

**A model of suboxic sedimentary diagenesis suitable for automatic tuning and  
gridded global domains**

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Manuscript and working model available on-line at

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## Abstract

We present a new model for oxic and anoxic diagenesis of shallow and deep-sea sediments based on an efficient solver for steady state pore water and solid phase diffusion/reaction/advection equations. The model, called "Muds", is orders of magnitude faster than solvers of the corresponding time-dependent equations. The model resolves Mn and Fe/S geochemistry as well as pore water pH and  $\text{CaCO}_3$  dissolution. The model speed opens application possibilities that are impossible for time-dependent models, including automatic tuning of uncertain parameters, and deployment of the model in gridded global domains.

The kinetic rate constants for respiration and bioturbation are parameterized as functions of the organic carbon rain to the sea floor, based on existing parameterizations in the literature. Seven uncertain model parameters, including many of the rate constant parameterizations, were tuned to minimize the misfit to observations from 53 sedimentary locations throughout the ocean. The model tuning knobs were the fractions of labile and refractory organic matter in the sedimenting material, the  $\text{NO}_3^-$ , Mn, Fe, and S respiration rate constant parameterizations, and the depth scales of respiration and of pore water irrigation. We searched for adequate fit values of these parameterizations using a simulated annealing method. The cost function (degree of misfit) was based on a comparison of pore water ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ) and solid phase (organic carbon and  $\text{MnO}_2$ ) model results with data. Many of the tuning parameters are constrained to  $\pm 50\%$  or better. The model is most skillful at predicting organic carbon concentration, depth of  $\text{NO}_3^-$  penetration, and pore water  $\text{Fe}^{2+}$ , and less so for  $\text{Mn}^{2+}$ ,  $\text{NH}_4^+$ , and solid phase  $\text{MnO}_2$ . The model misses some of the very high sediment surface  $\text{MnO}_2$  concentrations observed in, for example, the California Borderlands. We believe that these sites must receive a higher input of reactive Mn than the crustal abundance of the clay rain.

The model was deployed on every  $2^\circ \times 2^\circ$  gridpoint below 1000 m of the global sea floor, using gridded maps of organic carbon rain to the sea floor and overlying water chemistry. The deep sea carbon burial efficiency is 7%, with 95% of respiration by oxic metabolism. The model was also run against a new depth/oxygen hypsometry of the global ocean, with sediment area as a function of overlying oxygen concentration and average depth related to carbon fluxes, to include the effects of shallow water sediments. This analysis predicts that shallow waters (< 1000m) account for 88% of respiration, and oxygen accounts for 66% of respiration overall. Denitrification is closely coupled to organic nitrogen fluxes to the sediment, and the global rate is estimated to be  $1.4 \cdot 10^{14}$  mol yr<sup>-1</sup>, a factor of 6-8 higher than the corresponding estimate from Middelberg (1996), throwing the nitrogen cycle in the ocean into imbalance.

## **Introduction**

Oxidation/reduction chemistry of sediment is an integral part of the global carbon cycle, serving both as an indicator and as a player in processes that affect the  $PCO_2$  of the atmosphere. Many proposals for lowering  $PCO_2$  during glacial time invoke a more vigorous biological pump (Archer and Maier-Reimer, 1994; Archer et al., 2000; Broecker and Henderson, 1998; Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984), stimulated perhaps by an increase in iron deposition to the ocean surface (Mahowald et al., in press; Martin and Fitzwater, 1988; Peteet et al., 1990) or an increase in the global ocean inventory of  $NO_3^-$  (Broecker and Henderson, 1998; McElroy, 1983).

The biological pump may further affect atmospheric  $PCO_2$  indirectly by the mechanism of  $CaCO_3$  compensation, which controls the pH of the ocean (Archer and Maier-Reimer, 1994; Archer et al., 2000; Broecker and Peng, 1987). Oxic organic carbon respiration in sediments liberates carbon in the form of dissolved  $CO_2$ , acidifying the pore water and provoking the dissolution of  $CaCO_3$  (Emerson and Bender, 1981). The effect of suboxic

and anaerobic respiration on pore water pH is more complicated than for oxic respiration, but in general these reactions have the opposite (and perhaps a smaller) effect on pH and therefore  $\text{CaCO}_3$  preservation than oxic respiration (Berner et al., 1970; Canfield, 1989). The dominant suboxic electron acceptor in the redox conditions of the abyss, for example, is  $\text{NO}_3^-$ , which produces mostly  $\text{HCO}_3^-$ . Models of the  $\text{PCO}_2$  response to the strength of the biological pump must therefore consider the preservation of  $\text{CaCO}_3$  as a function of sediment redox chemistry (Archer et al., 2000).

Sinking organic matter carries with it an associated oxygen demand, such that an increase in biological sequestration of  $\text{CO}_2$  in the deep sea will be associated with a corresponding decrease in deep-sea oxygen (Sarmiento and Orr, 1991). The oxygen concentration beneath the sediment surface, recorded by sedimentary redox tracers, is determined by two factors, both of which can be affected by changes in the strength of the biological pump. One is the overlying water oxygen concentration, serving as the upper boundary condition for sedimentary diagenesis. The other is consumption within the sediment, determined by the balance between the downward fluxes of organic carbon vs. dissolved oxygen.

Many sedimentary redox tracers, such as manganese, organic carbon, and trace metals, cycle through geologic time, often correlated with global climate (Berger et al., 1983; Calvert and Padersen, 1993; Crusius et al., 1996; Dean et al., 1994; Dean et al., 1997; Francois, 1993; Nameroff, 1996; Rosenthal et al., 1995). The problem which invariably plagues studies of paleo sediment redox state is quantitative interpretation: Was the change in sediment chemistry caused by organic carbon rain to the sea floor, overlying water oxygen concentration, or both? For example, high concentrations of authigenic uranium found in Southern Ocean sediments might indicate either a stronger Southern Ocean biological pump (Anderson et al., 1998) or a poorly ventilated Southern Ocean (Francois et al., 1998). Morford and Emerson (1999) argue, based on global metal mass balances and V and Cd

concentrations observed in foraminifera, that the area of reducing sediments, where  $O_2$  penetrates less than 1 cm, cannot have more than doubled in the past 40,000 years. Again, however, their constraint reflects a combination of organic carbon rain and deep sea oxygen concentration.

We present a new sediment redox diagenesis model called Muds (just a name, not an acronym). Muds belongs to an efficient class of sediment diagenesis models which use relaxation methods to iterate to steady state solutions (Archer et al., 1993; Archer, 1991; Martin and Sayles, 1990; Soetaert et al., 1996). These methods reach the steady state orders of magnitude faster than time-dependent models can. Muds takes less than a minute to solve for pore water and solid phase steady state in the upper meter of the sediment. It is possible to use relaxation models in ways which are more difficult for time-dependent models, such as automatic tuning (Soetaert et al., 1996) and application to large gridded global domains (Archer, 1996b; Archer et al., 2000). Muds is the first of this class of models to resolve the suboxic manganese, iron, and sulfur redox systems. Pore water constituents include  $O_2$ ,  $NO_3^-$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $NH_4^+$ ,  $CO_3^{=}$ ,  $H_4SiO_4$ , and the solid phase includes two phases of organic carbon,  $MnO_2$ ,  $FeOOH$ ,  $CaCO_3$ ,  $SiO_2$ . The behavior of redox trace metals such as authigenic  $UO_2$  within Muds is described by Morford (1999) and will be published separately.

The rate constants for biologically mediated processes such as respiration and bioturbation are site-specific in the real ocean, generally correlated with overall sediment respiration or accumulation rate. We have attempted to generalize the model by parameterizing many of these rate constants as functions of the sediment respiration rate. These parameterization functions are tuned using automatic methods to minimize the misfit to a data set from 53 locations throughout the Atlantic and Pacific slope and abyss. Using these tuned parameterizations, we drive the model with gridded seafloor data (as (Archer, 1996b)) and predict global respiration and burial rates.

## Model Formulation

The Muds model is based on the steady-state diffusion / reaction equations for pore water and solid sediment. The model equations and reaction kinetics are similar to previously published sedimentary diagenetic models (Archer, 1991; Burdige and Geiskes, 1983; Cappellen and Wang, 1996) and are given in Table 1. Two types of organic carbon rain to the sea floor and react initially with  $O_2$  in the pore waters (Berner, 1980).  $NO_3^-$  serves as an electron acceptor below the depth where  $O_2$  is depleted. In this zone, solid  $MnO_2$  is also used as an electron acceptor for respiration, producing dissolved  $Mn^{2+}$ , which can precipitate to  $MnO_2$  in the oxic zone or  $MnCO_3$  at depth. Below the depth where  $NO_3^-$  is depleted  $SO_4^{2-}$  and solid  $FeOOH$  are used as electron acceptors, producing dissolved  $Fe^{2+}$  and  $HS^-$  which can either precipitate as  $FeS$  or diffuse to the oxic zone. Bioturbation can also expose solid  $FeS$  to oxidation. Irrigation of the pore water is simulated as a depth-dependent exchange with the overlying water, with an exchange rate parameterized as a function of organic carbon rain. Surface-active species such as  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $NH_4^+$ , and  $H^+$  can be adsorbed onto solid phases and transported by bioturbation or advection. Other solid phases include  $CaCO_3$  and  $SiO_2$ , which dissolve using first order dissolution kinetics, and nonreactive clay. The model does not currently simulate time-dependent behavior, such as the generation of relict manganese layers (Berger et al., 1983; Schmitz et al., 1999).

**Differential equations.** The equation for a pore water solute concentration,  $c$ , is

$$\phi \frac{\partial c}{\partial t} = 0 = \frac{\partial}{\partial z} \left( \frac{D_c}{F} \frac{\partial c}{\partial z} \right) + I_z (c_0 - c) + \frac{\partial}{\partial z} \left( D_B \frac{\partial c_{ads}}{\partial z} \right) - \Omega \frac{\partial c_{ads}}{\partial z} - J_c \quad (1)$$

where  $\phi$  is porosity,  $D_c$  is the diffusion coefficient for solute  $c$ ,  $F$  is the formation factor of the sediment (how much the solid matrix slows down diffusion), and  $z$  is depth (positive downwards).  $I_z$  is a depth-dependent irrigation coefficient with units of inverse time.

Adsorbed solute,  $c_{\text{ads}}$ , assuming equilibrium, is transported by bioturbation (using solid mixing rate  $D_B$ ) and burial ( $\Omega$ ); the divergence of  $c_{\text{ads}}$  is treated as a source or sink for  $c$ .  $J_c$  is the reaction rate, described below. The solid species are governed by the equation

$$(1 - \phi) \frac{\partial \%S}{\partial t} = 0 = \frac{\partial}{\partial z} \left[ D_B (1 - \phi) \frac{\partial \%S}{\partial z} \right] - \Omega \frac{\partial \%S}{\partial z} - J_S \quad (2)$$

where the units of the solid concentration,  $S$ , is g/g dry weight.  $D_B$  is the depth dependent solid diffusion (bioturbation) rate, and  $\Omega$  is the rate of sediment burial. In both types of equation, the time dependent terms equal zero, indicating that we seek the steady state profiles of all solid and pore-water constituents. The top boundary condition for solutes is the overlying water concentration, and for solids, the sediment rain rate. A condition of no gradient is imposed at the bottom boundary for all constituents.

**Discret equations.** The model is discretized on a 17-depth grid. The cell thickness ranges from 0.05 cm at the sediment surface to 35 cm in the deepest box, reaching a depth ( $z$ ) span of 100 cm. (In the discretized diffusion equation, the diffusive flux of oxygen can be no greater than

$$Flux_{\text{max}} = D \frac{\partial O_2}{\partial z} = D \frac{O_{2\text{bottom water}}}{\Delta z_{\text{top}}} \quad (3)$$

Thus  $\Delta z_{\text{top}}$ , the thickness of the top box, sets an upper limit on the diffusive flux of oxygen across the sediment-water interface. Fine grid spacing is desirable, but in time dependent models,  $\Delta z$  limits the time step, making detail in this region expensive to resolve. The relaxation method faces no such restriction.) Concentrations are defined in the box centers, burial rates at the cell bottoms. The model seeks the condition where fluxes across the cell boundaries are balanced against reaction rates within each box.

The model consists of a series of depth-dependent difference equations. These equations, one for each chemical species in the pore water or solid phase, are tightly and non-linearly coupled to each other by dissolution or precipitation reaction rates (for example, there is coupling between O<sub>2</sub> and organic carbon). In addition, the solid phases are all indirectly coupled to each other by solid phase advection, which is determined by the sum of the dissolution reaction rates, all of which depend in nonlinear ways on solid and solute concentrations. We attack this tangled mess of equations by successive approximation using a gradient-descent (Newton's) method.

One possible approach (which would be interesting to try as it might be faster) would be to simultaneously relax all concentration values at all depths (a linear algebra problem of  $n_z \times n_{\text{solvents}} \times n_{\text{solutes}}$  equations, in our case 3,332). We chose instead the strategy of separating the systems numerically wherever possible. The iteration proceeds in stages; first each pore water profile is iterated to steady state given the current guess for the solid phase profiles. Then the solid phase profiles are iterated a few times using the new reaction rates calculated from the pore water chemistry. For the systems Mn<sup>2+</sup>/MnO<sub>2</sub>/MnCO<sub>3</sub> and FeOOH/Fe<sup>2+</sup>/HS<sup>-</sup>/FeS, special steps had to be taken to reach solution; these will be described below.

For a solute  $c_i$  in box  $i$ , the model calculates the imbalance in the fluxes of the species ( $R_i$ ) as

$$\begin{aligned}
 R_i = & \frac{D_M}{\Phi_i \Delta z_i} \left( \frac{F_{i+1} + F_i}{\Delta z_{i+1} + \Delta z_i} (c_{i+1} - c_i) - \frac{F_i + F_{i-1}}{\Delta z_{i+1} + \Delta z_i} (c_i - c_{i-1}) \right) \\
 & + \frac{D_{B_{i+1}}}{\Delta z_i} \frac{2}{\Delta z_{i+1} + \Delta z_i} (c_{\text{ads}_{i+1}} - c_{\text{ads}_i}) - \frac{D_{B_{i-1}}}{\Delta z_i} \frac{2}{\Delta z_{i-1} + \Delta z_i} (c_{\text{ads}_i} - c_{\text{ads}_{i-1}}) \\
 & - \left( \Omega_{i-1} c_{\text{ads}_{i-1}} - \Omega_i c_{\text{ads}_i} \right) \frac{\Phi_i \rho_{\text{solid}}}{(1 - \Phi_i) \Delta z_i} + I_z (c_0 - c_i) + J_i
 \end{aligned} \tag{4}$$

where  $D_{B_i}$  and  $\Omega_i$  are defined at the bottom of box  $i$ ,  $\rho_{\text{solid}}$  is the dry density of solid material (2.5 g cm<sup>-3</sup>), and everything else is as defined above. For a solid, the residual  $R_i$  is calculated

$$R_i = \frac{1}{\Delta z_i (1 - \Phi_i)} \begin{pmatrix} D_{B_{i+1}} \frac{2(2 - \Phi_{i+1} - \Phi_i)}{\Delta z_{i+1} + \Delta z_i} (s_{i+1} - s_i) \\ -D_{B_i} \frac{2(2 - \Phi_i - \Phi_{i-1})}{\Delta z_i + \Delta z_{i-1}} (s_i - s_{i-1}) \\ -\frac{\Omega_{i+1}}{\rho_{\text{solid}}} s_{i+1} - \frac{\Omega_i}{\rho_{\text{solid}}} s_i + J_i \end{pmatrix} \quad (5)$$

The steady state solution is where all  $R_i=0$  for all species at all depths. The next guesses for each  $c_i$  and  $s_i$  are determined by a gradient-descent, or Newton's, method for finding the zero to a function. For an analogous one-dimensional system, we seek  $x$  such that  $f(x)=0$ . From an initial guess  $x$  we compute the next guess,  $x+\Delta x$ , as the zero intercept of the tangent to  $f(x_i)$

$$\Delta x = -f(x_i) \left( \left. \frac{\partial f}{\partial x} \right|_{x_i} \right)^{-1} \quad (6)$$

In the multidimensional system,  $n$  equations representing  $n$  boxes are solved simultaneously

$$\mathbf{J}(R, c) \cdot \Delta \mathbf{x} = -\mathbf{R} \quad (7)$$

where the Jacobian  $\mathbf{J}$  is a matrix of  $\partial R_i / \partial c_j$ , and  $\Delta \mathbf{x}$  and  $\mathbf{R}$  are vectors over all grid boxes  $i$ . The boundary conditions are built into the system of equations by modifying  $R_i$  in the sediment surface and deepest boxes to include diffusive flux or sediment rain at the top or zero diffusive flux at the bottom.

**Treatment of Monod kinetics.** Several chemical systems within the model are treated with zero-order "Monod" kinetics, where the reaction rate is independent of substrate concentration (zero order) as long as the concentration exceeds some critical value, but the reaction is forbidden when the reactant drops below that value (Devol, 1978; Postma and

Jakobsen, 1996). Taking oxygen as an example, in oxygenated sediments the consumption rate is

$$\text{rate} = k [\text{OrgC}] \quad (8)$$

but oxygen consumption ceases in anaerobic sediments. The rate constant  $k$  is therefore discontinuous across the anoxic boundary. We solve this type of system by iterating in this example  $z_{\text{oxic}}$ , the depth of oxygen penetration, to generate a reasonable oxygen profile. The rate within a grid box is proportional to the depth fraction of the box that is above the depth of oxygen penetration,  $z_{\text{oxic}}$  (implicitly assuming that organic carbon is well mixed within the box). The correct value for  $z_{\text{oxic}}$  produces the physically realistic solution with a non-negative concentration and zero flux at the bottom boundary,  $z_{\text{max}}$ . If the current guess for  $z_{\text{oxic}}$  is too deep, the no-flux condition requires a negative concentration at  $z_{\text{max}}$ . The next guess for  $z_{\text{oxic}}$  should be shallower. In oxygen-unlimited conditions, the correct solution is  $z_{\text{oxic}} = z_{\text{max}}$ . Similar tests and strategies are employed for the penetration depth of  $\text{NO}_3^-$ ,  $\text{MnO}_2$ , and  $\text{FeOOH}$ .

**Solute adsorption.** Steady state concentration profiles of several of the solutes need to be adjusted for adsorption onto solid surfaces. Adsorption may dominate the inventories of the surface active solutes in Muds:  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{NH}_4$ , and  $\text{H}^+$ . However, in the steady state, the salient comparison is not between the concentrations but rather between the vertical fluxes of adsorbed versus pore water solute. In the limit of no solid phase transport, where the only way to move  $\text{Fe}^{2+}$  for example is to diffuse it within the pore water, the pore waters will relax to the same concentration profile in the steady state regardless of adsorption. Adsorption alters the steady state pore water concentrations only insofar as vertical mixing or advection of the solid phase acts as a source or sink of solute. Given a current guess for the concentration of solute in the pore water, the model calculates the concentration of

adsorbed species assuming equilibrium,  $c_{ads}$  in equation 4, following (Wang and Cappellen, 1996). The vertical fluxes are then computed from the adsorbed concentration profile and the solid phase mixing and burial (advection) rates. Similarly, dissolved boron and protons diffuse in the pore waters, generating a source for alkalinity in the carbon chemistry routine, based on (Archer, 1991).

**Pore water irrigation.** In shallow-water sediments, it is observed that solute transport to the overlying water is enhanced by the action of benthic animals (Aller, 1980; Archer and Devol, 1992; Jorgensen and Revsbech, 1985). We simulate this process as a non-local fluid exchange between pore and overlying waters (Boudreau, 1984; Emerson et al., 1984). The highly reactive solutes  $Fe^{2+}$  and  $Mn^{2+}$  are assumed to oxidize to their solid forms, either at depth in the sediment or at the sediment surface, depending on the relative concentrations of oxidizers in the overlying water and reductants in the pore water, rather than escaping to the overlying water in dissolved form.

**Solute/solid coupling.** The reaction rates of the solid phases depend heavily on the pore water chemistry, for example oxic respiration depends on  $z_{oxic}$ , and calcite dissolution depends on  $CO_3^{=}$ . The model iteration scheme alternates between the solute and solid phase systems, seeking a coupled solution to both. Within each cycle, the solute profiles are relaxed completely to steady state, based on the current guess of the solid phase concentrations. Then the solid phases undergo 10 relaxation passes using the reaction rates calculated from the solute system, before returning to the solute routines. The solute and solid systems are coupled using a reaction rate "mail trolley" scheme which carries reaction rates from the subroutine where they are calculated (the oxygen routine, in this case) to the subroutine in which they are used (organic carbon). The mail trolley passes to each subroutine in the cycle, so that, for example,  $Mn^{2+}$  oxidation can contribute to the consumption of  $O_2$  on the next pass of the cycle, without requiring the  $O_2$  subroutine to know anything about  $Mn^{2+}$  chemistry.

Convergence is based on conservation of mass to within 2% for all solid phase and dissolved constituents (appropriate balances between rain, reaction, diffusion, and burial rates). Also, the sum of the solid phase concentrations provides a convergence diagnostic. Although the solid phase dry weight fractions initially total to 1 g/g, as the computation progresses they deviate, generally within the range of 0.5 - 1.5 g/g, then converge back toward a physically reasonable value of 1 g/g. Typically the model reaches convergence defined in these ways within 50-100 iterations.

### *Metal Subsystems*

The coupling between solid and dissolved species in the Mn and Fe cycles was found to be too intimate to allow their separation into isolated solid and pore water subroutines. Instead we combine the Mn species  $\text{Mn}^{2+}$ ,  $\text{MnO}_2$ , and  $\text{MnCO}_3$  into a manganese subroutine, and the Fe species  $\text{Fe}^{2+}$ ,  $\text{FeOOH}$ ,  $\text{FeS}$ ,  $\text{SO}_4^{2-}$ , and  $\text{HS}^-$ , into an iron subroutine. Each subroutine returns the steady state profiles for all the solid and dissolved profiles. The residuals for all species are computed simultaneously, and cross-term derivatives such as  $\partial R_{\text{MnO}_2} / \partial \text{Mn}^{2+}$  are included in the Jacobian matrix for computing the next guess concentrations. Manganese and iron respiration are first order in organic matter and zero order in oxide above the depth of oxide depletion. Currently sulfate depletion is not expected or allowed for.  $\text{MnCO}_3$  precipitation is first-order in  $\text{Mn}^{2+}$  concentration above an assumed saturation value of 150  $\mu\text{M}$ , and for simplicity independent of  $\text{CO}_3^{=}$  concentration.

$\text{FeS}$  precipitation is first order in both  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$ , with a rate constant of  $10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ .<sup>1</sup> Faster  $\text{FeS}$  precipitation kinetics would be more realistic, but numerically intractable by these methods. Our formulation has the desired property that generally either  $\text{Fe}^{2+}$  or  $\text{HS}^-$  is dominant in pore water while the concentration of the other is low enough that diffusive transport is negligible. Therefore we expect that the steady state concentration of the major constituent, generally  $\text{Fe}^{2+}$ , will be similar to what it would be if  $\text{FeS}$  precipitation kinetics

were faster. The algorithm is able to switch over smoothly from one regime to the other as the boundary conditions change.

$Mn^{2+}$  and  $Fe^{2+}$  oxidize quickly in the presence of  $O_2$  or  $NO_3^-$ , respectively, to yield the solid oxide forms. Estimates of the  $Mn^{2+}$  lifetime in an oxic water column range from 0.9-69 days (Wehrli et al., 1994), to as short as a few hours in surface sediments (Thamdrup et al., 1994). Iron oxidation lifetimes may be only a few minutes (Sung and Morgan, 1980). When we incorporated oxidation reactions into the residuals for dissolved and oxide forms of Mn and Fe, we found that the relaxation method does not converge unless the oxidation kinetics were slowed unacceptably. Instead, we adopted the following simplification. The concentration of dissolved metal within the oxic zone can be approximated by the equation

$$\frac{\partial m}{\partial t} = 0 = D \frac{\partial^2 m}{\partial z^2} - \lambda m \quad (9)$$

where  $D$  is a depth-independent diffusion coefficient and  $\lambda$  is a time constant for metal oxidation. The analytical solution to this equation is an exponential dropoff of the concentration  $m$  with height above the oxic boundary,  $z_{oxic}$ .

$$m(z) = m_{z_{oxic}} e^{-\sqrt{\frac{\lambda}{D}}(z_{oxic}-z)} \quad (10)$$

where  $m_{z_{oxic}}$  is the concentration of  $m$  at the oxic boundary  $z_{oxic}$ . The total rate of  $m$  oxidation can be calculated by integrating

$$\sum oxidation = \int_{z_{oxic}}^{-\infty} \lambda m dz = \sqrt{D \lambda} m_{z_{oxic}} \quad (11)$$

Since both  $D$  and  $\lambda$  are known at the outset,  $m_{z_{oxic}}$  can be determined by balancing the oxidation sink (or equivalently diffusion to the overlying water) against net production.

Determining  $m_{\text{oxic}}$  therefore completely specifies the concentration profile of  $m$  throughout the oxic zone.

Our scheme, which allows us to solve for fast oxidation kinetics, replaces the full treatment of transport and reaction in the calculation of the residuals for dissolved  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  (as in equation (4), above) with simple relaxation toward the concentration  $m$

$$R_{\text{Mn}^{2+}_i} = \text{Mn}_i^{2+} - m_i \quad (12)$$

### Tuning to Field Data

Various uncertain model parameters, such as kinetic rate constants, were tuned to optimize the fit to a 53-site data set compiled by *Morford* (1999), listed in Table 2. A plot of overlying water oxygen concentration vs. the rain of organic matter in Figure 1 serves as a cross-reference between the data listing in Table 2 and the model comparison plots presented below. The total flux of organic carbon is estimated from sediment respiration rates, or based on flux chambers or oxygen microelectrode profiles corrected for organic carbon burial. Overlying water  $[\text{O}_2]$  were taken from the *Levitus* (1993) annual mean data set when necessary. Overlying water  $[\text{NO}_3^-]$  were estimated from an empirical correlation of deep-water GEOSECS  $\text{NO}_3^-$  to  $\text{O}_2$  concentrations (Figure 2a), and clay accumulation rates were estimated from correlation with organic carbon rain in the dataset (Figure 2b).

The model was ground-truthed and tuned to these data using sediment rain rates (most importantly, organic carbon) and overlying water chemistry (most importantly, oxygen) as driving conditions. Model and data concentrations of organic carbon,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{HS}^-$ , the total (labile + refractory) particulate Mn were compared at 12 cm depth, along with sediment surface Mn and the depth of  $\text{NO}_3^-$  penetration. These comparisons were each normalized to the variance of the data and model output, and combined into a cost function

which we used to evaluate the overall model fit to data. Details of the cost function are given in the Appendix.

### *Parameterizations of Biologically Mediated Kinetics*

Rate constants for biologically mediated processes such as organic carbon respiration and bioturbation have been shown to co-vary in the natural world with water depth (Middelburg et al., 1997), sedimentation rate (Boudreau, 1994; Tromp et al., 1995), and organic carbon rain (Emerson, 1985). Organic carbon deposition is the energy source for benthic metabolism, and is a straightforward number to extract from ocean carbon cycle models. Therefore we based the parameterizations of biologically mediated kinetics on the organic carbon rain rate.

The rate of bioturbation at the sediment surface,  $D_{B_0}$ , was parameterized as a function of sediment accumulation rain by *Boudreau* (1994). We converted his parameterization to one based on organic carbon rain using the empirical relation between carbon and sedimentation from *Tromp* (1995), resulting in

$$D_{B_0} \left[ \frac{\text{cm}^2}{\text{yr}} \right] = 0.0232 \left( \text{Rain}_{\text{OrgC}} \left[ \frac{\mu\text{mol}}{\text{cm}^2 \text{yr}} \right] \right)^{0.85} \quad (14)$$

We attenuate the bioturbation rate with depth (from *Martin and Sayles* (1990)), and with overlying water oxygen concentration, as

$$D_B = D_{B_0} \times e^{-\left(\frac{z}{z_{\text{mix}}}\right)^2} \times \frac{[O_{2\text{BW}}]}{[O_{2\text{BW}} + 20\mu\text{M}]} \quad (15)$$

where the depth scale for bioturbation,  $z_{\text{mix}}$ , is taken to be 8 cm (*Martin and Sayles*, 1990) and the final factor attenuates bioturbation in low-oxygen conditions, with a half-saturation constant of 20  $\mu\text{M}$   $\text{O}_2$ .

The rate of pore water irrigation is based on comparisons of diffusive (microelectrode) and total (chamber) oxygen fluxes across the sediment water interface (Archer and Devol, 1992; Glud et al., 1994; Reimers et al., 1992) (Figure 3). In these locations O<sub>2</sub> penetrates only a few millimeters into the sediments, so the excess O<sub>2</sub> flux measured by the chamber is assumed to consist of an exchange of bottom water with anoxic pore water. Irrigation intensity correlates nicely with organic carbon rain, with the possible exception of low-O<sub>2</sub> environments; three out of four locations where O<sub>2</sub> < 30 μM showed anomalously high irrigation intensity. We parameterized irrigation intensity as

$$I_0 = 11 \left[ \frac{a \tan\left(5 \frac{Rain_{oc} - 400}{400}\right)}{\pi} + 0.5 \right] - 0.9$$

$$+ 20 \frac{O_{2_{BW}}}{O_{2_{BW}} + 10} e^{\left(\frac{-O_{2_{BW}}}{10}\right)} \frac{Rain_{oc}}{Rain_{oc} + 30}$$
(16)

where the first two terms of the right hand side generalizes the high O<sub>2</sub> conditions (solid line, Figure 3a), and the third term modifies the high O<sub>2</sub> result for low O<sub>2</sub> conditions (Figure 3b). The depth distribution of irrigation is assumed to follow a functional form

$$I(z) = I_0 e^{-\left(\frac{z}{z_{irrig}}\right)^2}$$
(17)

with the depth scale,  $z_{irrig}$ , selected by the tuner to be  $1.8 \pm 1$  cm (Table 3). This value is shallower than the 4 cm depth scale implied by <sup>222</sup>Rn measurements (Smethie et al., 1981) and used in a model of the Danish sites (Wang and Cappellen, 1996).

Organic carbon respiration is complicated by a range of organic carbon reactivities and by various electron acceptors. Model fits to data are improved when the organic carbon is

divided into fractions with different reactivities (Berner, 1980). In a steady state model, the salient impact of the degradation lifetime is the depth of organic carbon reaction. Fast degradation confines carbon to the sediment surface, while slower kinetics allow mixing to distribute carbon to deeper levels, where its effect on pore water chemistry will be stronger (Emerson and Bender, 1981). The depth distribution of oxic respiration can be estimated directly from oxygen microelectrode data, and appears to be consistent across a range of organic carbon rain rates [*B. Hales, personal communication, 1999*]. Hales finds that oxygen profiles from a range of locations can be fit with a double exponential, with two-thirds consumed on a depth scale of a few mm, and the rest over ~4 cm (Hales and Emerson, 1996; Hales and S.Emerson, 1997; Hammond et al., 1995). We find that the best fit for the carbon rain (as opposed to oxidation) requires  $50\pm 5\%$  reactive carbon, consistent with Hales if most of the carbon burial comes from the less labile carbon fraction. Using the bioturbation rate constants calculated as above, we calculate the oxic organic carbon degradation rate constants as

$$k_j = \frac{D_{B_0}}{z_{\text{scale},j}^2} \quad (18)$$

where  $z_{\text{scale},j}$  is the inferred  $O_2$  consumption scale depth from Hales, using the sediment surface value of  $D_B$ . As the organic carbon rain increases, so does  $D_{B_0}$  and therefore so does  $k_j$  (Figure 4). Note that the decrease in  $D_B$  with depth, and transport by burial, will distort the distribution of organic carbon relative to equation 17.

The reaction rates of the two organic carbon fractions with other electron acceptors are proportional to their reactivities with oxygen. Therefore a specification of the reaction rate of slow organic carbon with some electron acceptor determines the reaction rates of the fast fraction, as for example

$$k_{\text{NO}_3\text{fast}} = k_{\text{NO}_3\text{slow}} \times \frac{k_{\text{O}_2\text{fast}}}{k_{\text{O}_2\text{slow}}} \quad (19)$$

The rate constants for denitrification were selected by the tuner to be about an order of magnitude slower than the corresponding oxic degradation rates (Table 3). The zero-order rate constants for Mn, Fe, and S respiration were derived from *Toth and Lehrman (1977)* as

$$k_{\text{intermed}} [\text{s}^{-1}] = 1.0753 \times 10^{-16} \alpha \left( \text{Rain}_{\text{OrgC}} \left[ \frac{\mu\text{mol}}{\text{cm}^2\text{yr}} \right] \right)^{1.75} \quad (20)$$

where  $\alpha$  is a tunable parameter for each respiration reaction (Mn, Fe, or S). Fast and slow organic carbon reaction rate constants are derived analogously to equation 3. The best-fit values of  $\alpha$  for Mn, Fe, and S respiration rates were 1.9, 0.4, and 1.3, relative to the implicit *Toth and Lehrman (1977)* value of 1.0 (Table 3). It is interesting to note that the rate constants for oxic respiration exceeds those for alternate electron acceptors by 2-4 orders of magnitude (Figure 4), insuring that organic matter preservation will depend on overlying water oxygen concentration.

As long as some nonzero concentration of organic carbon remains at depth, the pore-water profiles of anaerobic decomposition products such as  $\text{NH}_4^+$  and  $\text{Fe}^{2+}$  depend on the depth of the model domain. To eliminate this model dependence, we introduced an  $e$ -folding depth for respiration, a single scale depth governing all respiration reactions. The rate of oxic carbon degradation at some depth  $z$  is then taken to be

$$k_z = k e^{-\frac{z}{z_{\text{resp.scale}}}} \quad (21)$$

where  $k$  is the value at the sediment surface, calculated as described above. The model best fit used a scale depth of  $3.5 \pm 1.4$  cm, on the shallow side of in situ measurements, which indicate 4-6 cm depth scales (Canfield et al., 1993a; Canfield et al., 1993b; Jorgensen et al., submitted-a). Estimates of sulfur respiration rates from deep in DSDP cores are orders of magnitude slower than sediment surface values, consistent with attenuation with depth as we have constructed it here (Canfield, 1991). It is not clear why bacterial metabolic rates should decrease with depth in surface sediments, but whatever the reason, this dropoff appears to have a major effect on the preservation of organic matter in sediments.

The model is sensitive to the rain rates of reactive  $\text{MnO}_2$  and  $\text{FeOOH}$ . We take the total rain rates of Mn and Fe to be the crustal abundance (Turekian and Wedepohl, 1961) multiplied by 50% bioavailability for Mn (Nameroff, 1996; Shaw et al., 1990) and 30% for Fe (Raiswell and Canfield, 1988; Raiswell et al., 1994). Of these, we have greater confidence for Mn; the fraction of labile Fe depends on laboratory technique. Both variables are probably spatially variable in the ocean, but we lack the information to resolve this. Oxidation of  $\text{Mn}^{2+}$  followed first-order kinetics with a mean lifetime of about 16 minutes. Precipitation of  $\text{MnCO}_3$  followed a first-order rate law, against a  $\text{Mn}^{2+}$  saturation concentration of  $150 \mu\text{M}$  with a rate constant of  $10^{-10} \text{ s}^{-1}$ .

### *Tuning Methods*

We minimized the cost function using a simulated annealing method ((Press et al., 1986)), the strength of which is finding global minima in a complicated cost-function terrain, i.e. with many local minima and maxima. Details, and a discussion of the uncertainties in the tunable parameters, are given in the Appendix.

## **Results**

Depth distributions of pore water and solid phase chemistry are compared between model and data in Figure 5. The Patten Escarpment is a deep, high respiration but well-oxygenated site; the San Nicolas Basin is similar but with lower overlying water oxygen

content (Shaw et al., 1990). The model does a reasonable job of capturing the depth dependence of the pore water data (Figure 5), but it underestimates the vertical gradients of  $\text{MnO}_2$  at these and other sites.

Model results are compared with the full data set in Figure 6. The smooth color fields on the left-hand sides of Figure 6 are the model sensitivity to overlying water  $[\text{O}_2]$  (10 to 300  $\mu\text{M}$  in steps of 3) and the rain of organic carbon (1 to 100  $\mu\text{mol cm}^{-2} \text{yr}^{-1}$  in steps of 1). Biologically mediated rate constants, overlying water  $\text{NO}_3^-$ , and clay rain rates are parameterized as functions of organic carbon rain as described above. The smooth fields show the systematic dependence of organic carbon,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Mn}^{2+}$ ,  $\text{MnO}_2$ , and  $\text{Fe}^{2+}$  on overlying water oxygen and organic carbon rain. Superimposed on the smooth model fields are data values plotted as color circles with black outlines. The data are located on the plot according to their overlying water  $\text{O}_2$  and organic carbon rain rate (Table 2) and colored on the same color scale as for the model fields underneath.

Model estimates are directly compared with data on the right-hand side of the figure. Each comparison on the plot is numbered according to the same site numbering system used in Table 2 and Figure 3. The 1:1 lines in most cases seem to bisect the model/data points (meaning that the model is not biased). The model skill is best for organic carbon. The depth of  $\text{NO}_3^-$  penetration is quite good for most sites, but in some locations the model predicts  $\text{NO}_3^-$  depletion by 25-75 cm that is not seen in the data.

The distributions of Mn in solid and dissolved form are less well predicted. The color plots suggest that some of the misfit is due to variability in the data. Model results vary smoothly as a function of overlying  $[\text{O}_2]$  and  $\text{Rain}_{\text{oc}}$ , while observed concentrations are not as well-sorted by these variables. This may be because metal concentrations in natural pore waters are not in steady state, or because of heterogeneity in metal deposition or geochemistry. The concentration of  $\text{Fe}^{2+}$  in pore waters, for example, varied by a factor of two between successive visits to the Patten Escarpment (Shaw et al., 1990; Zheng, 1999). In

addition, however, the model is unable to generate the intensity of surface  $\text{MnO}_2$  enrichment observed in, for example, the Patten Escarpment (Figure 5). We suspect that  $\text{Mn}^{2+}$  is released from nearby reducing sediments in the California Borderlands. This has been observed in shallow continental shelf sediments from the central California shelf via remineralization of sedimentary organic matter and calcium carbonate dissolution (Johnson et al., 1992).  $\text{MnO}_2$  rain rates are calculated according to the fraction of Mn assumed in the clay flux, whereas Mn associated with  $\text{CaCO}_3$  flux and organic carbon flux has been neglected.  $\text{MnO}_2$  rain rates must also be higher than crustal at Manop sites H and M, where sediment surface  $\text{MnO}_2$  reaches 20-50 ppt (a factor of 25-60 higher than crustal (Turekian and Wedepohl, 1961)).

Most of the organic carbon rain reacts with oxygen throughout the conditions simulated by the model (Figure 7). Nitrate metabolism reaches a maximum at intermediate organic carbon rain; at high rain sites the nitrate reacts instead with  $\text{Fe}^{2+}$  diffusing up from below. Mn metabolism is highest at the boundary of  $\text{MnO}_2$  depletion. In low oxygen conditions, half of the respiration may be attributed to anoxic metabolism.

### *Global Model Results*

One of the advantages of the efficient relaxation scheme we employ in the Muds model is the possibility of applying the model to gridded global domains such as global ocean carbon cycle models. We present two complimentary approaches of capturing the global sedimentary carbon cycle, one based on a spatially resolved map of sediment respiration, and another based on a new global oxygen-differentiated hypsometry of the sea floor.

The spatially resolved model is based a  $2^\circ \times 2^\circ$  gridded map of organic carbon rain to the deep sea floor generated by *Jahnke* (1996). The area-weighted mean organic carbon rain rate to the sea floor is  $22 \mu\text{mol C m}^{-2} \text{ yr}^{-1}$ . Rain rates of  $\text{CaCO}_3$  and opal are taken to be 1.4 and  $1.0 \times$  the molar ratio of  $\text{Rain}_{\text{oc}}$ . Clay rain rates are based on a gridded field generated by *Archer* (1996b) to drive a global model of  $\text{CaCO}_3$  preservation. Overlying

water chemistry boundary conditions ( $O_2$ ,  $NO_3^-$ , total  $CO_2$ , and  $\Delta CO_3^{=}$ ) were extracted from global gridded water column data sets (Archer, 1996a; Levitus et al., 1993). Rate constants are parameterized as a function of organic carbon rain, as above. The gridded field extends to 60° North and South, and contains 7387 sedimentary grid points. The simulation takes a few hours on a 16-node linux cluster.

Maps of organic carbon,  $CaCO_3$ , and labile  $MnO_2$  are shown in Figure 8. The model shows an interesting contrast between Atlantic and Pacific  $MnO_2$  concentrations, but no equatorial Pacific  $MnO_2$  enrichments (Mn nodules). The carbon burial efficiency is 11%, with 94% of respiration by oxic metabolism. Organic carbon is buried at a rate of  $6.0 \cdot 10^{12}$  mol yr<sup>-1</sup>, and the total rate of denitrification is  $4.3 \cdot 10^{12}$  mol yr<sup>-1</sup>. Morford and Emerson (1999) used the same carbon rain map and assumed oxic-only carbon degradation to calculate the area of sediments where oxygen penetrates 1 cm or less, conditions under which authigenic redox-sensitive trace metal enrichment or depletion is observed. The Muds model predicts a thin oxic zone in 3.2% of the sea floor, lower than the Morford and Emerson (1999) estimate of 4%, largely because of the effect of additional electron acceptors in Muds.

The gridded global domain presented above is limited to locations deeper than 1000 m, excluding shallow water sediments which are generally thought to comprise 80-90% of global carbon burial (Bernier, 1982; Hedges and Keil, 1995). In an attempt to rectify this omission, we created an oxygen-differentiated hypsometry of the sea floor, depositing carbon using an empirical relationship between organic carbon rain and water depth (Middelburg et al., 1997) (Figure 9a). The new hypsometry is constructed as a table of sediment area as a function of overlying water oxygen concentration and depth. These were derived from the 5° resolution ETOPO5 bathymetry, binned into the 33 depth-levels of the Levitus (1993) climatology (ranging from 10 meter resolution in the upper ocean to 500 m spacing in the deep sea). For each data point in ETOPO5, we searched for the closest

oxygen concentration from the Levitus annual mean field. According to our tabulation, the oxy-hypsometry of the ocean has three regions of maximum areal density (Figure 9b). Two are in the deep sea (at 150 and about 210  $\mu\text{M}$  oxygen content) and a third is shallower than 100 m (ranging from 150-350  $\mu\text{M}$   $\text{O}_2$ ).

The bathymetric model predicts that 88% of the global organic carbon burial occurs shallower than 1000 meters (Figure 9c). The total rate of carbon burial is  $2.1 \cdot 10^{14}$  mol  $\text{yr}^{-1}$ , a factor of 35 higher than the deep-sea based spatial model presented above. The discrepancy is due to shallow water sediments; if we restrict the bathymetric model to sediments deeper than 2500 meters, the area-weighted average organic carbon rain rate, and the total carbon burial rate, is similar to the results of the spatial model results. Suboxic and anoxic respiration become more important in shallower waters, but perhaps less so than expected (sulfate respiration accounts for 15% of the global respiration in the top 1000 meters, compared with estimates of 35-50% from from 0-200 m water depth and progressively less at deeper locations (Jorgensen, 1982). Overall, oxic respiration accounts for 66% of the total. Denitrification occurs primarily (88%) shallower than 1000 meters, and the global rate is  $1.45 \cdot 10^{14}$  mol  $\text{yr}^{-1}$ , a factor of 33 higher than the spatially resolved model. This estimate is also a factor of seven to ten higher than the estimate of Middelberg (1996) which was based on the same carbon rain / depth relationship. Much of the discrepancy is found in shallow waters, where the Middelberg model underestimates observed rates, and in the range of 500-1500 meters, where Muds overestimates the data (Figure 10). Globally, about 30% of denitrification occurs in the depth range of 200-2000 meters; if we decrease the Muds estimate by a factor of 3 in this range, the global total will be  $1.16 \cdot 10^{14}$  mol  $\text{yr}^{-1}$ , still six to eight times higher than Middelberg, and high enough to throw the nitrogen budget of the ocean completely out of balance. Finally, the bathymetric model finds that 20.6% of the sea floor is capped with less than 1 cm of oxic sediments, a

factor of 5 higher than the original Morford and Emerson (1999) estimate, emphasizing the importance of shallow sediments for global mass balances of redox-sensitive trace metals.

In its focus on the deep sea, the *Jahnke* (1996) gridded map of organic carbon rain to the sea floor resembles the output of a low-resolution ocean carbon cycle general circulation model. The comparison of gridded and bathymetric models of the global sea floor demonstrates the need to develop some parameterization of shallow-water sediments for GCM models of the ocean carbon cycle.

### **Summary**

We present a new model of oxic and suboxic sedimentary diagenesis which resolves the chemistry of  $\text{NO}_3^-$ , Mn, Fe, and S, and is efficient enough to incorporate into gridded global models of the sea floor. The model is tuned to solid and pore water data from a suite of 34 locations throughout the deep sea. The model does a good job of predicting the organic carbon distribution, somewhat more poorly at simulating solid phase Mn distribution. Many of the parameters are constrained to within  $\pm 50\%$ . The model is suitable for incorporation into heterogeneous gridded carbon cycle models, two examples of which we show here. In a gridded model of the deep sea floor, organic carbon burial efficiency is 7% and oxygen accounts for 95% of respiration. In a global model including shallow water sediments, we find that oxygen accounts for 66% overall, and that 88% of global nitrate consumption occurs in the top 1000 meters.

The Muds model can be run interactively on the web at <http://geosci.uchicago.edu/~archer/cgimodels/muds.html>.

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## Tables

Table 1. Sedimentary Model Reactions and Rate Expressions

Reaction	First Order	Zero Order
$\text{OrgC}^1 + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{NO}_3^-$	OrgC	
$\text{Mn}^{2+} + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$	$\text{Mn}^{2+}$	$\text{O}_2$
$\text{OrgC} + 236\text{MnO}_2 + 472\text{H}^+ \rightarrow 236\text{Mn}^{2+} + 106\text{CO}_2 + 16\text{NO}_3^-$	OrgC	$-\text{O}_2, +\text{MnO}_2$
$\text{OrgC} + 94.4\text{HNO}_3 \rightarrow 106\text{CO}_2 + 47.2\text{N}_2$	OrgC	$-\text{O}_2, +\text{NO}_3^-$
$5\text{Fe}^{2+} + \text{NO}_3^- \rightarrow \text{FeOOH} + \text{N}_2 + 9\text{H}^+$	$\text{Fe}^{2+}$	$+\text{NO}_3^-$
$\text{OrgC} + 472\text{FeOOH} + 960\text{H}^+ \rightarrow 106\text{CO}_2 + 472\text{Fe}^{2+} + 16\text{NH}_4^+$	OrgC	$-\text{NO}_3^-$
$\text{OrgC} + 59\text{SO}_4^{2-} + 75\text{H}^+ \rightarrow 106\text{CO}_2 + 16\text{NH}_4^+ + 59\text{HS}^-$	OrgC	$-\text{NO}_3^-$
$\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$	$\text{HS}^-$	$+\text{O}_2$
$\text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS} + \text{H}^+$	$\text{HS}^-, \text{Fe}^{2+}$	
$\text{FeS} + 4.5\text{O}_2 + \text{H}^+ \rightarrow \text{FeOOH} + \text{SO}_4^{2-}$	FeS	$+\text{O}_2$
$\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^-$	$\text{O}_3^-/[\text{CO}_3^-]_{\text{sat}}$	
$\text{SiO}_2 \rightarrow \text{H}_4\text{SiO}_4$	$[\text{SiO}_2], \Delta[\text{H}_4\text{SiO}_4]$	

1. OrgC = Redfield organic matter,  $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}$ .

(Weber et al., submitted)(Jorgensen et al., submitted-b)(Thamdrup et al., 2000)(Reimers et al., 1992)

(Canfield et al., 1993b)(Canfield et al., 1993a)(1989)(1987)(1999)(Christensen, 1989)  
(1982)(1982)(1984)(1984)(1984)(1990)(1988)(1990)(1998)(1996)(1999)(1992)(1993  
)

Table 3. Tunable Parameters in the Model

Parameter	Applied to	Best	Max.	Constr.	Min.	Constr.
$F_{\text{labile}}$	Fraction of labile organic rain	0.5	-10%	MnO <sub>2</sub>	+10%	OrgC, MnO <sub>2</sub>
$z_{\text{resp.}}$	Resp. scale depth	3.5 cm	-40%	Fe, Mn, MnO <sub>2</sub>	+40%	MnO <sub>2</sub> , NH <sub>4</sub>
$z_{\text{irrig.}}$	Porewater irrig. depth	1.8 cm	-60%	Fe, Mn, MnO <sub>2</sub> , H <sub>2</sub> S	+60%	NH <sub>4</sub> , MnO <sub>2</sub>
$\alpha_{\text{NO}_3}$	Relative to oxic	0.3	-80%	MnO <sub>2</sub>	+60%	$z_{\text{NO}_3}$
$\alpha_{\text{Mn}}$	Relative to <i>Toth and Lehrman</i> [1997] for S	1.9	-20%	MnO <sub>2</sub>	+10%	MnO <sub>2</sub> , Mn <sup>2+</sup>
$\alpha_{\text{Fe}}$	Relative to <i>Toth and Lehrman</i> [1997] for S	0.4	-10%	Fe <sup>2+</sup> , NH <sub>4</sub> <sup>+</sup>	+20%	Fe <sup>2+</sup>
$\alpha_{\text{SO}_4}$	Relative to <i>Toth and Lehrman</i> [1997]	1.3	-40%	NH <sub>4</sub> <sup>+</sup>	+60%	Fe <sup>2+</sup> , H <sub>2</sub> S

## Appendix. Automatic Tuning and Statistical Significance of the Cost Function

Throughout this and the next sections, subscript  $i$  denotes a data site or its model prediction,  $j$  denotes a chemical comparison, for example organic carbon concentration, and  $k$  denotes a tuning parameter, for example a rate constant.

### *The Cost Function*

After considerable experimentation, a cost function was defined as

$$C_j = \sqrt{\frac{\sum_i (m_{ij} - d_{ij})^2}{n_j} \left( \frac{1}{\sigma_{d_j}^2} + \frac{1}{\sigma_{m_j}^2} \right)} + 10 \left( \frac{\overline{m_j}^2 + \overline{d_j}^2}{\overline{m_j} \overline{d_j}} - 2 \right) + 10 \sum_i \frac{(d_{ij} - m_{ij})^2}{(d_{ij} + m_{ij} + \epsilon)^2} \quad (\text{A1})$$

The cost associated with comparison  $j$  is denoted  $C_j$ , where a better fit is less costly. Data values are  $d_{ij}$ ,  $m_{ij}$  is the model prediction, and  $n_j$  is the number of sites with data of type  $j$ . The first term on the right hand side is the RMS misfit between model and data, normalized to the variance of the model and the data,  $\sigma_{m_j}^2$  and  $\sigma_{d_j}^2$ . This term is analogous to the inverse of a correlation coefficient, with the added restriction that the data cluster around a 1:1 line. The second term strives to equate the mean values of the model and data,  $\overline{m_j}$  and  $\overline{d_j}$ . This term served to eliminate a relative minimum near a model solution with  $m_j$  values all near zero. The third term is minimized when the ratio of each pair of  $d_{ij}$  and  $m_{ij}$  is unity, where  $\epsilon$  is a small number to prevent division by zero. This term guards against the case where a single model overestimate at one location compensates in the mean (the second

term) for underestimates elsewhere. The total cost function is the sum over all chemical comparisons  $j$

$$C_{\Sigma} = \sum_j C_j \quad (\text{A2})$$

### *Automatic Tuning*

We sought optimum values of the input parameters using a simulated annealing algorithm (Press et al., 1986). The cost function was computed for an initial guess for each parameter  $P_k$  by running the model for each of the 53 data sites. Next each  $P_k$  was varied randomly and independently of the others through an RMS range of  $\pm 5\%$ . The new cost function is compared with the previous one, and the new  $P_k$  values are accepted if

$$e^{\left( \frac{C_{\text{init}} - C_{\text{new}}}{\alpha C_{\text{init}}} \right)} > \beta \quad (\text{A3})$$

where  $\beta$  is a random number between 0-1 and  $\alpha$  is temperature in the annealing analogy. In practice, if the new cost is lower than the old one, the new parameters are always chosen. If the new cost exceeds the old one, the new parameters might be chosen, with the probability governed by the temperature parameter  $\alpha$ . The strength of simulated annealing is its ability to escape from local minima by occasionally moving uphill temporarily to higher cost functions. We also tried gradient descent method, where each parameter is tuned according to the direction of steepest descent

$$P_k^{n+1} = P_k^n - \alpha_k \frac{\partial C_{\Sigma}}{\partial P_k} \quad (\text{A4})$$

where  $\alpha_k$  is chosen empirically to maximize stable convergence. However, we found that this method usually became trapped in local valleys, limiting its usefulness.

### *Uncertainties in Model Parameters*

We evaluate the uncertainties in the model input parameters by systematically varying them one at a time and recording the increase in the cost function as each parameter deviates from its best fit value. The uncertainty of an input parameter reduces to the statistical significance of the cost function; how much worse does the cost function have to be before it is considered significantly worse? As can be seen above, the cost function was formulated as a means of enforcing our subjective views of what the best-fit model solution should look like. The simplest cost function, a simple RMS deviation from the data, often led to solutions in which most of the error was carried by a single tracer,  $\text{NH}_4$ , for example, which we subjectively considered an unsatisfactory solution. Hence we will treat the significance of the cost function subjectively. The results of our analysis are presented in Table 3. Most of the model parameters are constrained to within  $\pm 50\%$  of their best fit value.

This analysis ignores the potential for co-dependence between model parameters; it could be that a simultaneous change in several parameters could still fall within the acceptable range in the cost function. Also, we are assuming that the model itself is correct, and choosing best-fit values of the input parameters given that limitation. This analysis tells us more about the sensitivity of the model than about the sensitivity of the real world.

## Figure Captions

Figure 1. Overlying water [O<sub>2</sub>] and organic carbon rain rates of the sedimentary locations in Table 2. Each location is plotted as the site number from Table 2, to enable cross-correlation with the data values in Figure 7.

Figure 2. Further parameterizations. a) Overlying water NO<sub>3</sub><sup>-</sup> as a function of overlying water O<sub>2</sub>, based on data from GEOSECS. Data are fit as  $\text{NO}_3^- = -0.0004 \text{ O}_2^2 + 0.03 \text{ O}_2 + 41$ . b) Clay rain (accumulation) rate from the data locations in Table 2 plotted against organic carbon rain. Clay rain (mg cm<sup>-2</sup> yr<sup>-1</sup>) = Org Rain (μmol cm<sup>-2</sup> yr<sup>-1</sup>) / 2. (Hartnett, 1998; Jahnke et al., 1989; Reimers et al., 1992).

Figure 3. Parameterization of pore water irrigation. (a) Depth integrated irrigation rate, cm<sup>3</sup> pore water exchanged per cm<sup>2</sup> sediment area per day, or cm day<sup>-1</sup>. Symbols are inferred from comparison of diffusive (microelectrode) versus total (benthic chamber) oxygen consumption rates. Solid line is the model parameterization in high-O<sub>2</sub> conditions (equation 16, first two terms). Four points, demarked by the oval, were determined where the overlying water [O<sub>2</sub>] was lower than 30 μM. Three of these had anomalously high irrigation intensities. (b) The third term in equation (16) is an oxygen dependent parameterization, to simulate the apparent enhancement of irrigation observed in the data.

Figure 4. Rate constants for organic carbon diagenesis as a function of organic carbon rain to the sea floor. Organic carbon is split into two fractions, Fast and Slow. Oxidic degradation rate constants for both fractions are compared with estimates of overall reactivity based on measured sediment organic carbon concentrations and respiration rates from Table 2. For suboxic reactions, only the Slow rates are shown; the ratio of Fast to Slow is the same as for oxic respiration.

Figure 5. Pore water and solid phase chemistry comparison with data from the California Borderlands and Aarhus Bay, Denmark. (a, b, and e) Patten Escarpment, and (c, d, and f)

San Nicholas Basin, from Shaw (Shaw et al., 1990). (g and h) From station S6, Aarhus Bay, Denmark (Canfield et al., 1993a; Canfield et al., 1993b).

Figure 6. Model comparison with data from all sites in Table 2. Continuous color plots on the left-hand side are model fields as a function of overlying water  $[O_2]$  and organic carbon rain. Circles are data, colored on the same color scale as the model fields. Scatter plots on the right-hand side are a direct comparison of model and data values, indexed by site number from Table 2 and Figure 3. (a) Organic carbon at 8 cm depth, % dry weight. (b) Depth of  $NO_3^-$  penetration, cm. (c)  $NH_4^+$  concentration at 8 cm depth,  $\mu M$ . (d)  $Mn^{2+}$  concentration at 8 cm depth,  $\mu M$ . (e)  $MnO_2$  concentration at the sediment surface, ppt Mn. (f)  $MnO_2$  concentration at 8 cm depth, ppt Mn. (g)  $Fe^{2+}$  concentration at 8 cm depth,  $\mu M$ . (h)  $H_2S$  concentration at 8 cm depth,  $\mu M$ .

Figure 7. Fraction of organic carbon respiration due to  $O_2$ ,  $NO_3^-$ , Mn, Fe, and S as a function of oxygen and carbon rain.

Figure 8. Global maps of (a) organic carbon (% dry weight), (b)  $CaCO_3$  (% dry weight), and (c)  $MnO_2$  (ppm dry weight) from the gridded deep sea model run.

Figure 9. Global oxygen-hypsometry model of sediment respiration. (a) An average organic carbon rain rate as a function of depth, from Middelburg (1997). (b) A new compilation of sediment area delineated by depth (from the ETOPO5 5 minute bathymetry of the ocean) and overlying water oxygen concentration (from the Levitus (1993) annual mean gridded distribution). Units are  $10^6 km^2$  per km of depth interval and per  $\mu M O_2$  concentration. Depth is binned into 33 ranges, corresponding to the vertical resolution of the Levitus (1993) climatologies, and oxygen is binned into 40 bins ranging from 0-400  $\mu M O_2$ , in increments of 10  $\mu M$ . (c) Cumulative fraction of carbon burial as a function of depth in the ocean, showing that 88% of carbon buried in the model occurs shallower than 1000 meters. (d) Respiration pathways as a function of depth. Shallower than 1000 meters,  $NO_3^-$  is consumed by upward diffusion of  $Fe^{2+}$ , rather than by respiration reactions. (e)

Ratio of sedimentary nitrate consumption to nitrogen rain to the sea floor in organic particles. In shallow waters, nitrate is extracted from overlying waters, but even here most denitrification is supported by organic nitrogen rain, consistent with Devol (1991). In deeper waters, only a fraction of nitrogen rain is lost to denitrification.

Figure 10. Comparison of sedimentary denitrification rates between Muds (solid lines), the Middelberg (1996) model (dashed lines), and data, tabulated by Middelberg (1996). (a) Linear axes, and (b) log axes.