Global-scale quantification of mineralization pathways in marine sediments: A reaction-transport modeling approach

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[1] The global-scale quantification of organic carbon (C_{org}) degradation pathways in marine sediments is difficult to achieve experimentally due to the limited availability of field data. In the present study, a numerical modeling approach is used as an alternative to quantify the major metabolic pathways of C_{org} oxidation (C_{ox}) and associated fluxes of redox-sensitive species fluxes along a global ocean hypsometry, using the seafloor depth (SFD) as the master variable. The SFD dependency of the model parameters and forcing functions is extracted from existing empirical relationships or from the NOAA World Ocean Atlas. Results are in general agreement with estimates from the literature showing that the relative contribution of aerobic respiration to C_{ox} increases from <10% at shallow SFD to >80% in deep-sea sediments. Sulfate reduction essentially follows an inversed SFD dependency, the other metabolic pathways (denitrification, Mn and Fe reduction) only adding minor contributions to the global-scale mineralization of C_{org}. The hypsometric analysis allows the establishment of relationships between the individual terminal electron acceptor (TEA) fluxes across the sediment-water interface and their respective contributions to the C_{org} decomposition process. On a global average, simulation results indicate that sulfate reduction is the dominant metabolic pathway and accounts for approximately 76% of the total C_{ox}, which is higher than reported so far by other authors. The results also demonstrate the importance of bioirrigation for the assessment of global species fluxes. Especially at shallow SFD most of the TEAs enter the sediments via bioirrigation, which complicates the use of concentration profiles for the determination of total TEA fluxes by molecular diffusion. Furthermore, bioirrigation accounts for major losses of reduced species from the sediment to the water column prohibiting their reoxidation inside the sediment. As a result, the total carbon mineralization rate exceeds the total flux of oxygen into the sediment by a factor of 2 globally.

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1. Introduction

[1] Early diagenetic processes in marine sediments are of considerable importance for the global cycling of many elements at the Earth’s surface. In sediments, the microbial degradation of organic carbon (C_organic) is a dominant process that determines either directly or indirectly many other biogeochemical reactions [e.g., Berner, 1980; Westrich and Berner, 1984; Middelburg, 1989; Boudreau and Ruddick, 1991]. The complex interplay between the major redox cycles (carbon, oxygen, nitrogen, manganese, iron and sulfur) that is triggered by organic matter decomposition has been investigated at numerous sites worldwide with the aim of establishing global budgets [e.g., Canfield, 1993, Tromp et al., 1995; Jahnke, 1996; Seiter et al., 2005; Hensen et al., 2006; Jorgensen and Kasten, 2006; Zabel and Hensen, 2006]. Yet, because of sampling difficulties and the complex pathways of early diagenesis, much of the available site specific benthic biogeochemical data do not provide sufficient information to describe the major benthic degradation processes. Perhaps more significantly, many sampling locations are not representative of the wider seafloor environment and are chosen on the basis of their unusual environmental characteristics. Thus, when extrapolated globally, these data sets introduce an unknown bias into C_organic mineralization budgets.

[1] Various experimental methodologies have been proposed to quantify the flux of reactive particulate C_organic from the surface layers down toward the seafloor. Direct estimations are obtained from export production and/or sediment trap deployments. Nonvertical particle settling and enhanced particle transport in benthic nepheloid layers can redistribute the benthic carbon oxidation demand over regional scales and so introduce large uncertainties in the final particle flux calculation [Jahnke et al., 1990; Reimers et al., 1992; Inthorn et al., 2006]. More often indirect approaches are employed, based on (1) time change in total dissolved organic carbon (TCO_2) flux from sediments, which requires corrections for CaCO_3 dissolution [e.g., Berelson et al., 1996], (2) dissolved oxygen uptake (DOU) by sediments using pore water O_2 microprofiles [e.g., Glud et al., 1994], and (3) total oxygen uptake (TOU) by sediment from the time change in bottom water oxygen concentration [e.g., Andersson et al., 2004]. The latter two methods are based on the premise that O_2 is the ultimate oxidant for C_organic and reduced metabolites in the sediment resulting from anaerobic carbon mineralization. Of these, TOU probably represents the most robust way to gauge C_organic flux because dissolved oxygen consumption by macrofauna [Glud et al., 1994] and transport of reduced species (NH_4^+, Mn^{2+}, Fe^{2+}, H_2S), termed oxygen demand units (ODU) by Soetaert et al. [1996], can constitute a large fraction of total O_2 demand. However, if a significant fraction of ODU are buried as sedimentary sulfides or lost to the seawater and not corrected for, then TOU can potentially underestimate the depth-integrated rate of C_organic mineralization. Perhaps not surprisingly, a combination of approaches and statistical analyses using various proxy parameters have been used to quantify spatially resolved C_organic fluxes at the global scale [e.g., Jahnke, 1996; Zabel and Hensen, 2006; Seiter et al., 2005].

[1] In the present study, we explore in more detail the global mineralization of C_organic in the seafloor using a reaction-transport model (RTM) approach. RTMs simulate the complex interplay between transport processes and biogeochemical transformations, which allow for a temporally and spatially resolved quantification of reaction rates and material fluxes. In recent years, RTMs have become an established tool for the simulation of redox-sensitive processes in marine sediments [e.g., Soetaert et al., 1996; Boudreau, 1996; Van Cappellen and Wang, 1996; Dhakar and Burdige, 1996; Berg et al., 2003; Thullner et al., 2005; Dale et al., 2008a, 2008b]. We employ the seafloor depth (SFD) as the master variable for all simulations, which implies that the principal model parameters and semiempirically determined functions (boundary conditions, transport and reaction rate parameters) change from coastal shelf environments (100 m) to the deep ocean (5000 m) in a predictive manner. Statistically
Table 1. Subdivision of the Ocean Floor Into Depth Provincesa

<table>
<thead>
<tr>
<th>Depth Range (m)</th>
<th>Model SFD (m)</th>
<th>% Global</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner shelf 0–150</td>
<td>100</td>
<td>5.8</td>
</tr>
<tr>
<td>Outer shelf 150–350</td>
<td>200</td>
<td>1.4</td>
</tr>
<tr>
<td>Upper slope 350–750</td>
<td>500</td>
<td>1.3</td>
</tr>
<tr>
<td>Midslope 750–1500</td>
<td>1000</td>
<td>2.6</td>
</tr>
<tr>
<td>Lower slope 1500–2750</td>
<td>2000</td>
<td>7.1</td>
</tr>
<tr>
<td>Abyss 2750–4250</td>
<td>3500</td>
<td>34</td>
</tr>
<tr>
<td>Abyss &gt;4250</td>
<td>5000</td>
<td>48</td>
</tr>
<tr>
<td>Global</td>
<td>—</td>
<td>3.3 x 10^18 km^2</td>
</tr>
</tbody>
</table>

aModel simulations for each depth area are performed using boundary conditions and forcings corresponding to the model seafloor depth (SFD) indicated. The total seafloor area and percentages used in this study correspond to the ocean between 60°S and 60°N.

robust relationships developed by Middelburg et al. [1997] and Meile and Van Cappellen [2003] suggest that this condition is largely met throughout the ocean, yet these relationships have not been tested in global-scale models. The use of SFD as a master variable is attractive since, as Middelburg et al. [1997] remarked, SFD is an independent variable and free from experimental error, which is not true for the direct methodologies for carbon flux determination listed above. The approach does neglect regional-scale heterogeneity, which could be overcome by demarcation of the seafloor into biogeochemical provinces [Longhurst et al., 1995]. However, our research interest in the present study is not to reproduce experimental data sets from specific sites or specific seafloor environments but first to compare the extent to which proposed SFD-dependent parameters support previous findings of global-scale POM mineralization and pathways along the global hypsometry. We will then investigate the fate and fluxes of ODUs generated in situ and discuss the validity of TOU as a proxy for organic carbon oxidation (C_{ocx}) rate. To our knowledge, this will provide the first detailed analysis of source and sink fluxes for NH₄⁺, Mn²⁺, Fe²⁺ and H₂S in marine sediments at the global scale.

2. Simulation Procedure

2.1. Model Approach

The RTM simulations are performed using boundary conditions and forcings corresponding to SFD of 100 m, 200 m, 300 m, 1000 m, 2000 m, 3500 m and 5000 m. These depths are representative of shelf, slope and abyssal sediments as described in Table 1. The relative contributions of each SFD interval to the total area of the seafloor are taken from the ETOPOS 5 x 5 min Navy bathymetry database [National Geophysical Data Center, 1993] available online (http://irdl.ldeo.columbia.edu/). The data analysis is restricted to latitudes between 60°S and 60°N and thus does not account for high latitude environments. These high latitudes represent only 13% of the global surface and ~10% of the total seafloor due to the relatively high abundance of landmasses at these latitudes.

For each selected SFD, geochemical processes in the sediments are quantified using the Biogeochemical Reaction Network Simulator (BRNS) [Regnier et al., 2002; Aguilera et al., 2005], an adaptative simulation environment suitable for large, mixed kinetic-equilibrium reaction networks [e.g., Thullner et al., 2005; Jourabchi et al., 2005; Dale et al., 2009]. For each dissolved species, i, the BRNS simulates the changes in pore water concentration, c_i, as a result of sediment burial, mixing due to molecular diffusion and bioturbation, bio-irrigation, and species production/consumption due to reactions. If sediment compaction and porosity changes are neglected, the mass conservation equation for c_i, reads:

\[
\frac{\partial c_i}{\partial t} - \nu_{bar} \frac{\partial c_i}{\partial x} + \frac{\partial}{\partial x} \left( D_i^* \frac{\partial c_i}{\partial x} \right) + \alpha \cdot (c_{i,0} - c_i) + R_i
\]

In equation (1), x and t are the vertical and temporal coordinates, \( \nu_{bar} \) is the burial velocity, \( D_i^* \) is the effective diffusion coefficient of species i, \( D_i \) is the bioturbation coefficient, \( \alpha \) is the bioirrigation coefficient, \( c_{i,0} \) is the dissolved concentration of at the sediment-water interface and \( R_i \) is the sum of all reaction rates consuming or producing species i. The spatial distributions of solid state species, l, are not influenced by molecular diffusion or bioirrigation and the mass conservation equation therefore reduces to:

\[
\frac{\partial c_l}{\partial t} = -\nu_{bar} \frac{\partial c_l}{\partial x} + \frac{\partial}{\partial x} \left( D_l \frac{\partial c_l}{\partial x} \right) + R_l
\]

where \( R_l \) is the sum of all reaction rates consuming and producing species l. \( R_l \) and \( R_i \) typically depend on other species concentrations than species i and l, respectively. Therefore, the reactions are coupled through the mass conservation equations (see below).

Boundary conditions at the seafloor (x = 0) are specified as constant concentrations \( c_{i,0} \) for dissolved species:

\[
c_i(x = 0) = c_{i,0}
\]
Table 2. Processes and Variables Implemented in the Reaction Network

<table>
<thead>
<tr>
<th>Description</th>
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<tbody>
<tr>
<td>Reactions: Primary redox (C&lt;sub&gt;ox&lt;/sub&gt; reactions)</td>
</tr>
<tr>
<td>Reactions: Secondary redox</td>
</tr>
<tr>
<td>Reactions: Nonredox</td>
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<tr>
<td>Variables</td>
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</tbody>
</table>

and as a constant depositional flux, \( J_l \) (mass per seafloor area per unit time), for solid species:

\[
J_l = \rho \cdot (1 - \Phi) \cdot \left( v_{\text{bar}} \cdot c_l - D_h \frac{\partial c_l}{\partial x} \right)_{x=0} \]  \hspace{1cm} (4)

where \( \rho \) is the density of the solid matrix and \( \Phi \) is the sediment porosity. At the lower boundary of the model domain (\( x_{\text{max}} = 50 \text{ cm} \)), a zero gradient condition (\( \frac{\partial c_l}{\partial x} = 0 \)) is applied for all species [Boudreau, 1997]. Specific values for all boundary conditions at the seafloor are discussed in section 2.3.2.

[9] Spatial discretization of equations (1) and (2) is performed using a one-dimensional finite difference scheme along an irregular grid composed of 111 nodes. The grid spacing increases from 1 mm at the sediment surface to 1 cm at \( x_{\text{max}} \). Transient simulations are carried out until steady state is reached using a time step of \( 10^{-7} \text{ y} \) for ocean margin sediments (SFD \( \leq 1000 \text{ m} \)) and \( 10^{-6} \text{ y} \) for deep sea sediments (SFD \( > 1000 \text{ m} \)). Mass balance in the system was always achieved with an accuracy of at least 0.1%.

2.2. Reaction Network and Definitions

[10] The reaction network implemented in the BRNS is taken from Van Cappellen and Wang [1995] and details on reaction stoichiometries, rate laws and equilibrium constraints can be found in Appendix A. In brief, the total \( C_{\text{ox}} \) rate, \( R_{C_{\text{ox}}} \), is simulated assuming a first order dependency with respect to labile particulate organic matter (POM), assumed to be (CH<sub>2</sub>O)<sub>106</sub>(NH<sub>3</sub>)<sub>12</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>). Other POM fractions which are not degraded within the 50 cm simulated domain are considered to be recalcitrant and not included in the simulations. The sequential contribution of the major metabolic pathways to the overall process of \( C_{\text{org}} \) decomposition (primary redox reactions) is controlled by empirical inhibition terms which ensure that \( R_{C_{\text{ox}}} = r_{O_2} + r_{NO_3} + r_{MnO_2} + r_{FeOHS} + r_{SO_4} \), where each \( r_{\ldots} \) denotes the rate of \( C_{\text{ox}} \) associated with a specific terminal electron acceptor (TEA). Secondary redox reactions, which mainly describe the reactions of the ODU produced by the primary reactions (NH<sub>4</sub><sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, H<sub>2</sub>S, and HS<sup>−</sup>) are also included in the reaction network. Nonredox mineral precipitation/dissolution processes and acid-base equilibria are considered (Table 2). Note that most model parameters which are associated with reactions not directly involved in \( C_{\text{org}} \) cycling are assumed to be independent or weakly sensitive to the SFD.

[11] The BRNS provides vertical profiles of individual species concentrations and reaction rates. From these profiles, the fluxes of dissolved species across the seafloor and (sediment) depth integrated reaction rates can be calculated. The depth-integrated \( C_{\text{org}} \) oxidation rate (mass per seafloor area per unit time) by each primary redox pathways, \( n \), is simply obtained by depth integration over the whole model domain, \( x_{\text{max}} \), which then allows calculating the total \( C_{\text{ox}} \) in the sediment:

\[
C_{\text{ox,total}} = \sum_n \int_0^{x_{\text{max}}} r_n dx \]  \hspace{1cm} (5)

In this study, the modeled sediment column is sufficiently large so that the labile carbon reaching the seafloor is completely degraded, i.e., there is no burial of labile \( C_{\text{org}} \) out of the last grid space in the model. Consequently, and considering that the ratio of carbon to oxygen during organic matter mineralization is 1:1 for a \( C_{\text{org}} \) oxidation state of zero, \( C_{\text{org}} \) flux in this study is assumed to be equivalent to the total oxygen uptake (TOU) of the sediment. We make this assumption because, in practical terms, TOU is normally considered to represent the depth integrated rate of \( C_{\text{ox}} \), which
requires that all the ODU produced from the primary redox reactions are oxidized back to \( \text{MnO}_2, \text{Fe(OH)}_3, \text{SO}_4^{2-} \) using \( \text{O}_2 \) as the ultimate TEA. Strictly, however, TOU is not equal to the flux of \( C_{\text{org}} \) remineralized in the seafloor for three reasons. First, some ODU escape reoxidation and are buried in the long term sedimentary record, mainly as particulate iron sulfides, and a correction to measured TOU may be necessary \[1996\]. Second, if all POM were to be degraded by denitrification, then the TOU will be zero since the \( \text{N}_2 \) product is not oxidized in the sediment or bottom water. Third, POM contains particulate organic nitrogen (PON), represented by \( \text{NH}_3 \). In our model, aerobic respiration is described as coupled oxidation and nitrification (Tables A1 and A2 in Appendix A) where PON is oxidized directly to \( \text{NO}_3^- \). Thus, if all POM were to be degraded aerobically, the TOU demand would be 1.22 times greater than TOU calculated on a carbon-only basis. Between these two end-member cases, other TOU values can be obtained when the oxidation of the \( \text{NH}_4^+ \) released during manganese, iron and sulfate reduction is not complete. Nonetheless, to avoid these complications and allow a more straightforward comparison with literature data, TOU in this study refers to the POC component of POM only:

\[ \text{TOU} = J_{\text{POC}} \]  

(6)

For similar reasons, we exclude \( \text{NH}_4^+ \) from the calculation of ODU:

\[ J_{\text{ODU}} = \frac{1}{2} \cdot J_{\text{Me}^{2+}} + \frac{1}{4} \cdot J_{\text{Fe}^{2+}} + 2 \cdot J_{\text{H}_2\text{S}} \]  

(7)

and \( \text{NH}_4^+ \) fluxes are discussed separately. Note that in equation (7) \( \text{H}_2\text{S} \) corresponds to total dissolved sulfide (\( \text{H}_2\text{S} + \text{H}^+ \)).

2.3. SFD-Dependent Parameters

\[12\] This section describes the general SFD dependency of all model parameters directly involved in \( C_{\text{org}} \) decomposition. A summary of all values selected for the variables, parameters and boundary conditions along the global hypsometry is given in Table 3. In the empirical relationships presented below the SFD is specified in meters (m).
2.3.1. Transport Parameters

[13] The global-scale relationship between burial velocity $v_{bur}$ (cm yr$^{-1}$) and SFD is taken from the statistically significant ($r^2 = 0.615$, $n = 220$, $p = 0.0000$) empirical relationship of Middelburg et al. [1997] (there presented as sediment accumulation rate):

$$v_{bur} = 3.3 \cdot 10^{-0.8748-0.0004351 \text{SFD}}$$  \hspace{1cm} (8)

[14] The bioturbation coefficient $D_b$ (cm$^2$ yr$^{-1}$) is similarly expressed as [Middelburg et al., 1997]:

$$D_b = 5.2 \cdot 10^{0.7624-0.0003972 \text{SFD}}$$  \hspace{1cm} (9)

$D_b$ values used in the regression analysis by Middelburg et al. [1997] are based on $^{210}$Pb measurements and depend significantly on SFD ($r^2 = 0.432$, $n = 132$, $p = 0.0000$). Studies suggest that the surface sediment mixed by bioturbation is approximately 10 cm thick and independent of the SFD [Boudreau, 1997; Van Cappellen and Gaillard, 1996]. Based on these results, a mixed layer depth of 10 cm is imposed for all simulations, an assumption generally supported by the more recent study of Teal et al. [2008], who presented a mixed layer depth of 6 ± 6 cm with only marginal dependency on SFD.

[15] The effective diffusion coefficient $D_i^*$ (cm$^2$ yr$^{-1}$) for each dissolved species $i$ is given by:

$$D_i^* = \frac{D_i(T,S)}{1 - \ln(\Phi^2)}$$  \hspace{1cm} (10)

where $D_i(T,S)$ (cm$^2$ yr$^{-1}$) is the species-dependent, molecular diffusion coefficient in seawater at a given temperature (T) and salinity (S) [Boudreau, 1997]. $D_i^*$ also depends on SFD through T (see below) and $\Phi$. Values of $\Phi$ are set to 0.85 for SFD ≤ 200 m and to 0.80 for SFD ≥ 200 m [Van Cappellen and Wang, 1995].

[16] The bioirrigation rate $\alpha$ (yr$^{-1}$) is calculated from the bioirrigation coefficient at the sediment surface ($\alpha_0$, yr$^{-1}$) and the bioirrigation attenuation depth length ($x_{irr}$, cm):

$$\alpha = \alpha_0 \cdot \exp\left(-x/x_{irr}\right)$$  \hspace{1cm} (11)

Due to a lack of data, $x_{irr}$ is assumed to be independent of the SFD and set to 3.5 cm. This irrigates the sediment down to ~15 cm depth, which although typical for shelf sediments [Van Cappellen and Wang, 1996; Meile et al., 2001; Burdige, 2006] may not be so for deeper environments. We discuss the ramifications of this approach below. We also assume that irrigation rates are identical for all species, although we recognize that some highly redox sensitive species such as Fe$^{2+}$ may be irrigated at much lower rates due to oxidation at the walls of animal burrows [Meile et al., 2005]. $\alpha_0$ is calculated from the mean bioirrigation coefficient in the aerobic sediment layer ($\pi$, yr$^{-1}$) and the penetration depth of O$_2$ into the sediment ($x_{O2}$, cm) [Meile and Van Cappellen, 2003]:

$$\alpha_0 = \frac{\pi \cdot x_{O2}}{x_{irr} \cdot \left(1 - \exp\left(\frac{x_{O2}}{x_{irr}}\right)\right)}$$  \hspace{1cm} (12)

where

$$\pi = -73.071 + 71.912 \cdot \exp\left(-0.0013846 \cdot \frac{J_{O2}}{1000}\right)$$  \hspace{1cm} (13)

$$x_{O2} = 0.5 \cdot \frac{2 \cdot \Phi \cdot c_{O2} \cdot D_{O2}^* \cdot J_{O2, diff}}{J_{O2, diff}^*} + 0.5 \cdot \frac{2 \cdot \Phi \cdot c_{O2} \cdot D_{O2}^* \cdot J_{O2}}{J_{O2, diff}^*} \cdot J_{O2}$$  \hspace{1cm} (14)

In equation (13) and (14), $J_{O2}$ (μmol cm$^{-2}$ yr$^{-1}$) and $J_{O2, diff}$ (μmol cm$^{-2}$ yr$^{-1}$) are defined as the total flux and the diffusive flux of O$_2$ across the sediment-water interface, respectively, $c_{O2}$ (μM) is the bottom water O$_2$ concentration, and the noninteger coefficients are empirically derived by Meile and Van Cappellen [2003].

[17] $J_{O2}$ is directly dependent on the SFD [Wijsman, 2000; Andersson et al., 2004]:

$$J_{O2} = J_0 \left[ (1 - p) \cdot \exp\left(-b_1 \cdot \text{SFD}\right) + p \cdot \exp\left(-b_2 \cdot \text{SFD}\right) \right]$$  \hspace{1cm} (15)

where $J_0$ is equal to $J_{O2}$ for SFD = 0 (986 μmol cm$^{-2}$ yr$^{-1}$), $p$ is a partitioning coefficient of $J_0$, equal to 0.14, and $b_1$ (0.017 m$^{-1}$) and $b_2$ (0.00047 m$^{-1}$) control the slopes of the exponen- tials (values taken from Wijsman [2000]). This relationship ($r^2 = 0.71$) is derived from more than 500 TOU estimates measured for SFD between 10 and 9000 m.

[18] Finally, $J_{O2, diff}$ in equation (14) is derived from $J_{O2}$, using the empirical relation derived by Meile and Van Cappellen [2003] based on a comparison of measured O$_2$ fluxes calculated by O$_2$ micro-
sensor profiles and in situ benthic chamber incubations \((n = 41, r^2 = 0.79)\):

\[
J_{O_2,\text{diff}} = \frac{500 \cdot J_{O_2}}{646 + J_{O_2}}
\]  

(16)

Table 3 shows that \(\alpha_0\) decreases by 2 orders of magnitude between 100 m and 5000 m, which reflects the lower availability of labile \(C_{\text{org}}\) with increasing SFD.

### 2.3.2. Upper Boundary Conditions

[15] Values for \(O_2\), \(NO_3^-\), \(T\) and \(S\) are taken from the NOAA World Ocean Atlas 2001 [Conkright et al., 2002], available online at the IRI/LDEO Climate Data Library (http://iridl.ldeo.columbia.edu/). In this database, the variables are reported with a 1° × 1° horizontal resolution and a vertical resolution which varies from 10 m close to the sea surface to 500 m for water depths >2000 m, up to a maximum depth of 5500 m. In the present study, the annual mean data recorded at the deepest water depth for any given horizontal coordinate is assumed to be representative of the seafloor conditions at this coordinate. Average bottom water values of \(O_2\) (µM), \(NO_3^-\) (µM), \(T\) (°C) and \(S\) are then calculated for each SFD interval as indicated by the polynomial data interpolation in Figure 1. Even though the data show a considerable degree of variability due to basin-wide differences in water masses, the interpolations capture the essential features such as the oxygen minimum zone on the continental slope. Due to the low variability with SFD, sulfate (\(SO_4^{2-}\)) and \(S\) along the global hypsometry were fixed to 28 mM and 35 for all simulations, respectively. For both \(S\) and \(T\), the upper boundary condition is applied over the entire sediment core.

[20] The flux of POM reaching the seafloor which is mineralized in the upper 50 cm is derived from the empirical relationship of Middelburg et al. [1997] between carbon mineralization rate and SFD \((r^2 = 0.69, n = 80, p = 0.0000)\). These authors split the total flux of POM reaching the seafloor into a nonreactive fraction that is buried and a degradable fraction that is mineralized (both fractions having similar magnitudes at the global scale). Assuming that the carbon mineralization rate provides a realistic estimate of the flux of degradable POM reaching the seafloor \((J_{POM, \mu M\ C\ cm^{-2}\ yr^{-1}})\), \(J_{POM}\) can be quantified by:

\[
J_{POM} = 1800 \cdot 10^{(0.5086 - 0.000389 \times \text{SFD})}
\]  

(17)

[21] Note that for water depths >1000 m, \(J_{POM}\) values predicted by equation (17) are in good agreement with the more recent sediment TOU curve developed by Andersson et al. [2004]. Higher fluxes are predicted by equation (17) for shallower water depths, which probably results from the different regression techniques employed in the two studies.

[22] Although the distribution of reducible manganese and iron in marine sediments is well documented at many individual sites [e.g., Canfield et al., 1993; Aller, 1994; Slomp et al., 1997], no estimate is currently available to constrain the deposition flux of the particulate metal oxide along the global hypsometry. We assume that the fluxes for 200 m and 5000 m SFD can be approximated by those derived from previous model studies for shelf and deep sea sediments, respectively [Van Cappellen and Wang, 1995]. Extrapolation to intermediate SFD is then obtained by exponential interpolation. Sensitivity analysis (not shown) revealed that the model output is insensitive to either an exponential or linear interpolation func-

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**Figure 1.** Imposed boundary conditions for \(O_2\), \(NO_3^-\), and temperature. Symbols and error bars show averages and standard deviations of global values.
tion. In view of the uncertainty in constraining the fluxes of Mn and Fe oxides to the seafloor and as using original flux values from Van Cappellen and Wang [1995] led to negligible contribution of these pathways to total POM, these original values are arbitrarily increased by a factor of 100 to increase their sensitivity on POM degradation rates.

2.3.3. Rate of POM Degradation

The oxidation of POM is simulated using a 1-G model approach [Berner, 1980], which assumes a single pool of degradable organic matter of uniform reactivity, described by first order kinetics with respect to POM. The rate constant, \( k_C \) (yr\(^{-1}\)), is obtained from Boudreau [1997] using an expression relating \( k_C \) to \( v_{bur} \):

\[
k_C = 0.38 \cdot v_{bur}^{0.59}
\]

This rate constant is applicable to the more reactive carbon fractions which are degraded within the top 10–20 cm of sediments and more recalcitrant fractions are not considered. As Boudreau admits, this relationship may be biased toward the type of environmental settings from where the data originate. We nonetheless choose to employ this relationship since it is our prime interest to observe how this type of simple relationship impacts carbon degradation globally. Possible artifacts are discussed further below.

3. Results and Discussion

3.1. Concentration and Rate Distributions

Simulated depth concentration profiles of POM, \( O_2 \), \( NO_3^- \), and \( SO_4^{2-} \) for 100, 2000, 3500 and 5000 m are shown in Figures 2a–2d, and respiration pathways are shown in Figures 2e–2h. As expected, the highest surface POM concentrations are found at 100 m water depth (1200 \( \mu mol \) g\(^{-1}\)) compared to the deep ocean (400 \( \mu mol \) g\(^{-1}\)). The POM concentration profiles do not reproduce residual POM concentrations since recalcitrant POM pools are not included and assumed to be nonreactive within the 50 cm model domain. In
general, the flux of POM to the seafloor, which decreases by 2 orders of magnitude from 100 to 5000 m (Table 3), has a greater impact on POM concentrations than its reactivity, which decreases by only 1 order of magnitude. Yet, bioturbation is clearly an important transport mechanism for mixing reactive POM down below the oxic layer where burial velocities in the deep ocean are extremely low (Table 3). For all water depths, the POM concentration is reduced by >99% of the surface concentration by 30 cm depth.

The rate of POC mineralization ($C_{ox}$) is around 50 times greater at 100 m than at 5000 m (Figure 2e). The model-derived rate profiles in Figures 2f–2h show that aerobic respiration is the main pathway for POM degradation if $O_2$ is present (Figure 2b), which is a direct result of the inhibition of carbon degradation by other electron acceptors if $O_2$ is above 8 $\mu$M (see Appendix A). The spatial domain of aerobic respiration increases from <1 cm at 100 m SFD to >10 cm at 5000 m SFD. The large oxygen penetration depths are typical for deep water sediments [Ghed et al., 1994; Glud, 2008]. Simulated oxygen penetration depths also agree well with the global-scale predictions of Meile and Van Cappellen [2003] (Figure 3). Only, at 5000 m SFD, Meile and Van Cappellen [2003] predict a large (>5 cm), yet finite oxygen penetration depth whereas our model predicts oxygen throughout the sediment at very low concentrations. A likely explanation for this artifact is the simulation of a single labile POM pool only. Furthermore, in these deep waters, NO$_3^-$ also persists throughout the sediment and inhibits sulfate reduction (Figure 2c). The zone of denitrification extends from about 8–16 cm in the deep ocean and overlaps the zone of aerobic respiration (Figure 2g). The subsurface preponderance of oxic and suboxic conditions is a characteristic feature of deep sea sediments [e.g., Jørgensen, 1982; Canfield, 1989; Tromp et al., 1995; Jørgensen and Kasten, 2006]. Although barely discernible in Figure 2, in situ production of NO$_3^-$ from biogenic nitrogen causes a slight increase in NO$_3^-$ with depth below the sediment surface (Figure 2c). This simulated effect is in agreement with experimental observations, which show that the subsurface increase in NO$_3^-$ may be even more pronounced. For example, in the deep Pacific Ocean the subsurface NO$_3^-$ increase is >20 $\mu$M within 2 cm below the seafloor [Berelson et al., 1990]. The small increase in NO$_3^-$ in the model simulation results could be because our bottom water $O_2$ concentration at 5000 m (150 $\mu$M) is lower than measured in the Pacific Ocean.

When NO$_3^-$ is exhausted, sulfate reduction is the main pathway for POM mineralization with decreasing rates with increasing water depth (Figure 2h). Overall, the simulated shift from predominant sulfate-based carbon mineralization to aerobic respiration with increasing SFD is in qualitative agreement with field evidence [e.g., Canfield, 1989; Cai and Reimer, 1995; Thamdrup and Canfield, 1996; Jahnke, 1996; Ferdelman et al., 1999; Canfield et al., 2005] and earlier modeling studies [Van Cappellen and Wang, 1995; Tromp et al., 1995; Soetaert et al., 1996]. It is also interesting to observe that, with the exception of the deep abyss (>4250 m, Table 1), downward mixing of labile carbon stimulates sulfate reduction within the mixed layer despite the very low bioturbation rates (1.2 cm$^2$ yr$^{-1}$, Table 3). In all cases, SO$_4^{2-}$ concentration remains above 26 mM (Figure 2d) in the simulated sediment column. In nature it is likely that sulfate concentrations will further decrease with sediment depth due to the oxidation of refractory organic carbon in deeper sediment layers, a process not considered in this study.

Note that on the axes scales of the plots, the depth of aerobic respiration and denitrification consistently exceed the apparent depth of $O_2$ and NO$_3^-$ penetration, although the rates do show a dramatic decrease below the observed penetration depth (Figures 2b and 2f). Solutes are transported to these deeper sediments by bioirrigation, and the incongruities in the concentration and rate profiles are due to rapid turnover of $O_2$ and NO$_3^-$. Meile et
al. [2001] calculated that only 10–20% of total O$_2$ influx is delivered to the aerobic zone, with the remainder being transported by nonlocal mechanisms to greater depths. Overall, the relative importance of bioirrigation to the total solute flux to the sediment is largest at 100 m SFD for O$_2$ and NO$_3$ where it contributes ~50% and 90% of the total flux into the sediment, respectively (Figures 4a and 4b). TOU:DOU ratios above 1 are characteristic of sediments receiving high fluxes of labile carbon [Seiter et al., 2005]. Between 200 m and 3500 m, the relative importance of bioirrigation is much lower for O$_2$ (25%) and NO$_3$ (60%), and at 5000 m, it accounts for <10% of total O$_2$ influx. This agrees with Glud et al. [1994], who showed that that depth-integrated O$_2$ consumption is not statistically different from DOU in deep sea sediments. No data are plotted for NO$_3$ for the deep abyssal sediments because the net solute flux of NO$_3$ is to the ocean (Figure 2c) [Hammond et al., 1996; Hensen et al., 1998].

Bioirrigation is even more important for SO$_4^{2-}$ and accounts for all of the input throughout the ocean (Figure 4c). Even though this may not be wholly representative of coastal sites where highly reactive POM fractions drive a larger diffusive flux gradient, bioirrigation is still a major transport pathway for SO$_4^{2-}$. Recent modeling studies of coastal sediments calculate that 80–90% of SO$_4^{2-}$ transport into the sediment from the seawater occurs through nonlocal processes [Dale et al., 2008a, 2008b]. The increasing importance of bioirrigation to the total rate of solute input follows the order SO$_4^{2-}$ > NO$_3$ > O$_2$ which generally reflects their depth of consumption by C$_{ox}$. For example, aerobic respiration begins immediately at the sediment-water interface, which induces a steeper concentration gradient and, consequently, a higher diffusive flux than both NO$_3$ and SO$_4^{2-}$. The latter is not consumed in the uppermost sediment layers and displays much more vertical concentration gradients (Figure 2d). Transport into the sediment must therefore be dominated by irrigation.

### 3.2. Global Hypsometric Analysis of TEA Fluxes and C$_{ox}$ Rates

Simulated depth-integrated C$_{ox}$ rates (µmol C cm$^{-2}$ yr$^{-1}$) by the primary redox pathways along the global hypsometry are shown in Figures 5a–5e, and the corresponding total fluxes of dissolved (O$_2$, NO$_3$ and SO$_4^{2-}$) and solid (MnO$_2$ and Fe(OH)$_3$) TEAs to the sediment directly from the ocean are shown below in Figures 5f–5j in terms of carbon oxidation potential (µmol C cm$^{-2}$ yr$^{-1}$). TOU is also compared in Figure 5f to the empirical TOU-SFD relationship derived by Andersson et al. [2004]. The solute fluxes are driven by the chemical gradients in the sediment through bioirrigation and diffusion, whereas the solid fluxes are directly determined by the applied boundary conditions.

The C$_{ox}$ rates by each pathway display a decrease with SFD, with the exception of MnO$_2$ reduction which displays an unusual behavior owing to secondary redox cycling (Figures 5a–5e). The decrease is consistent with the imposed decrease of POM flux and reactivity with increasing SFD (Table 3). Observational data for comparison, which are taken from the database compiled by Middelburg et al. [1996, 1997], are only available for aerobic respiration, denitrification and sulfate reduction.
For the shelf sediments (0–350 m water depth), the agreement between the model and observations is favorable for sulfate reduction, but less favorable for aerobic respiration and denitrification whereby the model predicts lower values by up to 200–400 mol cm⁻² yr⁻¹. Note that the average sum of measured rates of aerobic respiration, denitrification and sulfate reduction for the shelf (∼900 μmol C cm⁻² yr⁻¹; Figures 5a, 5b, and 5e) is much higher than the total carbon mineralization rate reported in the same database. The latter is ∼500 μmol cm⁻² yr⁻¹ [Middelburg et al., 1997], which compares well to our modeled TOU mineralization rate (Figure 5f). A similar mineralization rate of 400 μmol cm⁻² yr⁻¹ is also predicted by predicted by the model of Andersson et al. [2004] (Figure 5f).

![Figure 5](image1)

Figure 5. (a–e) Modeled (lines) profiles of carbon mineralization rates along the global hypsometry and (f–j) modeled (lines, open symbols) fluxes of O₂, NO₃⁻, metal oxides, and SO₄²⁻ to the sediment (the rates are converted to carbon units using the stoichiometry of POC degradation; see Appendix A). The diamonds in Figures 5a, 5b, and 5e represent observations taken from the database compiled by Middelburg et al. [1997]. Also plotted in Figure 5f are the TOU estimates using the relationship of Andersson et al. [2004] (denoted “TOU (observed)”) and POC flux in this study (≡TOU) (denoted “TOU (model)”). The points in Figure 5g are observed NO₃⁻ fluxes taken from Middelburg et al. [1996].

![Figure 6](image2)

Figure 6. (a) The relative contribution of O₂, NO₃⁻, and SO₄²⁻ to the total flux of TEAs into the sediment (expressed as a fraction of the total carbon oxidation capacity). (b) The relative contribution of aerobic respiration, denitrification, and sulfate reduction to CO₂. Manganese and iron oxide play a negligible role and are not shown.
for SFD of 0–350 m. When considered collectively, our model provides a good correspondence for TOU at these water depths compared to Middelburg et al. [1997] and Andersson et al. [2004].

The modeled data in Figure 5 are summarized in Figure 6a and Figure 6b as the fractional contribution of each dissolved TEA ($O_2$, $NO_3^-$, $SO_4^{2-}$) to the total electron acceptor flux and $C_{ox}$ rate as a function of SFD, respectively. Both plots are presented on a carbon-equivalent basis. The contribution of $O_2$ to the total TEA flux becomes progressively more important with increasing SFD, from 35% at 100 m to 100% at 5000 m SFD. However, $O_2$ contributes less than 10% to the $C_{ox}$ rate at 100 m SFD (Figure 6b) because most is used to oxidize reduced metabolites (see section 3.3). The contribution of $NO_3^-$ to the TEA flux and $C_{ox}$ rate is less variable, being around 5–10% in both cases which agrees with previous estimates [Middelburg et al., 1996]. Iron oxide contributes only <1% of the TEA and $C_{ox}$ rate, and that of manganese reduction is an order of magnitude lower (data not shown). Because the depositional fluxes of iron and manganese oxide are poorly constrained, the significance of these latter values is uncertain, and important contributions of iron and manganese reduction may be highly localized [Canfield et al., 1993; Van Cappellen and Wang, 1996]. Around 60% of total carbon oxidation potential between 100 and 2000 m is supplied by $SO_4^{2-}$ (Figure 6a), yet in situ sulfide oxidation leads to sulfate-based carbon mineralization rates which contribute ~80% to the total $C_{ox}$ rate at these depths. The relative importance of $SO_4^{2-}$ decreases sharply below 2000 m, and at 5000 m $SO_4^{2-}$ is not used in carbon mineralization.

Globally integrated fluxes and carbon mineralization rates are presented in Table 4. The continental shelf between 0 and 150 m, corresponding to ~6% of the seafloor (Table 1), is responsible for 52% of global sulfate reduction (8 Tmol $SO_4^{2-}$/yr$^{-1}$) and 45% of the global TOU of 21 Tmol yr$^{-1}$. Considering that TOU is equivalent to POC flux and ignoring the small loss of ODU released as $N_2$ during denitrification (~3% of total carbon equivalents), the inner shelf thus also receives 45% of the global deposition flux of POC. The continental shelf as a whole is responsible for 55% of total $O_2$ uptake and 64% of sulfate reduction. This compares to 61% and 64%, respectively, for the shelf (0–200 m) calculated by Jørgensen and Kasten [2006] for the data compiled by Canfield [1993] and Canfield et al. [2005]. The shelf is also highly significant for reactive iron input (84% of total flux) and reduction rates (83% of total). Denitrifi-
cation, on the other hand, is more evenly distributed throughout the ocean, with 34% taking place on the shelf, 29% on the slope and 37% in the abyss. Over half of all denitrification occurs at SFD below 1500 m by virtue of the large expanse of slope and abyssal sediments. Denitrification removes around 1.1 Tmol NO$_3^-$/C yr$^{-1}$ from the ocean, which is less than 1.6–2 Tmol yr$^{-1}$ calculated by the model of Middelburg et al. [1996], who considered the degradable POC to consist of two pools with different reactivity. In the deepest SFD interval, comprising 48% of the seafloor, oxidation of reduced biogenic nitrogen sustains a small efflux of NO$_3^-$ from the sediment equivalent to 2% of global benthic NO$_3^-$ uptake. Further, because the POM reaching the seafloor is particularly recalcitrant (Table 3), these deep abyssal sediments consume only 11% of the global O$_2$ flux.

Further insight into the model performance can be gained by comparison with the literature TOU data (Figure 7a). Even though the relative TOU distribution with SFD discussed above compares well to other studies, it can be seen that the model predicts higher values than those observed by Andersson et al. [2004] for the outer shelf and midslope to upper slope and lower values for the lower slope and the abyss. Additionally, the model always predicts higher TOU than predicted by Canfield et al. [2005]. The implications of this are twofold. First, assuming that the true TOU lies somewhere between the Canfield and Andersson models, the global statistical relationship for quantifying reactive carbon fluxes based on SFD (equa-

![Figure 7.](image)

**Figure 7.** (a) Experimentally derived TOU data grouped according to ocean margin type from two literature sources versus TOU data derived for the reaction-transport model approach. The arrow indicates possible downslope transport of carbon from the shelf in nepheloid layers. (b) Rates of sulfate reduction converted to carbon units by multiplying by 2 versus TOU data grouped according to ocean margin type. The black diamonds are data from Canfield et al. [2005] modified after Jørgensen and Kasten [2006], and the white diamonds are model data. No sulfate reduction is predicted for the deep abyss by the model, and this point is located on the TOU axis.
Figure 5e, where modeled rates (10–100 cm$^{-2}$ m$^{-1}$ yr$^{-1}$) are greater than the values reported in the data set of Canfield et al. [2005]. The straight lines on the log-log plot represent equal TEA fluxes and $C_{ox}$ rates by each primary redox pathway is positively correlated with the total flux of TEA into the sediment. The model-derived data across the SFD intervals are synthesized into a normalized plot of $C_{ox}$ rate versus TEA flux, both axes presented on a carbon-equivalent basis (Figure 8). The 1:1 line indicates equal TEA fluxes and $C_{ox}$ rates. The $C_{ox}$ rate for each primary redox pathway is positively correlated with the total flux of TEA into the sediment. No correlation was obtained for MnO$_2$. For O$_2$, the rate of aerobic respiration is a factor of 5 smaller than the O$_2$ flux (slope = 0.18). In contrast, the $C_{ox}$ rates using NO$_3^-$, Fe(OH)$_3$ and SO$_4^{2-}$ are larger than 1. In situ production of NO$_3^-$, Fe(OH)$_3$ and SO$_4^{2-}$ through oxidation of NH$_4^+$, Fe$^{2+}$, FeS and H$_2$S by O$_2$ explains these observations. This is clearly an important source of SO$_4^{2-}$, considering the large contribution of sulfate reduction to carbon respiration (Figure 6 and Table 4). The steep slope for Fe(OH)$_3$ reflects intense recycling within the sediment, and indicates that each iron atom is recycled about 8 times before burial or transport back to the water column. The production of NO$_3^-$ from biogenic nitrogen (i.e., NH$_4^+$) occurs at all SFD, and the slope of 1.29 indicates that biogenic nitrogen is a significant source of NO$_3^-$ but remains quantitatively less important by a factor of 4 than the influx of NO$_3^-$ from the ocean. The fraction of the depth-integrated denitrification rate supported by biogen-
ic nitrogen may be significantly higher in oxygen minimum zones over the continental margins [Devol, 1991; Archer et al., 2002]. Data compiled by Canfield [1993] seem to suggest that when O$_2$ availability falls below ~20 μM a greater fraction of carbon oxidation occurs with NO$_3^-$ than with O$_2$. These low concentrations are not globally representative, however, and in our simulations O$_2$ was always above 100 μM.

The sink pathways of NH$_4^+$, Mn$^{2+}$, Fe$^{2+}$ and H$_2$S with SFD are shown in Figure 9 as relative and absolute values. The data exclude the 5000 m SFD interval because the high O$_2$ penetration depth (Figure 2b) prohibits significant production of these reduced species in the surface sediments. Major sinks on shelf and slope sediments (SFD < 2000 m) include bioirrigation out of the sediment for NH$_4^+$ and H$_2$S, and oxidation for Mn$^{2+}$ and Fe$^{2+}$. Losses by diffusion across the sediment-water interface are only important for NH$_4^+$. Precipitation of FeS accounts for 30% of the H$_2$S sink in shallow water depths, yet as precipitation takes place in the bioturbated zone 99% of the FeS is subsequently reoxidized to sulfate by O$_2$ (resulting in maximum concentrations of buried FeS around 10 μmol g$^{-1}$ at shallow SFD; data not shown). The reoxidation of Fe$^{2+}$ to Fe(OH)$_3$ by MnO$_2$ demonstrates a close coupling of the manganese and iron cycles. Relatively less Fe$^{2+}$ is oxidized by O$_2$ because MnO$_2$ is the first oxidant encountered by Fe$^{2+}$ as it diffuses upward. The model does not consider Fe$^{2+}$ oxidation by NO$_3^-$, which may also compete with MnO$_2$ for Fe$^{2+}$ [Dhakar and Burdige, 1996].

It is important to note that direct losses of H$_2$S to the ocean by diffusion and bioirrigation are a significant sink of reducing equivalents throughout most of the ocean (Figure 9d). This ODU loss is equivalent to 11 Tmol O$_2$ yr$^{-1}$ (Table 4), and means that DOU measurements would account for 50% of TOU. The additional flux of NH$_4^+$ originating from PON, which is not included in the ODU flux value in Table 4, is equal to 3.2 Tmol O$_2$ yr$^{-1}$. It is thus remarkable that approximately half of the oxygen demand which enters the
sediment as POC is lost from the sediment by efflux to the ocean as ODU. This effect decreases with SFD (Figure 9) because higher O₂ penetration effectively traps the ODUs in the sediment by oxidation and prevents their escape to the water column. This important result requires that the imposed rate of bioirrigation determined from semiempirical statistical functions [Meile and Van Cappellen, 2003] and, more importantly, the irrigation attenuation with depth (3.5 cm⁻¹ assumed constant throughout the ocean) are realistic. If the irrigation depth is too high, then H₂S will be flushed from the system and escape in situ oxidation. While data from the oligotrophic Bermuda Time Series site suggest that diffusion dominates solute transport in the deep sea [Sayles and Martin, 1995], Glud et al. [1994] observed that TOU exceeded DOU in deep Atlantic sediments by 1–3 times. In this case though, they attributed the excess oxygen uptake to the formation of oxic surfaces on burrow walls as well as respiration by the animals rather than sulfide escape. The fact remains that reliable and spatially resolved data of irrigation depths calculated using geochemical tracers (e.g., Br⁻) in the different biogeochemical provinces of the seafloor [e.g., Seiter et al., 2005] is not available. It is our view that this is currently the largest obstacle to be surmounted before a global assessment of subsurface solute transport and nonlocal solute exchange with bottom waters can be made.

[39] The results nevertheless allow us to speculate on the role of bioirrigation in more practical terms. On the basis of benthic chamber TOU experiments, it has been argued that up to 95% of sulfide produced in marine sediments is oxidized to sulfate [Jorgensen, 1977a, 1977b]. This figure is derived from mass balance closure of the sulfur cycle as the difference between sulfur burial and sulfate reduction. Our model provides further insight into the sulfur cycle, and predicts that 30% of sulfide (as H₂S and FeS) is oxidized in situ, with the remainder lost to the ocean by bioirrigation of H₂S. Laying aside for the moment the concerns over the depth-integrated bioirrigation rate, if this sulfide were to be rapidly oxidized in the overlying water then by mass balance closure our model would predict that close to 100% of sulfide is oxidized and that a large fraction of the O₂ flux (76%) is involved in the reoxidation of sulfide. It is generally assumed that the contribution to TOU by sulfide oxidation takes place in the oxic and suboxic surface sediment layers, although on the basis of the model results presented here we would argue that the largest proportion is oxidized above the sediment. Dissolved sulfide is not routinely measured in chambers, although Linke et al. [2005] showed that sulfide may not become detectable until O₂ is depleted. Rapid chemical sulfide oxidation by O₂ [Millero et al., 1987; Buisman et al., 1990] could potentially maintain very low concentrations of sulfide above the seafloor and disguise the sulfide irrigation flux. Again, more information on irrigation depths would resolve this issue definitively.

3.4. Uncertainty of Model Predictions

[40] The presented model predictions (as is the case for model predictions in general) are subject to uncertainties introduced during the model design and parameterization. Simplifications in model structure concern the choice of the reaction network and the description of transport and reaction processes which inadvertently lead to idealized representations of reality. For instance, nutrients such as phosphorus [e.g., Katsev et al., 2006] or trace elements [e.g., Canavan et al., 2007] are excluded from the reaction network. This choice was guided by the lack of evidence for a major, global control of these species on the primary and secondary redox reactions investigated here. Precipitation/dissolution processes of alkaline earth metal minerals [e.g., Luff and Wallmann, 2003; Arndt et al., 2006], adsorption kinetics [e.g., Van Cappellen and Wang, 1996], and redox reactions involved in methane cycling [e.g., Dale et al., 2008a, 2008b] are ignored here. The dissolved concentration of iron and manganese may nevertheless be affected directly or indirectly by precipitation or sorption, but because of the high uncertainty in the boundary conditions for metal oxides, it was chosen to ignore the influence of these additional processes on iron and manganese cycling. Furthermore, methanogenesis only really needs to be considered when combined with the degradation of refractory carbon at larger sediment depths, and is considered to account for 5% of total carbon mineralization [Jorgensen and Kasten, 2006].

[41] Simplifications concerning the rate laws are primarily centered on the 1-G description of the carbon degradation model. This approach is conceptually attractive since more complex formulations require additional parameters which are
unknown in the context of global-scale applications. The 1-G model neglects, however, the very labile organic material which is decomposed close to the sediment surface as well as the recalcitrant carbon pools present at large sediments depths. The degradation of these highly reactive and refractory pools would have opposite effects on the relative contribution of the various metabolic pathways of organic matter decomposition. Higher rates near the SWI would steepen oxygen profiles and, thus, promote higher oxygen fluxes and aerobic degradation rates. Carbon oxidation at large depth would lead to increased sulfate-reduction rates and, eventually, to the onset of methanogenesis and methane oxidation [Dale et al., 2008b]. A decrease of POM oxidation rate for the different degradation pathways along the redox gradient would have similar effects. Yet, the overall quantitative effect of these additional carbon pools on redox cycling cannot currently be predicted at the global scale. It is, however, likely that the results will ultimately depend on choice of which carbon degradation model (e.g., multi-G [Westrich and Berner, 1984]; power law [Middelburg, 1989]; reactive continuum [Boudreau and Ruddick, 1991; Tromp et al., 1995]) is most adequate to describe the complexity of organic matter degradation [e.g., Brüchert and Arnosti, 2003]. Furthermore it has not yet been determined whether model predictions would be affected by the explicit inclusion of microbial biomass into reaction kinetics as suggested elsewhere [Wirtz, 2003; Thullner et al., 2005, 2007].

Uncertainties have also been introduced during the implementation of transport processes and include the assumption of constant porosity and the use of simplified functional dependencies to define bioirrigation and bioturbation intensities with depth. As in the upper most part of the sediment the latter two processes have been shown here to be dominant for species transport, whereas the variations in advection through burial triggered by porosity changes will only have a minor impact on the model results. It should be noted that the volume of the solid matrix can change significantly due to porosity variations but the combined effect of porosity and bioturbation on the distribution of solid species is not straightforward [Mulson et al., 1998] even though bioturbation is dominant in the uppermost part of the sediment. Teal et al. [2008] showed that global-scale estimates for bioturbation depths and intensities are subject to high uncertainties caused among others by measurement results depending on the applied experimental method and by sampling sites unevenly distributed at the global scale. An increase in bioturbation is assumed to shift carbon degradation activities toward larger sediment depths, a process which would favor sulfate reduction over aerobic degradation [Meysman et al., 2005]. Bioirrigation is a major transport process for dissolved species, especially at shallow SFD (Figure 4). In the absence of bioirrigation, the dominance of sulfate reduction would even be more pronounced (results not shown). Higher bioirrigation rates than those used here would increase the supply of oxygen to the sediment, hence favoring aerobic degradation.

All parameters used in this study are subject to uncertainties. Intuitively, model results should be most sensitive to variations in parameters that are directly controlling the fluxes of POM and TEAs as well as the rate of organic carbon oxidation. For instance, using a power law dependency instead of an exponential dependency of POM fluxes on SFD as done previously [e.g., Middelburg et al., 1997] and also adopted in this study would lead to a greater contribution of deep sea sediments to global carbon oxidation and to much higher global carbon mineralization rates [Glud, 2008] than reported elsewhere. Consequently, the contribution of the different degradation pathways at the global scale would be altered. However, advanced sensitivity analyses of complex nonlinear systems have revealed that a priori ranking of parameters concerning the associated uncertainty of model results is not recommendable [e.g., Holstein and Wirtz, 2009]. Detailed and systematic sensitivity analyses should thus be performed in the future to determine if the most poorly constrained parameters (e.g., depth of irrigation and bioturbation, carbon reactivity, boundary conditions for iron and manganese and rate constants for secondary reaction rates) are also the largest sources of uncertainty for the shown model results. Future research should also address how the uncertainty in model prediction could be reduced most, especially whether more detailed models depending on a large number of poorly constrained parameters are better suited than simplified models depending on less, better constrained parameter values when it comes to improving confidence in model predictions.
3.5. Synthesis and Implications

[44] Using a reaction-transport model approach, we have quantified the global benthic carbon mineralization in the seafloor (21 Tmol C yr$^{-1}$). This flux, assumed to be equivalent to carbon-based TOU, is in good agreement with previous experimental estimates of TOU on a global basis and in satisfactory agreement with TOU estimates on a depth-resolved basis. This lends support to a controversial finding of this study, that is, carbon degradation is dominated by sulfate reduction at all SFD except in the deep abyss. The global contribution of sulfate-based POC mineralization (76%) is higher than previous estimates (25–65%) because of the higher contribution from deep sea sediments (~2750–4250 m). Aerobic respiration becomes increasingly important with SFD, yet accounts for only 15% of global POC mineralization. Higher rates of aerobic mineralization at the expense of sulfate reduction would bring our model predictions of sulfate-based carbon mineralization into line with the literature.

[45] Current estimates of integrated sulfate reduction rates for the deep sea, where sulfate penetrates $10^1$–$10^2$ m, are mainly inferred from the diffusive flux calculated from deep sea drilling project (DSDP) pore water concentration profiles well below the surface [Canfield et al., 2005]. This provides an estimate for net sulfate reduction rates and is only valid if no production or consumption occurs over the linear concentration gradient from which the flux is calculated. Sulfide oxidation in reducing microenvironments within the sulfate reduction zone [Jorgensen, 1977b] or by reactive iron mineral phases [Raiswell and Canfield, 1996] could lead to an underestimation of sulfate reduction rates calculated in this way. Our model provides an additional indication that sulfate reduction could be occurring in deep sea sediments relatively close to the sediment-water interface where sulfate concentration profiles are vertical (Figure 2d). Detection of sulfate reduction from dissolved sulfide concentrations may also not be possible because of sulfide trapping into iron sulfides followed by mixing into the suboxic surface layers by bioturbation and reoxidation. This could potentially allow sulfate reduction to bypass visual inspection or even experimental detection [Froelich et al., 1979]. Along similar lines, the strikingly linear sulfate concentration profiles in slope sediments of the southeast Atlantic published by Fossing et al. [2000] and attributed to bioirrigation of sulfate suggests much lower rates of sulfate reduction than were measured by $^{35}$S incubation studies. A careful assessment of sulfate reduction rates in lower slope and abyssal sediments, if at all possible using current analytical methodologies given the above complicating factors, should be viewed as a research priority.

[46] All the above brings into question previous results which show that 100 to 1000 times more POC is oxidized by $O_2$ than by sulfate in deep sea sediments [Canfield et al., 2005]. Mackin and Swider [1989] used an analytical model to determine the controls on aerobic respiration versus sulfate reduction. Through sensitivity analysis, they noted that respiration of $C_{org}$ by $O_2$ will only exceed 20% of $C_{ox}$ if (1) the reactive carbon attenuates rapidly with depth, (2) $C_{ox}$ is very low, and (3) bioturbation is prevalent. These effects will increase the penetration of oxygen in the sediment and, consequently, the oxygen exposure time (OET). Increased OET enhances $C_{org}$ degradation [Hartnett et al., 1998], and so will reduce the fraction degraded by sulfate. Implementation of the OET concept in the model can be done simply by defining a higher rate constant (equation (18)) for aerobic mineralization [Tromp et al., 1995] or by including an additional labile pool of $C_{org}$ [Middelburg et al., 1996; Soetaert et al., 1996; Archer et al., 2002]; see also section 3.4. Our view is that first resolving the discrepancies in irrigation depth and deep-sea sulfate reduction rates is needed before addressing the question of the appropriate carbon degradation model.

4. Summary and Conclusions

[47] In the present study early diagenetic processes in marine sediments and the resulting fluxes of reactive species were simulated using a reactive transport modeling approach. Using the SFD as master variable and defining globally averaged environmental conditions as input data for the simulation of individual SFD intervals resulted in realistic concentration and reaction rate profiles inside the sediment. When making a SFD resolved comparison between experimental data presented in the literature and simulated sediment depth integrated carbon oxidation rates and fluxes of species across the sediment-water interface, some quantitative discrepancies between our
### Table A1. Primary Cools Pathways, Stoichiometries, and Rate Laws $r_i$, Implemented in the Reaction Network

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Stoichiometry</th>
<th>Reaction Rate (per Mol Carbon) $r_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic degradation</td>
<td>$\text{HCO}_3^{-} + \text{O}_2 + 2\text{H}^+ \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>$r_{\text{OA}} = k_{\text{OA}} \cdot c_{\text{HCO}<em>3^{-}} \cdot c</em>{\text{O}_2}$</td>
</tr>
<tr>
<td>Denitrification</td>
<td>$\text{HPO}_4^{2-} + 2\text{NO}_3^{-} + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{N}_2 + 2\text{CO}_2 + \text{O}_2$</td>
<td>$r_{\text{DN}} = k_{\text{DN}} \cdot c_{\text{HPO}<em>4^{2-}} \cdot c</em>{\text{NO}_3^{-}}$</td>
</tr>
<tr>
<td>Manganese reduction</td>
<td>$\text{MnO} + \text{HPO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{Mn}^{2+} + 2\text{CO}_2$</td>
<td>$r_{\text{MnR}} = k_{\text{MnR}} \cdot c_{\text{MnO}} \cdot c_{\text{HPO}_4^{2-}}$</td>
</tr>
<tr>
<td>Iron reduction</td>
<td>$\text{Fe(OH)}_3 + \text{H}_2\text{PO}_4^{-} + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{Fe}^{3+} + 2\text{CO}_2 + \text{O}_2$</td>
<td>$r_{\text{FeR}} = k_{\text{FeR}} \cdot c_{\text{Fe(OH)}<em>3} \cdot c</em>{\text{H}_2\text{PO}_4^{-}}$</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>$\text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} + 2\text{CO}_2$</td>
<td>$r_{\text{SR}} = k_{\text{SR}} \cdot c_{\text{SO}_4^{2-}}$</td>
</tr>
</tbody>
</table>

- $k_{\text{DN}}$, $k_{\text{MnR}}$, and $k_{\text{FeR}}$ are first-order rate constants.
- The half-saturation constant (see Table A3) and $k$ is a first-order rate constant.
- The Redfield ratio $x/y/z$ is set to 106/12/1. Phosphate concentration changes are not included into the simulations.

[48] The results of our study indicate that in marine sediments at the global-scale sulfate reduction might be a more important organic oxidation pathway than previously assumed. Although the deep abyss is characterized by mainly aerobic conditions, the high total oxidation rates in shelf sediments results in these shallow (mainly sulfate reducing) SFD being responsible for most of the global carbon oxidation and resulting fluxes of redox species. Furthermore, bioirrigation is a major contributor to dissolved species fluxes across the sediment-water interface. This indicates that flux estimates based on diffusion profiles might lead to an underestimation of species fluxes. Bioirrigation also allows reduced species to be transported back to the water column before their reoxidation in the sediment. This can lead to an inequality between net oxygen uptake into the sediments and total carbon oxidation rates and thus to a potential underestimation of carbon oxidation rates in marine sediments if they are derived from dissolved oxygen uptake.

[49] Future steps to improve the validity of the model predictions on global mineralization pathways and species fluxes would include a regionalization of the SFD-parameter relations used in this study. This regionalization should focus mainly on shelf sediments, as these sediments contribute most to the global rates and species fluxes and are most affected by terrestrial and climatic influences resulting in a higher variability than observed for deeper SFD. In addition, more experimental data on the relevance of bioirrigation and of individual carbon oxidation pathways at various environmental conditions would help to improve our understanding of these sediment systems and their contribution to global element cycles.

### Appendix A: Reaction Network and Reaction Rate Parameters

[50] Tables A1 and A2 provide a list of stoichiometries and rate laws for all reactions implemented in the model (reaction network from Van Cappellen and Wang [1995]). Parameter values for the reac-
<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 ( \text{NH}_3^+ + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{CO}_2 + 3\text{H}_2\text{O} )</td>
<td>( r_1 = k_1 \cdot c_{\text{NH}<em>3^+} \cdot c</em>{\text{O}_2} )</td>
</tr>
<tr>
<td>R2 ( \text{Mn}^{2+} + 1/2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{MnO}_2 + 2\text{CO}_2 + \text{H}_2\text{O} )</td>
<td>( r_2 = k_2 \cdot c_{\text{Mn}^{2+}} \cdot c_{\text{O}_2} )</td>
</tr>
<tr>
<td>R3 ( \text{Fe}^{2+} + 1/4\text{O}_2 + 2\text{HCO}_3^- + 1/2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{CO}_2 )</td>
<td>( r_3 = k_3 \cdot c_{\text{Fe}^{2+}} \cdot c_{\text{O}_2} )</td>
</tr>
<tr>
<td>R4 ( 2\text{Fe}^{2+} + \text{MnO}_2 + 2\text{HCO}_3^- + 2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + \text{Mn}^{2+} + 2\text{CO}_2 )</td>
<td>( r_4 = k_4 \cdot c_{\text{Fe}^{2+}} \cdot c_{\text{MnO}_2} )</td>
</tr>
<tr>
<td>R5 ( \text{H}_2\text{S} + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{SO}_4^{2-} + 2\text{CO}_2 + \text{H}_2\text{O} )</td>
<td>( r_5 = k_5 \cdot c_{\text{H}<em>2\text{S}} \cdot (c</em>{\text{H}<em>2\text{S}} + c</em>{\text{HCO}_3^-}) )</td>
</tr>
<tr>
<td>R6 ( \text{H}_2\text{S} + \text{MnO}_2 + 2\text{CO}_2 \rightarrow \text{Mn}^{2+} + \text{S}^0 + 2\text{HCO}_3^- )</td>
<td>( r_6 = k_6 \cdot c_{\text{MnO}<em>2} \cdot (c</em>{\text{H}<em>2\text{S}} + c</em>{\text{HCO}_3^-}) )</td>
</tr>
<tr>
<td>R7 ( \text{H}_2\text{S} + 2\text{Fe(OH)}_3 + 4\text{CO}_2 \rightarrow 2\text{Fe}^{2+} + \text{S}^0 + 4\text{HCO}_3^- + \text{H}_2\text{O} )</td>
<td>( r_7 = k_7 \cdot c_{\text{Fe(OH)}<em>3} \cdot (c</em>{\text{H}<em>2\text{S}} + c</em>{\text{HCO}_3^-}) )</td>
</tr>
<tr>
<td>R8 ( \text{FeS} + \text{O}_2 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} )</td>
<td>( r_8 = k_8 \cdot c_{\text{FeS}} \cdot c_{\text{O}_2} )</td>
</tr>
<tr>
<td>R9 ( \text{Mn}^{2+} + 2\text{HCO}_3^- \rightarrow \text{MnCO}_3 + \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>( r_9 = \left( k_9 \cdot H^+ \left( \frac{c_{\text{Mn}^{2+}} \cdot c_{\text{CO}<em>3^-} \cdot 1}{K</em>{\text{MnCO}<em>3}} \right) \right) \cdot \left( \frac{c</em>{\text{Mn}^{2+}} \cdot c_{\text{CO}<em>3^-} \cdot 1}{K</em>{\text{MnCO}_3}} \right) )</td>
</tr>
<tr>
<td>R10 ( \text{Fe}^{2+} + 2\text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>( r_{10} = \left( k_{10} \cdot H^+ \left( \frac{c_{\text{Fe}^{2+}} \cdot c_{\text{CO}<em>3^-} \cdot 1}{K</em>{\text{FeCO}<em>3}} \right) \right) \cdot \left( \frac{c</em>{\text{Fe}^{2+}} \cdot c_{\text{CO}<em>3^-} \cdot 1}{K</em>{\text{FeCO}_3}} \right) )</td>
</tr>
<tr>
<td>R11 ( \text{Fe}^{2+} + \text{H}_2\text{S} + 2\text{HCO}_3^- \rightarrow \text{FeS} + 2\text{CO}_2 + 2\text{H}_2\text{O} )</td>
<td>( r_{11} = \left( k_{11} \cdot H^+ \left( \frac{c_{\text{Fe}^{2+}} \cdot c_{\text{H}<em>2\text{S}} \cdot 1}{K</em>{\text{FeH}<em>2\text{S}}} \right) \right) \cdot \left( \frac{c</em>{\text{Fe}^{2+}} \cdot c_{\text{H}<em>2\text{S}} \cdot 1}{K</em>{\text{FeH}_2\text{S}}} \right) )</td>
</tr>
<tr>
<td>R12 ( \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} )</td>
<td>thermodynamic equilibrium</td>
</tr>
<tr>
<td>R13 ( \text{H}^+ + \text{CO}_3^- \leftrightarrow \text{HCO}_3^- )</td>
<td>thermodynamic equilibrium</td>
</tr>
<tr>
<td>R14 ( \text{H}^+ + \text{H}_2\text{S} \leftrightarrow \text{H}_2\text{S} )</td>
<td>thermodynamic equilibrium</td>
</tr>
</tbody>
</table>

\(^a\) (R1)–(R8), secondary redox reactions; (R9)–(R11), nonredox mineral precipitation/dissolution; (R12)–(R14), acid-base equilibria. \( H^+ \) is the Heaviside operator with \( H^+(x) = 1 \) for \( x \geq 0 \), and \( H^+(x) = 0 \) for \( x < 0 \). \( k_i (i = 1, \ldots 11) \) denote all reaction rate parameters.
tion rate laws are given in Table A3 as function of the seafloor depth (SFD).

## Acknowledgments

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