (e.g., oxygen, sulfate) concentration. However studies clearly show that this is not an appropriate assumption under all conditions.

In this talk we will present the results of modeling studies we are currently carrying out to examine these problems. We will discuss the implications of these results on several aspects of sedimentary iron and manganese redox cycling.

The model. The model we have developed (Dhakar and Burdige, 1994a,b) is an advection/diffusion/reaction model based on those discussed in Berner (1980). The model consists of eight equations for solid phase organic carbon, manganese, iron and dissolved (pore water) oxygen, nitrate, ammonium, manganese, and iron. Because of the nature of the kinetic expressions used in the equations, the model consists of a series of coupled, non-linear differential equations that have no analytical solutions in either the steady-state or the time-dependent case. The equations are therefore solved numerically using an implicit finite difference procedure (Crank, 1975; Rabouille and Gaillard, 1991).

Molecular diffusion, advection driven by sediment accumulation and bioturbation are the transport processes included in the model. Bioturbation is assumed to be a random, diffusion-like process (e.g., Berner, 1980) which is both depth and oxygen dependent. Biogeochemical reactions included in the model

are: organic matter oxidation by oxygen, nitrate, manganese and iron oxides (i.e., oxic and sub-oxic remineralization); Fe(II), Mn(II), and ammonium oxidation by O₂; Fe(II) oxidation by manganese oxides and nitrate; ammonium oxidation by nitrate.

Results. *Steady-state manganese redox cycling and the formation of manganese rich layers in sediments.* In many marine sediments (e.g., Froelich *et al.*, 1979), a solid phase manganese peak is often observed just above the sediment redox boundary (SRB, defined here as the depth in the sediments where pore water oxygen goes to zero). Early models of manganese cycling in sediments that neglected bioturbation (e.g., Burdige and Gieskes, 1983) predicted the occurrence of this manganese peak near the SRB. However, the inclusion of bioturbation in later models (e.g., Rabouille and Gaillard, 1991) suggested that sediment mixing disperses this manganese peak, and instead leads to manganese-rich surficial sediments. In our model, we observed that such a manganese peak can form in bioturbated sediments depending on the depth zonation of bioturbation and manganese oxidation, and the depth of the SRB (which is ultimately controlled by the bottom water oxygen concentration and the magnitude of the organic carbon flux to the sediments).

Iron and manganese redox cycling, and the nature of the oxidants and reductants associated with the reactions. In most marine sediments, oxygen is assumed to be the primary oxidant of pore water manganese (Burdige, 1993). In contrast, at least in pelagic sediments, pore water iron profiles suggest that compounds other than O₂ (i.e., manganese oxides and nitrate) are likely more important oxidants of Fe(II) during sedimentary iron cycling (Burdige, 1993).

There are several possible mechanisms of manganese and iron reduction in sediments, although few studies have conclusively demonstrated the occurrence of a particular mechanism in a given sediment. These mechanisms include microbial reduction coupled to organic matter oxidation, microbial reduction coupled to sulfide oxidation (manganese oxides only), and abiotic

(chemical) reduction by compounds such as sulfide, nitrite, Fe(II) (manganese oxides only), and certain organic compounds (see references in Burdige,1993).

Manganese reduction is generally considered less efficient than denitrification (i.e., nitrate reduction), although there can be a certain degree of overlap between both the energetics of these processes, and their depth zonation in sediments (Burdige,1993). In addition, pore water data sometimes suggest the possibility of overlap between the zones of manganese and iron reduction. However, Fe(II) is known to chemically reduce both nitrate and manganese oxides (Burdige,1993), and these reactions may contribute to the appearance of a more distinct boundary between the zones of iron reduction and other sub-oxic processes.

In many pelagic and hemi-pelagic sediments, the apparent upper boundary of the iron reduction zone occurs below the manganese reduction zone and at the depth of complete nitrate removal (i.e., below the zone of denitrification). While this observation is consistent with thermodynamic arguments (e.g., Froelich *et al.*,1979), the exact mechanism by which iron reduction is inhibited by the presence of electron acceptors such as nitrate and manganese oxides is unclear. These electron acceptors may directly inhibit microbial iron reduction in a way similar to that in which O₂ inhibits sub-oxic remineralization processes. It is also likely that microbial iron reduction may occur concurrently with denitrification and microbial manganese reduction. However, because of reactions between ferrous iron and manganese oxides and nitrate, any Fe(II) produced by iron reduction in the presence of manganese oxides or nitrate will be re-oxidized back to iron(III) oxides, rather than accumulate in the pore waters. The lack of linear pore water Fe(II) profiles through the zones of manganese reduction and denitrification provides evidence in support of reactions between ferrous iron and manganese oxides and nitrate, and for the fact that the oxidant of the upwardly diffusing Fe(II) is likely not oxygen but is either manganese oxides or nitrate.

In our model we assumed that denitrification, manganese and iron reduction can all co-occur, although the inclusion of chemical reactions between Fe(II) and manganese oxides and nitrate leads to a spatial separation between the zone of net iron reduction and other sub-oxic remineralization processes. In our model results Fe(II) did not accumulate in pore waters in the presence of nitrate and manganese oxides (as is generally observed in field data), and the net iron reduction in the zones of manganese reduction and denitrifica-

tion was essentially zero. At the same time, the occurrence of these reactions in sediments has not been demonstrated, although they have important implications on the dynamics of carbon oxidation and metal redox cycling in sediments.

Non-steady state manganese redox cycling. A common observation in many pelagic and hemipelagic sediments is the presence of multiple manganese peaks. Such peaks are observed over a variety of depth and time scales, and can have important paleoceanographic significance (see the discussion in Burdige,1993). Under steady-state conditions only one manganese peak should be observed in sediments (Burdige and Gieskes,1983; also see above), and the existence of multiple peaks has been attributed to non-steady state conditions. In the simplest sense, this may result from the net migration (relative to the sediment-water interface) of the SRB, since under steady-state conditions the SRB moves upwards at a rate equal to the sedimentation rate and remains at a fixed depth in the sediments. The depth of the SRB will increase with time (i.e., occur at deeper depths) if, for example, bottom water oxygen concentrations increase or the flux of organic carbon to the sediments decreases. Similarly, the depth of the SRB will decrease if these quantities change in the opposite direction (Burdige,1993).

In recent work we have modified our steady-state model to examine such time dependent situations. Preliminary work has involved model runs in which either bottom water oxygen concentrations or the flux of organic carbon to the sediments are instantaneously changed in ways that, under steady-state conditions, should lead to a several cm shift in the depth of the SRB. We observed that it takes several hundred to thousands of years for the SRB to adjust to such external changes. The apparent sluggishness of sediments to respond to these changes appears to be related to the fact that the reservoir of organic carbon in the mixed (bioturbated) layer of the sediment acts to dampen the rate of upshift or downshift of the SRB. Under certain circumstances, these changes can also lead to the in-growth, on similar time scales, of a second manganese peak in the sediments. However, the ways in which this occurred were slightly different than those described in previous qualitative models proposed to explain the formation of multiple manganese peaks in sediments (e.g., Burdige,1993). Current work with our model involves more detailed studies aimed at quantitatively examining these previous models, along with studies examining specific geochemical data sets that suggest the occurrence of non-steady state manganese cycling (e.g., Froelich *et al.*,1979; also see Burdige,1993).