Methane efflux from marine sediments in passive and active margins: Estimations from bioenergetic reaction–transport simulations

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Abstract

A simplified version of a kinetic–bioenergetic reaction model for anaerobic oxidation of methane (AOM) in marine sediments (Dale, A.W., Regnier, P., Van Cappellen, P., 2006. Bioenergetic controls on anaerobic oxidation of methane (AOM) in coastal marine sediments: a theoretical analysis. Am. J. Sci. 306, 246–294.) is used to assess the impact of transport processes on biomass distributions, AOM rates and methane release fluxes from the sea floor. The model explicitly represents the functional microbial groups and the kinetic and bioenergetic limitations of the microbial metabolic pathways involved in AOM. Model simulations illustrate the dominant control exerted by the transport regime on the activity and abundance of AOM communities. Upward fluid flow at active seep systems restricts AOM to a narrow subsurface reaction zone and sustains high rates of methane oxidation. In contrast, pore-water transport dominated by molecular diffusion leads to deeper and broader zones of AOM, characterized by much lower rates and biomasses. Under steady-state conditions, less than 1% of the upward dissolved methane flux reaches the water column, irrespective of the transport regime. However, a sudden increase in the advective flux of dissolved methane, for example as a result of the destabilization of methane hydrates, causes a transient efflux of methane from the sediment. The benthic efflux of dissolved methane is due to the slow growth kinetics of the AOM community and lasts on the order of 60 years. This time window is likely too short to allow for a significant escape of pore-water methane following a large scale gas hydrate dissolution event such as the one that may have accompanied the Paleocene/Eocene Thermal Maximum (PETM).

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1. Introduction

Anoxic marine sediments constitute by far the largest methane (CH₄) reservoir on Earth, either dissolved in the interstitial water or as condensed gas hydrates. On a global scale, the latter contain between 10,000 and 22,000 Gt of carbon (Gt=10¹⁵ g) (Dickens, 2001), with a mean ¹³C isotopic composition of −60‰ (Kvenvolden et al., 1993). Fluxes of CH₄ to the atmosphere from hydrates have been suggested to be a key forcing of the climate system (Archer and Buffett, 2005) and associated with climatic oscillations in the geological past (Kennett et al., 2000). Modern marine sediments, however, account for only 3% of the global CH₄ flux to the atmosphere (Reeburgh, 2003) because most of the CH₄ is consumed before reaching the seafloor through anaerobic oxidation of methane (AOM). Despite its global significance, the mechanism of AOM is still uncertain (Boetius et al., 2000;
Hinrichs et al., 1999). It is thought to be carried out by a syntrophic association of methane-oxidizing archaea and sulfate-reducing bacteria (Boetius et al., 2000). The net AOM reaction consumes methane and sulfate (SO\textsuperscript{2−}) and produces sulfide (HS\textsuperscript{−}) and carbonate alkalinity (HCO\textsubscript{3}\textsuperscript{−}), according to:

\[
\text{CH}_4(aq) + \text{SO}_4^{2−}(aq) \rightarrow \text{HS}_2(aq) + \text{H}_2\text{O}(l) + \text{HCO}_3^−(aq)
\]  

(1)

The highest AOM rates are found in cold-seep environments, where high CH\textsubscript{4} fluxes are sustained by upward advection of pore-water flow (Luff and Wallmann, 2003). The upward fluid flow may arise from a variety of processes, such as hydrate dewatering induced by tectonic uplift or hydrate dissolution due to geothermal gradients (Suess et al., 1999). The dissolved CH\textsubscript{4} is then mostly consumed at a geochemical boundary termed the sulfate-methane transition zone (SMTZ), where SO\textsubscript{4}\textsuperscript{2−} concentrations typically fall from seawater values (~28 mM) to sub-mM levels within a few cm below the sea floor. Biomass concentrations also show maximum values in this highly active zone and may form a thick mat at the sediment surface (Treude et al., 2003).

From a global perspective, however, the bulk of AOM occurs in passive continental shelf sediments where pore-water solute transport occurs mainly by molecular diffusion. In these systems, the SMTZ extends over a greater depth interval, and is generally located between 1–10 m below the sediment surface.

Despite considerable effort to quantify CH\textsubscript{4} flux from the sea floor (Luff and Wallmann, 2003; Tryon and Brown, 2001; Wallmann et al., 2006; Torres et al., 2002; Mau et al., 2006; Haese et al., 2003; Linke et al., 2005; Sommer et al., 2006), the effects of the macroscopic transport regime on the AOM efficiency and CH\textsubscript{4} turnover remain equivocal. Early diagenetic models of CH\textsubscript{4} generally assume a steady-state biomass and ignore the role of microbial bioenergetics. Most commonly, a bimolecular expression for AOM rate (Luff and Wallmann, 2003; Haese et al., 2003; Sommer et al., 2006; Wallmann et al., 2006; Van Cappellen and Wang, 1996) is used:

\[
\text{Rate} = k_{\text{AOM}}[\text{SO}_4^{2−}][\text{CH}_4]
\]  

(2)

where \(k_{\text{AOM}}\) is an apparent second-order rate constant (concentration\textsuperscript{−1}time\textsuperscript{−1}). In the case of AOM, the very small energetic yields and low growth rates are likely to play a major role in the response of AOM to changes in the fluid flow regime and CH\textsubscript{4} transport rates. These effects, however, cannot be accounted for by the above rate equation.

In this work, a model coupling microbial activity and transport is used to explore the impact of externally-impressed fluid flow on biomass distributions, metabolism and, ultimately, on CH\textsubscript{4} fluxes in marine sediments. A reduced version of the reaction network developed by Dale et al. (2006) was incorporated into a reactive-transport model software (Aguilera et al., 2005). The model explicitly simulates functional biomasses, and accounts for kinetic and bioenergetic constraints on biomass synthesis and substrate turnover. The first part of the paper investigates two representative steady-state baseline scenarios with contrasting macroscopic transport regimes; a passive, non-seep, margin in which transport is dominated by molecular diffusion (diffusion-dominated system, DDS), and an active seep system in which upward advection of pore water is the dominant solute transport term (advection-dominated system, ADS). The second part focuses on the transient evolution of biomass distribution and CH\textsubscript{4} efflux following changes in the upward advective CH\textsubscript{4} supply. Finally, the biomass response to fluid flow is used to assess the importance of AOM in delivering large quantities of isotopically-light carbon to the ocean–atmosphere during hydrate dissolution scenarios.

2. Modeling strategy

2.1. Physical aspects

The biomass-explicit model simulates the depth profiles of the pore-water concentrations of methane (CH\textsubscript{4}), sulfate (SO\textsubscript{4}\textsuperscript{2−}) and hydrogen (H\textsubscript{2}), as well as the microbial biomasses of sulfate-reducing bacteria (\(B_{\text{SRB}}\)), methanogenic archaea (\(B_{\text{MET}}\)) and methane-oxidizing archaea (\(B_{\text{MOA}}\)). The biomasses are assumed to be attached to particle surfaces. Three microbially-mediated reactions are considered: hydrogenotrophic sulfate reduction (hySR), hydrogenotrophic methanogenesis (hyME) and AOM (Table 1).

The one-dimensional mass-conservation equations for the solutes and biomasses are (Berner, 1980; Boudeau, 1997):

\[
\phi \frac{\partial C_j}{\partial t} = \frac{\partial}{\partial x} \left( \phi \rho D_s \frac{\partial C_j}{\partial x} \right) - \frac{\partial (\rho \cdot v \cdot C_j)}{\partial x} + \phi R_j
\]  

(3a)

Biomasses:

\[
(1 - \phi) \frac{\partial B_i}{\partial t} = (1 - \phi) R_i
\]  

(3b)

where \(x\) is depth (positive downwards), \(\phi\) is porosity, \(t\) is time, \(C_j\) and \(B_i\) are the time- and depth-dependent
concentrations of the solutes and biomass groups considered, $D_S$ is the tortuosity-corrected molecular diffusion coefficient (see Appendix), $v$ is the vertical upward fluid flow velocity, $R_J$ is the rate of change of $C_J$ due to biogeochemical reactions, and $R_I$ is the net growth or decay rate of $B_I$ (see Section 2.2). Note that although $v$ has a negative sign, all fluid flow velocities are reported from here on as absolute values. For the DDS and ADS baseline scenarios, $v$ equals 0 and 10 cm y$^{-1}$, respectively.

In Eqs. (3a) and (3b) bioturbation and bioirrigation are not considered. Biologically-enhanced transport was found to be negligible at Hydrate Ridge seeps (Luff and Wallmann, 2003), while in the DDS simulations the depth of the SMTZ is typically well-below the mixed and irrigated sediment layers. Sediment burial is also ignored because it has a negligible effect on the modeled spatial distribution of biomasses (results not shown). The time-dependent change in $B_I$ thus only depends on the net growth rate (Eq. (3b)). Omission of the additional transport mechanisms does not affect the main conclusions of the paper. Further details of the model including the calculation of solute fluxes across the sediment–water interface are given in the Appendix.

### 2.2. Biogeochemical aspects

The biogeochemical reaction network (Table 1) is a reduced version of the model developed by Dale et al. (2006). Microbial growth depends on the energy-generating reaction between an electron donor and acceptor (the catabolic reaction), whose rate is a function of kinetic and bioenergetic factors. The two electron donors considered here are CH$_4$ and H$_2$. Hydrogen is a ubiquitous product of organic matter fermentation and a major energy source for a wide range of microorganisms (Schink, 1997). Sulfate-reducing bacteria compete with methanogenic archaea for H$_2$ (Lovley and Goodwin, 1988), whereas their relationship with methane oxidizers is synergistic; AOM only occurs when the sulfate reducers consume H$_2$ to low enough levels for AOM to become thermodynamically viable (Dale et al., 2006; Hoehler et al., 1994). In view of mounting evidence, we assume that reverse bicarbonate methanogenesis (i.e. hyME in Table 1 written from right-to-left) is a feasible pathway for AOM (Krüger et al., 2003; Hallam et al., 2004), although this has been questioned (Nauhaus et al., 2002). Simultaneous AOM and hyME is thus impossible, since they have equal and opposite Gibbs energy yields.

The depth-dependent production of H$_2$ from fermentation of organic matter is treated as a forcing function in the model, given by:

$$H_2 \text{input} = \gamma \exp^{-ax}$$

where $\gamma$ is the rate of H$_2$ production at the sediment surface (mM y$^{-1}$, Table A1) and $a$ (cm$^{-1}$) is a depth attenuation coefficient. The exponential function reflects the decreasing abundance and reactivity of organic matter with depth in sediments (Middelburg, 1989).

The rate of catalysis is linked to the rate of biomass synthesis (Dale et al., 2006) via the growth yield (mole C biomass produced per mole electron donor consumed). The macrochemical equations, which couple catalysis to the microbial growth of each biomass species (anabolism) (Dale et al., 2006), are also shown in Table 1. Note that a cellular composition of C$_4$H$_7$O$_2$N is assumed (Rittmann and McCarty, 2001). This cellular composition is close to the reported average composition (C$_4$H$_2$O$_2$N) for chemolithoautotrophic microorganisms in anoxic environments (McCollom and Amend, 2005).

### Table 1

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Catabolic reaction</th>
<th>Stoichiometry</th>
<th>$\Delta G^{\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{SRB}$</td>
<td>Sulfate reduction (hySR)</td>
<td>$\frac{1}{2}H_2SO_4^{(aq)}+e^-+H_2\rightarrow \frac{1}{2}H_2S^{(aq)}+\frac{1}{2}H_2O$</td>
<td>-27.73</td>
</tr>
<tr>
<td>$B_{MET}$</td>
<td>Methanogenesis (hyME)</td>
<td>$\frac{1}{2}H_2+\frac{1}{2}HCO_3^{(aq)}+\frac{1}{2}e^-=\frac{1}{2}CO_2+\frac{1}{2}H_2O$</td>
<td>-23.91</td>
</tr>
<tr>
<td>$B_{OMA}$</td>
<td>Methane oxidation (AOM)</td>
<td>$\frac{1}{2}CH_4+\frac{1}{2}H_2O\rightarrow \frac{1}{2}H_2+\frac{1}{2}HCO_3^{(aq)}$</td>
<td>+23.91</td>
</tr>
</tbody>
</table>

For each process, the upper equation is the catabolic energy-generating reaction. The lower equation corresponds to the macrochemical pathway. The standard Gibbs energies ($\Delta G^{\circ}$, kJ e–mol$^{-1}$) of the catabolic reactions are calculated using the data in (Amend and Shock, 2001) and corrected for biologically neutral pH conditions ($pH = 7.37$) at 278 K and 1 bar with the transformation $\Delta G^{\circ'} = \Delta G^{\circ} - RT\ln[Kw^{0.5}]$, where $Kw$ is the stoichiometric coefficient of H$^+$ in the reaction Amend and Shock (2001) and Kw is the ion product. Pressure effects for the passive and active seep environments are neglected in the calculations.

* An explanation of how the growth equations are established is given by Dale et al. (2006).
The net growth rate of a given biomass group \( i \) (mol C g\(^{-1}\) y\(^{-1}\)) is represented in the model by:

\[
\frac{dB_i}{dt} = \mu_{\text{max},i} \cdot B_i \cdot F_{K,i} \cdot F_{T,i} - \mu_e \cdot B_i
\]

(5)

where \( \mu_{\text{max},i} (\text{y}^{-1}) \) is the maximum specific growth rate and \( \mu_e (\text{y}^{-1}) \) the maximum specific decay rate of the biomass group (Jin and Bethke, 2005). \( F_{K,i} \) and \( F_{T,i} \) are the kinetic and thermodynamic driving forces for microbial growth (see below). Values of \( \mu_{\text{max}} \) for \( \text{hySR, hyME and AOM} \) of 26.1, 23.2 and 18.3 \( \text{y}^{-1} \), respectively, were calculated by Dale et al. (2006) from generalized principles of microbial metabolism (Rittmann and McCarty, 2001). Biomass decay represents a first-order loss term due to, among others, cell death, lysis and trans-membrane leakage of metabolites. Values of \( \mu_e \) are assumed to be 0.1 \( \text{y}^{-1} \) for all species, which falls within the range 0.04–0.32 \( \text{y}^{-1} \) of Dale et al. (2006). A central working hypothesis of the present paper is that the same set of microbial parameter values applies to the ADS and DDS scenarios. This assumption is necessary because comparable data of microbial growth rates in diffusive and cold-seep environments are currently lacking.

The kinetic and bioenergetic controls on biomass growth are included in Eq. (5) through the \( F_{K,i} \) and \( F_{T,i} \) terms, which are given by:

\[
F_{K,i} = \frac{[E_D]}{K^{ED}_{S,i} + [E_D]} \cdot \frac{[E_A]}{K^{EA}_{S,i} + [E_A]}
\]

(6)

\[
F_{T,i} = 1 - \exp \left( \frac{\Delta G_{\text{NET}}}{\chi R T} \right) \quad \text{if} \ \Delta G_{\text{NET}} < 0
\]

(7a)

\[
F_{T,i} = 0 \quad \text{if} \ \Delta G_{\text{NET}} > 0
\]

(7b)

and

\[
\Delta G_{\text{NET}} = \Delta G_{\text{INSITU}} + \Delta G_{\text{BO}}
\]

(8)

In Eq. (6), \( K^{ED}_{S,i} \) and \( K^{EA}_{S,i} \) are the half-saturation constants for the electron donor ([\( E_D \)]) and electron acceptor ([\( E_A \)]) (mol L\(^{-1}\)), respectively. In the reaction network considered, the only electron acceptor which may be rate-limiting is \( \text{SO}_4^{2-} \). In Eqs. (7a) and (7b) and (8), \( \Delta G_{\text{NET}} \) is the net Gibbs energy (kJ e-mol\(^{-1}\)) which is channeled into microbial growth, while \( \Delta G_{\text{INSITU}} \) (kJ e-mol\(^{-1}\)) is the in situ Gibbs energy yield of the corresponding catabolic reaction and \( \Delta G_{\text{BO}} \) (kJ e-mol\(^{-1}\)) is the bioenergetic energy minimum (see below). \( \chi \) is the average stoichiometric number; equivalent to the number of protons translocated across the cell membrane during catabolism and is assumed to be equal to 1 per electron transferred (Jin and Bethke, 2005). \( F_T \) and \( F_K \) are dimensionless functions and vary between 0 (complete kinetic/thermodynamic limitation) and 1 (no kinetic/thermodynamic limitation). The incorporation of the \( F_T \) term in Eq. (5) accounts for the limiting effect on the catabolic reaction rate by the accumulation of reaction products.

For each catabolic reaction, \( \Delta G_{\text{INSITU}} \) is calculated from the activity quotient of the solutes involved in the reaction and the standard Gibbs energy of catabolism, \( \Delta G^0 \) (kJ e-mol\(^{-1}\), Table 1). \( \Delta G_{\text{BO}} \) is defined as the minimum conservable energy needed to maintain continuous microbial activity (Hoehler, 2004). It is often quoted to be equal to 15–20 kJ per mol per formula reaction, that is, the energy required to synthesize 1/3 to 1/4 mol ATP (Schink, 1997). However, these very high values of \( \Delta G_{\text{BO}} \) are measured under optimal laboratory conditions (Schink, 1997), and their extrapolation to field conditions is questionable (LaRowe and Helgeson, 2007). For the catabolic processes considered here, \( \Delta G_{\text{BO}} \) is estimated to be much lower, on the order of 0.5 kJ e-mol\(^{-1}\), based on the modeling work by Dale et al. (2006). Note that \( \Delta G_{\text{BO}} \) is defined here as a positive value and represents a fixed loss of \( \Delta G_{\text{INSITU}} \) which has a negative value when the reaction is thermodynamically favored. The minimum energy limitation is accounted for in the model such that \( F_T = 0 \) if \( \Delta G_{\text{NET}} > 0 \) (Eqs. (7a) and (b)).

3. Model application: steady-state scenarios

3.1. DDS and ADS baseline simulations

Model results are in order-of-magnitude agreement with typical integrated AOM rates (\( \Sigma \text{AOM} \), \( \text{CH}_4 \) efflux from sediments and biomass concentrations observed in a variety of DDS and ADS environments (Table 2). In the DDS (Fig. 1a–d), the sediment is characterized by a sulfate-reducing zone extending from 0 to 400 cm and a methanogenic zone from 400 to 500 cm. \( \text{CH}_4 \) is almost entirely consumed in the SMTZ (arbitrarily defined where AOM rate >0.01% of maximum rate) and does not escape the sediment. The maximum (0.2 nmol cm\(^{-3}\) d\(^{-1}\)) and integrated (0.04 nmol m\(^{-2}\) d\(^{-1}\)) AOM rates are largely determined by the magnitude of the upward diffusive \( \text{CH}_4 \) flux. Above and below the SMTZ, fermentative \( \text{H}_2 \) production drives \( \text{hySR} \) (0.1–0.2 nmol cm\(^{-3}\) d\(^{-1}\)) and \( \text{hyME} \) (0.1 nmol cm\(^{-3}\) d\(^{-1}\)). The \( \text{H}_2 \) concentration exhibits values characteristic of sediments where sulfate reduction (0.1–0.2 nM) and methanogenesis (7 nM) are the dominant microbial metabolic pathways (Lovley and Goodwin, 1988).
Table 2

CH4 efflux rates, integrated AOM rates (ΣAOM) and biomasses (ΣB) and mean biomass concentration ([B]) in passive and active margins compared to model-predicted values in this work (in bold).

<table>
<thead>
<tr>
<th>Value (mmol m⁻² d⁻¹)</th>
<th>Passive margins site</th>
<th>Method</th>
<th>Value</th>
<th>Passive margins site</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4 efflux</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.9-90</td>
<td>Hydrate Ridge</td>
<td>Benthic chamber</td>
<td>5.0 x 10⁻⁴</td>
<td>ADS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>0.6</td>
<td>Hydrate Ridge</td>
<td>Model</td>
<td>No data</td>
<td>DDS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>12.1</td>
<td>Costa Rica MV</td>
<td>Model</td>
<td>0.24</td>
<td>White Oak River Estuary</td>
<td>ΣQ² profile; ³⁵S</td>
</tr>
<tr>
<td>8.3</td>
<td>Dvurechenskii MV</td>
<td>Model</td>
<td>0.4</td>
<td>DDS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>ΣAOM (mmol m⁻² d⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>ADS (this study)</td>
<td>Model</td>
<td>0.04</td>
<td>Danish coast</td>
<td>Model</td>
</tr>
<tr>
<td>16.3</td>
<td>Kazan MV</td>
<td>SOQ² profile</td>
<td>0.05</td>
<td>[B. Cragg, pers. comm.]</td>
<td>Model</td>
</tr>
<tr>
<td>5.2-140</td>
<td>Hydrate Ridge</td>
<td>Model; ³⁵S</td>
<td>0.1</td>
<td>Black Sea</td>
<td>ΣQ² profile</td>
</tr>
<tr>
<td>16.1</td>
<td>Costa Rica MV</td>
<td>Model</td>
<td>0.24</td>
<td>Namibian shelf</td>
<td>ΣQ² profile; ³⁵S</td>
</tr>
<tr>
<td>31.1</td>
<td>Dvurechenskii MV</td>
<td>Model</td>
<td>0.4</td>
<td>White Oak River Estuary</td>
<td>Model</td>
</tr>
<tr>
<td>ΣB (cells cm⁻²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5-1.8 x 10¹¹</td>
<td>Hydrate Ridge</td>
<td>AODCᵇ</td>
<td>1.0 x 10¹⁰</td>
<td>DDS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>7.4 x 10¹¹</td>
<td>ADS (this study)</td>
<td>Model</td>
<td>1.0 x 10¹⁰</td>
<td>Surface sediments</td>
<td>Model</td>
</tr>
<tr>
<td>2.1 x 10¹⁰</td>
<td>Hydrate Ridge</td>
<td>FISHᶠ</td>
<td>0.5-2.2 x 10⁶</td>
<td>Coastal sediments</td>
<td>AODCᵇ</td>
</tr>
<tr>
<td>3.8 x 10¹⁰</td>
<td>Hydrate Ridge</td>
<td>AODCᵇ</td>
<td>5.0 x 10⁹</td>
<td>DDS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>2.7 x 10⁹</td>
<td>Gulf of Mexico</td>
<td>FISHᶠ</td>
<td>2.0 x 10⁷</td>
<td>DDS (this study)</td>
<td>Model</td>
</tr>
<tr>
<td>7.4 x 10¹⁰</td>
<td>ADS (this study)</td>
<td>Model</td>
<td>ΣQ²</td>
<td>Danish coast</td>
<td>Model</td>
</tr>
</tbody>
</table>

(MV = mud volcano).

a Calculated from total aggregates, assuming that 1 aggregate contains 300 cells (Boetius et al., 2000).

b Acridine orange direct counts (AODC).

c Fluorescence in situ hybridization.

d Mean value over the top 10 cm where highest rates of microbial activity occur (Boetius et al., 2000; Luff and Wallmann, 2003; Orcutt et al., 2005).

The distributions of $B_{MOA}$ and $B_{SRR}$ in the SMTZ mirror the corresponding rate profiles, with maximum concentrations of 0.23 and 4.5 x 10⁸ cells cm⁻³, respectively (Fig. 1d). Methanogenic biomass within the SMTZ is very low and only accumulates where SO₄²⁻ is depleted (Dale et al., 2006; Lovley and Goodwin, 1988). Total biomass concentration integrated over the SMTZ equals 2.8 x 10⁹ cells cm⁻² (4.4 x 10⁻⁶ mol C cm⁻²), equivalent to 28% of the total sediment biomass ($ΣB=1.0 x 10¹⁰$ cells cm⁻² or 1.6 x 10⁻⁵ mol C cm⁻²). The calculated mean biomass concentration, [B], (2.0 x 10⁷ cells cm⁻³ or 3.2 x 10⁻⁸ mol C cm⁻²) is 1-2 orders-of-magnitude lower than reported values for surface sediments along passive margins (Table 2) because many more microorganisms inhabit these sediments than those considered here. This discrepancy does not occur for the ADS (see below), because sulfate reducers and methane oxidizers dominate the biomass in seep environments.

The results for the baseline ADS scenario (Fig. 1e-h) are a striking contrast to the DDS due to the upward fluid flow of 10 cm yr⁻¹ imposed at the lower boundary. Almost all sulfate reduction is coupled to AOM, and SO₄²⁻ drops to 1 mM at 3 cm below the sediment surface, in line with observations at Hydrate Ridge seeps (Luff and Wallmann, 2003). The vertical advective flux of dissolved CH₄ effectively forces the SMTZ to be positioned immediately below the sediment–water interface and exhibits a distinct peak in coupled hySR–AOM rates at 3 cm. Maximum hySR and
AOM rates of \( \sim 5.0 \, \mu \text{mol cm}^{-3} \, \text{d}^{-1} \), again similar to observations at Hydrate Ridge (Treude et al., 2003), are 4 orders-of-magnitude larger than in the DDS. \( \text{CH}_4 \) as the terminal electron donor accounts for approximately 99% of hySR in the SMTZ in the ADS, compared to only 60% in the DDS.

As a direct consequence of the intense \( \text{CH}_4 \) and \( \text{SO}_4^{2-} \) fluxes, over 98% of the biomass is located within the SMTZ (Fig. 1h). The simulated mean \( \langle B \rangle \), \( 7.4 \times 10^{10} \, \text{cells cm}^{-3} \) and integrated biomass concentrations \( \Sigma B \), \( 7.4 \times 10^{11} \, \text{cells cm}^{-2} \) agree well with cell numbers reported for seeps (Table 2). The high build-up of sulfate-reducing and methane-oxidizing biomasses prevents \( \text{CH}_4 \) escape to the ocean, even when order-of-magnitude higher flow rates are imposed (Fig. 2). In reality, the high temporal and spatial variability of fluid flow (Tryon and Brown, 2001) complicates the accurate assessment of the in situ methane oxidation efficiency, and the latter may be low where focused fluid flow is able to bypass the microbial filter via sediment fractures and conduits (Torres et al., 2002; Mau et al., 2006). Sommer et al. (2006) predicted 96% efficiency of \( \text{CH}_4 \) consumption for advective flows of 10 cm y\(^{-1} \) at Hydrate Ridge. Lower efficiencies of 27–47% have been estimated for mud volcanoes, however (Linke et al., 2005; Wallmann et al., 2006). Assuming that these systems are at steady-state and that the microbial growth rates are comparable, this broad range of AOM efficiencies in seep environments could be explained by non-laminar pore-water transport through the sediment contaminating the measured \( \text{CH}_4 \) profiles. Alternatively, microscale diffusion limitations may lower the efficiency of the AOM microbial filter.
under high flow rate conditions. Further work is required to identify the role of these mechanisms.

In the framework of the bioenergetic model, low AOM efficiencies require $\mu_{max}$ values that are an order-of-magnitude lower (Fig. 2) than those used in the baseline simulation. However, we are confident that the baseline $\mu_{max}$ values are correct to within an order-of-magnitude; they are based on fundamental principles of microbial metabolism (Dale et al., 2006; Rittmann and McCarty, 2001) and have been successfully used to simulate measured CH$_4$ turnover rates in a range of marine depositional environments (Dale et al., in press).

The relationship between the advective flow velocity ($v$) and the integrated biomass concentration ($\Sigma B$), relative to $\Sigma B$ in the baseline ADS scenario ($v=10$ cm y$^{-1}$), is shown in Fig. 3. Even at very low flows (0.03 cm y$^{-1}$) there is a 4-fold increase in $\Sigma B$ compared to the DDS, and a large decrease in the width of the SMTZ from 112 to 23 cm. Thereafter, $\Sigma B$ increases proportionally with fluid flow, which shows that the biomass responds directly to the advective CH$_4$ flux. As advective flow increases, the SMTZ is pushed closer to the sediment surface (data not shown), yet upward migration of the SMTZ becomes hindered by an increasingly sharp SO$_4^{2-}$ gradient, causing the biomass density to progressively increase.

3.2. Kinetic and bioenergetic limitations to biomass growth

By definition, $F_K$ and $F_T$ for AOM are dependent on the pore-water chemistry, the substrate uptake rates and...
Fig. 5. Effect of $\Delta G_{BQ}$ for AOM ($kJ$ e-mol$^{-1}$) on AOM rates (nmol CH$_4$ cm$^{-3}$ d$^{-1}$), $\Delta G_{NET}$ ($kJ$ e-mol$^{-1}$) and anaerobic methane-oxidizing biomass concentration ($B_{MOA}$, $10^8$ cells cm$^{-3}$) in the DDS (upper panels) and ADS (lower panels). The dashed horizontal lines indicate the boundaries of the SMTZ and the dotted horizontal line shows the depth of maximum AOM rate.

Efficiencies of the organisms and the accumulation of metabolic products of the given catabolic process (Fig. 4). Yet, $F_K$ and $F_T$ show remarkably similar values in the ADS and DDS: in the DDS, $F_K$ and $F_T$ at the depth of maximum AOM rate equal 0.11 and 0.05 (Fig. 4a,b), respectively, which compares to 0.08 and 0.07 in the ADS (Fig. 4c,d). AOM is thus severely limited, thermodynamically as well as kinetically, in the ADS and DDS. For hySR, $F_K$ and $F_T$ are 0.01 and 0.36 in the DDS, and 0.01 and 0.35 in the ADS. Therefore, hySR is less thermodynamically limited than AOM. However, the hySR and AOM rates (Fig. 1) are only ~1% of their respective maximum rates (i.e. when $F_K \times F_T = 1$) for the DDS and ADS, despite large differences in SO$_4^{2-}$ and CH$_4$ fluxes to the SMTZ. Growth of the microorganisms in both settings is thus strongly limited (Nauhaus et al., 2007), yet they are able to colonize the sediment and function as an efficient barrier against CH$_4$ flux to the water column. Dale et al. (in press) arrived at essentially the same conclusions applying a similar kinetic–bioenergetic model to data from sediments in the Skagerrak.

The bioenergetic threshold for AOM ($\Delta G_{BQ}$) is a key control on CH$_4$ fluxes in marine sediments (Dale et al., 2006). However, a sensitivity analysis (Fig. 5) shows that the DDS and ADS respond differently to changes in this parameter. For the DDS, the highest threshold at which methane oxidizers are able to metabolize ($\Delta G_{NET} < 0$) is around 1.0 $kJ$ e-mol$^{-1}$ (Fig. 5a,b). Catabolism ceases ($\Delta G_{NET} = 0$) at higher thresholds because the bioenergetic barrier becomes too high. In contrast, methane oxidizers can be active in the ADS with thresholds as high as 3.0 $kJ$ e-mol$^{-1}$ (Fig. 5d,e). The higher biomass in the ADS effectively buffers the effect of bioenergetic limitation, whereas the lower CH$_4$ flux in the DDS makes methane-
oxidizing biomass more sensitive to collapse for the same increase in $\Delta G_{BO}$ (Fig. 5c,f). These results emphasize the need for better constraints on the value of $\Delta G_{BO}$ applicable to marine environments.

4. Model application: transient scenarios

The steady-state results show that the abundance and distribution of methane-oxidizing biomass in passive and active margin sediments are largely determined by the dominant macroscopic transport processes which supply electron donors and acceptors to the microorganisms. There is almost complete CH$_4$ oxidation under steady-state conditions, preventing CH$_4$ escape to the water column. In what follows, the effect of abrupt changes in the transport regime on biomasses and CH$_4$ efflux is investigated.

4.1. Comparison of biomass-explicit and -implicit models

Luff and Wallmann (2003) applied a reactive-transport model to Hydrate Ridge seep sediments to investigate the role of advective fluid flow on CH$_4$ flux across the sediment–water interface. They showed that for an increase in fluid flow from ~30 to 240 cm y$^{-1}$ over 20 days, the theoretical CH$_4$ escape flux to the water column was only significant when advective flow exceeded 100 cm y$^{-1}$. However, in their model, the AOM rate was dependent solely on the CH$_4$ and SO$_4^{2-}$ concentrations (Eq. (2)) with a bimolecular rate constant, $k_{AOM}$ equal to 10$^5$ M$^{-1}$ y$^{-1}$. The implicit assumption was, therefore, that the microbial biomasses responded instantaneously to the changing CH$_4$ influx.

The results of Luff and Wallmann (2003) prompted us to assess the time-lag between an abrupt onset of advective flow in a diffusive system and the subsequent readjustments of the biomass concentrations, AOM rate and CH$_4$ flux across the diffusive boundary layer. Starting with the steady-state DDS as the initial condition, the advective flow rate was increased instantaneously from 0 to 10 cm y$^{-1}$ at time $t=0$, while the CH$_4$ boundary concentration at the lower boundary was switched to a fixed concentration of 70 mM. The model output was tracked until a new steady-state was reached (the ADS scenario in Fig. 1) — defined as the time when the annual CH$_4$ efflux changed by <1%. Note that we chose this particular transient scenario because measured field data of biomasses and AOM rates are well-constrained for the two end-members of the simulation, that is, the DDS and the ADS with advective flow of ~10 cm y$^{-1}$ (e.g. Luff and Wallmann, 2003; Treude et al., 2003).

Fig. 6 shows the transient response to the increased advective flow according to the biomass-explicit model. The CH$_4$ efflux to the overlying water column increases roughly linearly for 12 y after $t=0$ y (Fig. 6a), in parallel to the CH$_4$ concentration immediately below the sediment surface (Fig. 6b). During this time, however, the rate of the efflux remains a very small percentage of the advective CH$_4$ influx at the base of the sediment column (Fig. 6a). Sulfate concentrations progressively decrease throughout the sediment as the CH$_4$-rich pore water is forced upwards (results not shown) and coupled AOM-hySR in the original SMTZ (~300 cm, Fig. 1c) effectively ceases after 12 y (Fig. 6c). Consequently, the biomasses of the sulfate-reducing and methane-oxidizing microorganisms at depth slowly decrease (Fig. 6d).

After $t=12$ y, the CH$_4$-rich pore water reaches the surface layer and at $t=29$ y up to 16% of the CH$_4$ escapes the sediment at a total rate of ~1.1 mol m$^{-2}$ y$^{-1}$ (Fig. 6a). Between $t=12$ and 29 y the biomass concentration in the uppermost sediment layer is too low to consume the CH$_4$, and the biomass concentration increase lags behind the efflux by about 4 y (Fig. 6e). After 29 y, the increase in biomass concentration causes the efflux rate to decrease sharply (Fig. 6e). Critically, once the CH$_4$ front is held in position at the surface by the opposing SO$_4^{2-}$ gradient, the biomasses undergo log-phase growth with a progressive shoaling toward the surface (Fig. 6d,e). At this point a new surface SMTZ is established, as evidenced by the increase in biomasses and AOM rate in the upper sediment layers (Fig. 6c,d).

After 70 y the CH$_4$ efflux levels out to 0.03 mol m$^{-2}$ y$^{-1}$ and >99% of the upward CH$_4$ flux is being oxidized. This phase is associated with a new steady-state in surface biomass concentration (Fig. 6d). Therefore, the time between the arrival of the CH$_4$ front at the surface (~12 y) and the establishment of a new steady-state microbiological community (70 y) represents the grow-in time of the biomass in response to the increased CH$_4$ supply. This represents the time window during which CH$_4$ can escape to the water column. It reflects the growth kinetics of the AOM community and is essentially independent of the flow rate itself. As a result, the magnitude of the CH$_4$ efflux across the diffusive boundary layer during the grow-in time is proportional to the advective pore-water CH$_4$ flux (results not shown). Clearly, active venting of CH$_4$ gas via sediment conduits would represent an additional source of CH$_4$ to the water column (Torres et al., 2002).

Fundamentally different results are obtained when the AOM rate is formulated using the biomass-implicit model (Eq. (2)) (Fig. 7). For the first 12 years in the low $k_{AOM}$ (10$^5$ M$^{-1}$ y$^{-1}$) scenario, the CH$_4$ efflux remains
negligible and increases rapidly once the CH$_4$-charged pore water arrives at the surface (Fig. 7a). Steady state is reached after 70 y, and CH$_4$ efflux across the diffusive boundary layer equals 5.6 mol m$^{-2}$ y$^{-1}$, so that AOM consumes only 20% of the upward CH$_4$ flux. In contrast, with the high $k_{AOM}$ (10$^{5}$ M$^{-1}$ y$^{-1}$) all the CH$_4$ is consumed within the sediment, making AOM 100% efficient (Fig. 7b). Unlike in the biomass-explicit model, when using the bimolecular rate expression there is no delay of the increase in surface $\Sigma AOM$ rates (Fig. 7c,d) following the arrival of the CH$_4$ front (Fig. 7e,f).

In the biomass-implicit model, the maximum rate and the efficiency of AOM are rigidly constrained by $k_{AOM}$, which also defines the threshold flow rate at which CH$_4$ emissions from the sea floor will begin (100 cm y$^{-1}$, Luff and Wallmann, 2003). The inflexibility of the bimolecular rate formulation restricts its use to steady-state early diagenetic applications where SO$_4^{2-}$ and CH$_4$ data are available for calibrating the pore-water profiles (e.g. Wallmann et al., 2006). Our model results caution against the use of Eq. (2) in transient applications where changes in the localized supply of CH$_4$ may trigger large changes in biomass density, particularly given the severe kinetic and bioenergetic limitations to growth of AOM communities, as evidenced by the long in situ doubling times implied by laboratory studies (Nauhaus et al., 2007; Girguis et al., 2005). A flow-variable bimolecular rate constant in Eq. (2) may thus be a better alternative to a fixed value in transient flow applications. Nonetheless, the explicit modeling of the evolution of microbial biomasses under transient conditions may be critical for assessing methane release from sediments on decadal or perhaps centennial time scales (Hensen et al., 2003).

4.2. Global-scale methane release from hydrates

Based on empirical evidence (see Higgins and Schrag, 2006 for an in-depth overview), it has been estimated that 55 Ma ago, large amounts ($1.5 \times 10^{18}-4.5 \times 10^{18}$ g) of isotopically-light carbon entered the
Fig. 7. Results of the transient scenario in which an advective flow of 10 cm y$^{-1}$ was imposed at time $t=0$ y, using the biomass-implicit biomolecular AOM rate (Eq. (2)). (a,b) CH$_4$ efflux from the sediment (mol m$^{-2}$ y$^{-1}$) and CH$_4$ escape (percentage of the upward advective flux), (c,d) integrated AOM rate, $\Sigma$AOM (mol CH$_4$ m$^{-2}$ y$^{-1}$) between 0–50 and 51–500 cm, and (e,f) CH$_4$ concentration at 0.1 cm (M). The left and right panels correspond to a biomolecular rate constant ($k_{AOM}$) of 10$^2$ and 10$^5$ M$^{-1}$ y$^{-1}$, respectively.

Ocean–atmosphere system in response to a 4–5 °C warming of ocean bottom waters (Zachos et al., 2003; Dickens et al., 1995; Röhl et al., 2000). This resulted in a ~200 ky period of extreme global warming known today as the Paleocene–Eocene Thermal Maximum (PETM) (Zachos et al., 2003; Dickens et al., 1995; Röhl et al., 2000). Massive release of CH$_4$ from gas hydrates equivalent to 1.3–3.8 x 10$^{17}$ mol CH$_4$, either by gas eruptions or massive slope failure (Higgins and Schrag, 2006; Kennett and Stott, 1991; Bice and Marotzke, 2002; Katz et al., 2001), and subsequent aerobic oxidation to CO$_2$ has been proposed as the source of the $^{13}$C-depleted carbon (Dickens, 2001; Zachos et al., 2003; Röhl et al., 2000). It has further been suggested that the resulting CO$_2$ dissolution in the oceans and the decrease in oceanic pH, caused a shoaling of the calcite
compensation depth, and the partial or total corrosion of sedimentary carbonate beds (Zachos et al., 2003). On the basis of our model results, we assess how effective the AOM barrier to CH$_4$ efflux could have been during the PETM.

According to our model results, the microbial response time to a change in fluid flow conditions is on the order of 60 y. This lag time is essentially instantaneous compared to the 10 ky onset of the PETM (Zachos et al., 2003; Dickens et al., 1995; Dickens, 2003), during which a more gradual hydrate dissolution and subsequent upward flux of dissolved CH$_4$ would be expected. Thus, we hypothesize that methane-oxidizing communities would be well-established at the sediment surface during the PETM with AOM acting as an efficient sink for upward advecting pore-water CH$_4$.

The efflux of isotopically-light carbon which entered the ocean from marine sediments during the PETM can be estimated by assuming that the global sea floor coverage by seeps 55 Ma ago was similar to today (7.5×10$^{11}$ m$^2$ Hinrichs and Boetius, 2002). Using the above range for hydrate dissociation during the PETM anomaly, an efflux in the range of 1.7–5×10$^5$ mol CH$_4$ m$^{-2}$ or 17–50 mol CH$_4$ m$^{-2}$ y$^{-1}$ is estimated. This value is only a factor of 3–8 higher than the modern day global AOM rate of 6.5 mol CH$_4$ m$^{-2}$ y$^{-1}$ (Hinrichs and Boetius, 2002), even without accounting for the fraction of CH$_4$ which escaped the sediment via fractures and conduits (Table 2).

The order-of-magnitude similarity of PETM and modern CH$_4$ fluxes agrees with the hydrate capacitor model of Dickens (2003), in that the PETM may not have arisen from an extraordinarily catastrophic release of CH$_4$ from the sea floor, but rather from the natural cycle of the global gas hydrate reservoir. Our model results also suggest that the potential importance of AOM as an efficient barrier to CH$_4$ efflux during the PETM anomaly may have been overlooked. This does not, however, conflict with the well-documented global-scale calcite dissolution which occurred during the PETM. Studies show that almost all the sulfide produced by AOM (Eq. (1)) is oxidized either biologically in situ or chemically in the water column (Luff and Wallmann, 2003; Sommer et al., 2006). The net combined effect of AOM and sulfate oxidation would be CO$_2$ production and a lowering of the calcite saturation index similar to that of aerobic methane oxidation. The addition of (13C-depleted) dissolved inorganic carbon to the ocean and the impact on the calcite saturation state is thus largely independent of the methane oxidation pathway.

5. Conclusions

A biomass-explicit bioenergetic reaction–transport model is used to investigate how the macroscopic (from cm to m) transport regime affects the distributions of biomasses and methane fluxes in marine sediments. Two end-member cases are considered: a diffusion-dominated system where externally-impressed flow is absent and an advection-dominated system where pore-water flow causes upward advective transport of methane. At steady-state, the kinetic and bioenergetic driving forces for AOM are similar in both cases, despite the markedly different transport properties. The methane-oxidizing communities act as an efficient benthic filter and prevent significant escape of dissolved methane to the overlying water column. In other words, given enough time, the microorganisms build-up sufficient biomass to entirely consume the upward methane flux.

In contrast, methane efflux to the water column may be significant following an abrupt increase of advective flow. Using the best current estimates of parameter values affecting microbial growth rates, transient simulations predict a lag time on the order of 60 y between the onset of increased advective flow and the establishment of a new, steady-state AOM biomass. During this time window, a significant fraction of the upward flux of methane may escape from the sediment. The lag time reflects the slow growth kinetics of the methane-oxidizing communities, and is independent of the flow regime.

From a geological perspective, the model-predicted microbial lag time of ~60 years to changes in methane supply is near instantaneous. In particular, it appears too short to allow for an escape of dissolved methane of the magnitude postulated to be released from gas hydrate dissolution during the Paleocene/Eocene Thermal Maximum (PETM). For the estimated time scale of methane generation at the onset of the PETM (~10 ky), AOM should have remained an effective barrier, limiting the amount of dissolved methane reaching the water column. However, even in that case, gas hydrate dissolution would have caused an efflux of 13C-depleted dissolved inorganic carbon, and lowered the CaCO$_3$ saturation state of the oceans.

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Table A1
Chemical and physical parameters used in the baseline simulations

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Upper boundary conditions

- B: Upper boundary condition for biomass
- Cw-SO₄²⁻: Upper boundary condition for SO₄²⁻
- Cw-H₂: Upper boundary condition for H₂

Lower boundary conditions

- B, SO₄²⁻, H₂: Lower boundary condition dC/dx=0 for B, SO₄²⁻ and H₂
- CH₄ (DDS): Lower boundary condition dCH₄/dx=0 for CH₄ in DDS
- CH₄ (ADS): Lower boundary condition CH₄=0 for CH₄ in ADS

Solute fluxes across the sediment–water interface, originating from the sum of advective and diffusive fluxes in the sediment, are assumed to be equal to the total transport flux across the diffusive boundary layer (DBL). Advevtive flow and eddy diffusion become insignificant in the DBL (Boudreau, 1997) and molecular diffusion dominates vertical solute transport, provided that the Peclet number is smaller than one. In an active vent system characterized by sufficiently slow vertical fluid flow, the non-dimensional Peclet number, Pe, is defined as

\[
Pe = \frac{|v| z_{\text{diff}}}{D_W}
\]

where \(v\) is the advective flow rate at the surface, \(z_{\text{diff}}\) is the thickness of the DBL, and \(D_W\) is the molecular diffusion coefficient of the solute in seawater (Schulz, 2000). For reasonable DBL thicknesses (<0.1 cm) and values of \(v<2000\) cm y⁻¹, \(Pe<1\) and the transport of solutes through the DBL is diffusion controlled (Linke et al., 2005). Here the DBL thickness is taken to be 0.04 cm (Linke et al., 2005).
The upper boundary condition for the concentration of any dissolved species, \( C \), can thus be defined by equating the flux across the DBL with the sum of advective and diffusive fluxes at the sediment surface:

\[
D_W \cdot \left( \frac{C_0 - C_W}{z_{\text{diff}}} \right) = \varphi_0 \cdot \left( D_S \cdot \frac{\partial C}{\partial x} \bigg|_{x=0} - v \cdot C_0 \right)
\]  

(14)

where \( C_0 \) is the solute concentration immediately below the DBL (that is, at the sediment surface), \( C_W \) is the concentration in the bottom water, \( \varphi_0 \) is the sediment porosity at the surface, and \( \frac{\partial C}{\partial x} \bigg|_{x=0} \) is the concentration gradient immediately below. \( C_W \) is imposed explicitly in the model, whereas \( C_0 \) is calculated. Molecular diffusion coefficients for the sediment \( (D_S, \text{cm}^2 \text{y}^{-1}) \) at in situ temperature \( (278 \text{ K}) \) and salinity \( (35.5) \) are calculated using a tortuosity correction \( (D_S = D_W/(1 - \ln^2)) \) (Boudreau, 1997) and assuming constant porosity \( (0.75) \). A more complete form of Eq. (14) would also include non-local solute transport by bioirrigation and bioturbation. However, Luff and Wallmann (2003) showed that their importance is not expected to be significant in seep systems.

The continuous differential equation of the upper boundary condition can be approximated in discretized form as:

\[
D_W \cdot \left( \frac{C_0 - C_W}{z_{\text{diff}}} \right) = \varphi_0 \cdot \left( D_S \cdot \frac{C_1 - C_0}{\Delta x} - v \cdot C_0 \right)
\]  

(15)

where \( C_1 \) is the solute concentration at the grid node immediately below \( C_0 \). After some manipulation, Eq. (15) gives the following algebraic equation:

\[
C_0 \cdot \left( \frac{\varphi_0 \cdot D_S}{\Delta x} + \varphi_0 \cdot v + \frac{D_W}{z_{\text{diff}}} \right) + C_1 \cdot \left( -\frac{\varphi_0 \cdot D_S}{\Delta x} \right) = \frac{D_W \cdot C_W}{z_{\text{diff}}}
\]  

(16)

Typical seawater concentrations are used for the bottom water concentrations \( (C_W) \). Solid biomass concentrations at the surface are defined as constant concentrations (Dirichlet boundary conditions). Initial biomass concentrations are set to low values \( (1 \times 10^{-9} \text{ mol C g}^{-1}) \), and only increase provided there is sufficient kinetic and thermodynamic drive for growth. At the lower boundary, zero concentration gradients (Neumann conditions) are prescribed for all species, with the exception of CH\(_4\) in the ADS. Here, CH\(_4\) was set to 70 mM to consider the effect of ascending CH\(_4\) on the pore-water profiles and biomass distribution. This concentration is reasonable for hydrate-bearing seep systems of water depths of ~500 m. The fluid flow velocity, \( v \), for the ADS baseline steady-state scenario \( (10 \text{ cm y}^{-1}) \) is a typical value for seep systems (Tryon and Brown, 2001; Torres et al., 2002; Haese et al., 2003).

Concentrations of bicarbonate \( (\text{HCO}_3^-) \) and sulfide \( (\text{HS}^-) \) are required for the calculation of \( \Delta G_{\text{INSITU}} \) (Eq. (8)). Concentrations of 10 mM \( \text{HCO}_3^- \) and 2 mM \( \text{HS}^- \) are used for the thermodynamic calculations, which are order-of-magnitude values for the SMTZ in seep and non-seep sediments [e.g. Luff and Wallmann, 2003; Van Cappellen and Wang, 1996]. Sensitivity analyses (not shown) reveal that \( \Delta G_{\text{INSITU}} \) is largely insensitive to reasonable concentration variations of these species. Activity coefficients required for \( \Delta G_{\text{INSITU}} \) (Eq. (8)) are calculated using the HCH software package (Shvarov and Bastrakov, 1999).

The time-dependent concentrations of solutes and biomasses are modeled on a pore water \( (\text{e.g. mol L}^{-1} \text{ pore water}) \) and solid phase basis \( (\text{e.g. mol g}^{-1} \text{ dry sediment}) \), respectively. Relevant unit conversions are used to scale the reaction rates of solute production and consumption to biomass growth. Biomass is reported as cells \( \text{cm}^{-3} \) assuming a cellular carbon content of 19 fg C cell\(^{-1} \) (Schippers et al., 2005). Vertically-integrated rates are expressed per area of total sediment.

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