ABSTRACT. A one-dimensional reactive transport model including mass, momentum and volume conservation for the solid, aqueous, and gaseous phases is developed to explore the fate of free methane gas in marine sediments. The model assumes steady-state compaction for the solid phase in addition to decoupled gas and aqueous phase transport, instigated by processes such as buoyancy, externally impressed flows and compaction. Chemical species distributions are governed by gas advection, dissolved advection and diffusion as well as by reaction processes, which include organoclastic sulfate reduction, methanogenesis and anaerobic oxidation of methane (AOM). The model is applied to Eckemförde Bay, a shallow-water environment where acoustic profiles confirm a widespread occurrence of year-round biogenic free methane gas within the muddy regions of the sediment, and where subsurface methanogenesis, overlaid by a zone of AOM has been reported. The model results reveal that, under steady-state conditions, upward gas migration is an effective methane transport mechanism from oversaturated to undersaturated intervals of the sediment. Furthermore, sensitivity tests show that when methanogenesis rates increase, the gas flux to the AOM zone becomes progressively more important and may reach values comparable to those of the aqueous methane diffusive flux. Nevertheless, the model also proves that the gas transport rates always remain smaller than the removal rates by combined gaseous methane dissolution and oxidation. Consequently, for the range of environmental conditions investigated here, the AOM zone acts as an efficient subsurface barrier for both aqueous and gaseous methane, preventing methane escape from the sediments to the water column.

INTRODUCTION

The production of biogenic methane (CH₄) in marine sediments through the methanogenesis of organic carbon deposited on the sea floor is an ongoing and important process in the global methane and carbon cycles (Reeburgh, 2003). Marine sediments contain approximately 5 to 53 percent of the total global carbon reservoir, mostly in the form of methane gas hydrate (Milkov, 2004). Although marine and freshwater deposits contain three orders of magnitude the quantity of methane with respect to that of the atmosphere (Reeburgh, 2003), studies have shown that the contemporary contribution of these sediments to the total atmospheric CH₄ input ranges represents only around 2 percent of global emissions (Reeburgh, 2007). This low contribution is a consequence of anaerobic oxidation of methane (AOM) coupled to sulfate reduction (Alperin and Reeburgh, 1985; Boeiu and others, 2000), an
efficient process which may consume up to 90 percent of the total CH$_4$ produced in situ (Iversen, 1996). The efficiency of this subsurface methane barrier depends, however, on the relative magnitude of the rates of upward methane migration and its microbial consumption through AOM.

In saturated porous media, methane may be present not only in aqueous and hydrate forms but also as free methane gas (CH$_4^{(g)}$). Environments where CH$_4^{(g)}$ has been observed include shallow marine sediments (Martens and others, 1998), rice paddies (Lu and Conrad, 2005), landfills (Bogner and Matthews, 2003) and wetlands (Reeburgh, 2003). Deep-sea sediments overlying shallow gas hydrates may also contain a significant proportion of CH$_4^{(g)}$ (Tryon and others, 2002). In these gassy environments, it is therefore important to take into account both CH$_4^{(g)}$ advection and dissolved CH$_4$ transport. The latter typically occurs due to diffusion through molecular processes, mixing by faunal activity, and aqueous advection through compaction and externally impressed flows. At high rates of gas transport, CH$_4^{(g)}$ can escape from the sediment (Jackson and others, 1998; Martens and others, 1998) a process here defined as ebullition.

Despite the potential widespread importance of CH$_4^{(g)}$ dynamics to quantifying methane fluxes, modeling studies which have employed an explicit gas phase as part of a continuous 3-phase system (solid, liquid, gas) have mainly been confined to soils and aquifers (Xu and Pruess, 2001; Molins and Mayer, 2007). Here, volume conservation within the pore spaces was accounted for by utilizing a solid matrix that, while having the ability to fracture, was static. This approach is unsuitable for marine sediments that undergo sediment compaction and transport of the solid matrix by burial and biologically-induced mixing (Berner, 1980). Clathrate modeling studies such as the one of Davie and Buffet (2001) have explicitly accounted for the fate of CH$_4^{(g)}$ during diagenesis in marine sediments. However, the CH$_4^{(g)}$ fraction was assumed to be buried along with the sediment, which is generally not the case observed in shallow marine environments (Anderson and others, 1998; Whiticar, 2002; Boudreau and others, 2005). Previous diagenetic modeling studies of methane dynamics have thus either (i) excluded the gas phase (Luff and Wallmann, 2003), (ii) included the gas phase implicitly by imposing instantaneous loss to the water column (Martens and others, 1998) or as a source for the dissolved methane pool (Haeckel and others, 2004), (iii) assumed that gas transport follows burial (Davie and Buffett, 2001), (iv) described transport as a pseudo-diffusive process without explicitly accounting for the volume of the free gas (Dale and others, 2008), or (v) considered gas phase transport explicitly with bubble transport through tube structures (Haeckel and others, 2007).

At a smaller scale, the mechanism for discrete gas bubble production and ebullition in muddy marine sediments has been proposed to follow linear elastic fracture mechanics (LEFM) (Boudreau and others, 2005). In brief, this theory states that the sediment responds elastically towards the expanding bubbles until a critical pressure threshold is reached, at which point the sediment fractures. Bubble growth then occurs along the fracture and bubble movement (ascension) is instigated through fracture propagation. The growth of a gas bubble thus depends on the elastic and fracture properties of the sediment, such as the critical stress intensity factor and Young's modulus. In heterogeneous sediments, these properties can have high spatial variability and may lead to zones of gas accumulation (Boudreau and others, 2005). Moreover, channel vents can form in systems where the viscous pressure gradient exceeds the hydrostatic pressure gradient (Stöhr and Khalili, 2006). In such cases, the flow of the gas phase is enhanced, implying that CH$_4^{(g)}$ escapes rapidly from the sediment and plays a lesser role in benthic methane cycling.

Nevertheless, in contrast to sediments subject to active venting, shallow methane environments are able to entrap significant quantities of free gas. For instance, in
Methane gas-phase dynamics in marine sediments: A model study

Eckernförde Bay sediments (Kiel Bight, Germany), which is the study-site adopted in this manuscript, a well-defined bubble horizon is located some decimeters below the sediment-water interface (SWI) (Wever and Fiedler, 1995; Martens and others, 1998; Silva and Brandes, 1998; Wever and others, 1998, 2006). Here, Anderson and others (1998) proceeded to characterize the shape and average size of individual bubbles through computed tomographic scans of sediment cores and observed that the gas phase was present as isolated bubble clusters. They described a whole range of elongate shapes for individual bubbles, from coin-shaped to near-spherical, with mm-scale (equivalent) radii. Although these studies provided a thorough description of the gas phase characteristics in Eckernförde Bay, the movement of the gaseous phase has yet to be well constrained. Indirect evidence for migration has been reported by Whiticar (2002), who suggested that gas transport and dissolution in methane-starved areas was responsible for the steep dissolved methane concentration gradients near the sulfate-methane transition zone (SMTZ—here defined as the surface of equimolar sulfate and methane). Furthermore, Treude and others (2005) postulated that unusual spatial and temporal AOM rate distributions were due to gas migration through the SMTZ. Gas ebullition, however, has only been occasionally observed in some locations of the Eckernförde Bay basin (Schlüter and others, 2004). Although Wever and others (2006) postulate that pressure drops and the subsequent degassing could cause ebullition, they did not report any major ebullition events at a gassy site over a 4-month period of hourly echo-sounder mapping within the central basin of Eckernförde Bay. It is also worth noting that at sites where methane ebullition fluxes have been observed, estimates from sonar acoustic data fall within a low range confined between 3 μmol m⁻² d⁻¹ (Jackson and others, 1998) and 20 μmol m⁻² d⁻¹ (Wilkens and Richardson, 1998). The high rates of methanogenesis (in the mM d⁻¹ range) both observed and modeled in the zone of gas production (Martens and others, 1999), in addition to the small variation observed in dissolved methane profiles (Wever and others, 1998) clearly contrast with these negligible ebullition fluxes, suggesting that methanogenesis is leading to CH₄(g) which in greater part is not escaping the sediment. Moreover, Martens and others (1999) specifically reported no ebullition taking place over a two year period at their study site.

To help explain the discrepancy between high rates of gas production and very low ebullition rates as well as elucidate the role of the gas phase in methane cycling, we developed a 1-D numerical reactive-transport model (RTM) which explicitly accounts for CH₄(g) generation and transport in marine sediments. It differs from previous modeling approaches in that it tackles the movement of a collective gas bubble phase in an unconsolidated sediment matrix, imparting from the fundamental conservation laws of mass and momentum applied to the total solid, aqueous and gaseous phases. The approach is volume conservative, such that the growth of (spherical) gas bubbles displaces the aqueous phase. In addition, the aqueous phase is allowed to invade the void created when bubbles dissolve in undersaturated pore water. Although our model does not account for the complex physics behind the LEFM for discrete propagation of single bubbles, our bubble growth rates were calibrated with the results reported under the diffusion limited constant eccentricity (DLCE) and the LEFM models of Gardiner and others (2003) at an Eckernförde Bay site. It can thus be considered as a sediment model of intermediate complexity which allows the physical description of a dynamic 3-phase system in a 1-D framework. The biogeochemical dynamics of the sediment are included by calibrating the model to measured geochemical profiles taken from Martens and others (1998), whereas the physical parameters in the model were calibrated with measured data (grain size, water content profiles) from Silva and Brandes (1998). Finally, the importance of the feedbacks on the CH₄(g) phase on both the physics and the biogeochemistry of the sediment are investigated by comparing the
model predictions to an additional gas implicit model where such feedbacks are absent.

MODEL THEORY

In this section, the model theory based on conservation of mass and momentum is described. Our approach follows that of L'Heureux and Fowler (2000) and Davie and Buffett (2001) for 2 and 3-phase systems, respectively. However, the gas phase in Davie and Buffett (2001) is buried along with the sediment using the assumption that the gas velocity is equal to the sediment accumulation rate, and the rates of gas formation are equal to those for hydrate formation. Here, the ultimate objective is to derive separate equations for the velocity and volume fraction of the solid, aqueous and gas phases in a system with depth-variable porosity, with particular reference to marine sediments. We begin by detailing the phase conservation equations in the three-phase system (§ Phase Conservation Equations) followed by describing the physics used to derive the time-dependent (transient) porosity profiles (§ Transient Porosity Profile) and, finally, the specific case of porosity profiles generated under steady-state compaction (§ Steady-State Compaction). We then introduce the concept of gas volume fraction (§ Gas Volume Fraction), the governing equation for the advective gas phase velocity (§ Gas Velocity), and, as a final point, we discuss the numerical approach to solve the resulting set of equations (§ Numerical Solution). Tables 1 and 2 summarize all variables, rates, and concentrations used in this paper with their respective symbols and corresponding units.

Phase Conservation Equations

In a one-dimensional vertical system composed of a solid (s), an aqueous (a), and a single-species gaseous (g) phase, mass conservation for each individual phase is dictated by the following continuity equations:

$$\frac{\partial \phi_{s} \rho_{s}}{\partial t} = - \frac{\partial \rho_{s} \phi_{s} v_{s}}{\partial z} + \rho_{s} \Sigma R_{s}$$  \hspace{1cm} (1)

$$\frac{\partial \phi_{a} \rho_{a}}{\partial t} = - \frac{\partial \rho_{a} \phi_{a} v_{a}}{\partial z} - \nu_{s} R_{g} - \rho_{s} \Sigma R_{s}$$  \hspace{1cm} (2)

$$\frac{\partial \phi_{g} \rho_{g}}{\partial t} = - \frac{\partial \rho_{g} \phi_{g} v_{g}}{\partial z} + \nu_{s} R_{g}$$  \hspace{1cm} (3)

where $t$ is time, $z$ is the vertical coordinate defined as positive downwards from the sediment-water interface (SWI), and $\rho$, $\phi$, $v$ represent the phase-specific density, volume fraction, and velocity due to sediment burial, respectively. Note that $\phi_{a}$ and $\phi_{g}$ are termed volume fractions of the aqueous and gas phases, rather than porosities. Also, mathematically, the solid, aqueous, and gas volume fractions are quantities that refer to the averaging from a 3-D system to a 1-D system. $R_{g}$ represents the gas molar production rate (conversely, $-R_{g}$ represents the gas molar dissolution rate) from the aqueous phase per total sediment volume, $v$ is the gas molar volume whereas $\Sigma R_{s} = \sum_{j} v_{j} W_{j}$ describes the net molar transfer rate between all solid phases and the aqueous phase. In the above expression, $v_{j}$ is the molar volume of solid species $j$, and $W_{j}$ represents the rate of production ($>0$) and/or consumption ($<0$) of the solid phase $j$ due, for example, to mineral precipitation and/or dissolution. No mass transfer between the solid and the gas phases is assumed.

The following relationships for the phase-specific volume fractions can also be defined:
### Table 1

**Nomenclature used for model development**

<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic response coefficient</td>
<td>$b$</td>
<td>$T^2LM^{-1}$</td>
</tr>
<tr>
<td>Average grain-size diameter</td>
<td>$d$</td>
<td>L</td>
</tr>
<tr>
<td>Hydrodynamic dispersion coefficient for substance i</td>
<td>$D_i$</td>
<td>$L^2T^{-1}$</td>
</tr>
<tr>
<td>Molecular diffusion coefficient for substance i</td>
<td>$D_i$</td>
<td>$L^2T^{-1}$</td>
</tr>
<tr>
<td>Gravity constant</td>
<td>$g$</td>
<td>LT$^{-2}$</td>
</tr>
<tr>
<td>Bubble nucleation rate</td>
<td>$J$</td>
<td>$L^3T^{-1}$</td>
</tr>
<tr>
<td>Bubble density</td>
<td>$n$</td>
<td>$L^3$</td>
</tr>
<tr>
<td>Pore fluid pressure</td>
<td>$P$</td>
<td>$ML^{-1}T^{-2}$</td>
</tr>
<tr>
<td>Average bubble radius</td>
<td>$r$</td>
<td>L</td>
</tr>
<tr>
<td>Salinity</td>
<td>$S$</td>
<td>$MM^{-1}$</td>
</tr>
<tr>
<td>Time</td>
<td>$t$</td>
<td>T</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>K</td>
</tr>
<tr>
<td>Velocity of p-phase</td>
<td>$v_p$</td>
<td>$LT^{-1}$</td>
</tr>
<tr>
<td>Depth</td>
<td>$z$</td>
<td>L</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>$\alpha$</td>
<td>L</td>
</tr>
<tr>
<td>Kinetic mass transfer coefficient</td>
<td>$\beta$</td>
<td>LT$^{-1}$</td>
</tr>
<tr>
<td>Surface tension</td>
<td>$\gamma$</td>
<td>$MT^{-2}$</td>
</tr>
<tr>
<td>Carman-Kozeny dimensionless parameter</td>
<td>$\varepsilon$</td>
<td>(-)</td>
</tr>
<tr>
<td>Viscosity of p-phase</td>
<td>$\eta_p$</td>
<td>$ML^{-1}T^{-1}$</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>$\theta$</td>
<td>(-)</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>$K$</td>
<td>LT$^{-1}$</td>
</tr>
<tr>
<td>Permeability</td>
<td>$\kappa$</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Diffusive boundary layer</td>
<td>$\lambda$</td>
<td>L</td>
</tr>
<tr>
<td>Density of p-phase</td>
<td>$\rho_p$</td>
<td>$ML^{-3}$</td>
</tr>
<tr>
<td>Effective stress</td>
<td>$\sigma$</td>
<td>$ML^{-1}T^{-2}$</td>
</tr>
<tr>
<td>Molar gas volume</td>
<td>$\upsilon$</td>
<td>$L^3mol^{-1}$</td>
</tr>
<tr>
<td>Volume fraction of p-phase</td>
<td>$\phi_p$</td>
<td>(-)</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\phi$</td>
<td>(-)</td>
</tr>
<tr>
<td>Mass transfer rate</td>
<td>$\psi$</td>
<td>$LT^{-1}$</td>
</tr>
<tr>
<td>Sedimentation accumulation rate</td>
<td>$\omega$</td>
<td>$LT^{-1}$</td>
</tr>
<tr>
<td>Total stress</td>
<td>$\Omega$</td>
<td>$ML^{-1}T^{-2}$</td>
</tr>
</tbody>
</table>

**Concentrations and saturation constants**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic matter concentration</td>
<td>$C_{CH_4O}$</td>
<td>mol/g</td>
</tr>
<tr>
<td>Sulfate concentration</td>
<td>$C_{SO_4^{2-}}$</td>
<td>mM</td>
</tr>
<tr>
<td>Methane concentration</td>
<td>$C_{CH_4}$</td>
<td>mM</td>
</tr>
<tr>
<td>Methane saturation concentration</td>
<td>$C_{CH_4}^*$</td>
<td>mM</td>
</tr>
<tr>
<td>Methane half – saturation constant</td>
<td>$H_{CH_4}$</td>
<td>mM</td>
</tr>
<tr>
<td>Sulfate half – saturation constant</td>
<td>$H_{SO_4^{2-}}$</td>
<td>mM</td>
</tr>
</tbody>
</table>

---

$^a$ Expressed in fundamental dimensions: $M = \text{Mass}, T = \text{Time}, L = \text{Length}, K = \text{Temperature}, \text{mol} = \text{mol}$

$^b$ Phases: $a = \text{aqueous}, s = \text{solid}, g = \text{gaseous}$
TABLE 2
Rates, fluxes and rate constants

<table>
<thead>
<tr>
<th>Rate</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of POC</td>
<td>$F_{CH_2O}$</td>
<td>mol/(m² a)</td>
</tr>
<tr>
<td>Rate of change in organic matter concentration</td>
<td>$\sum R_{CH_2O}$</td>
<td>mol/(g a)²</td>
</tr>
<tr>
<td>Rate of change in sulfate concentration</td>
<td>$\sum R_{SO_4}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>Rate of change in methane concentration</td>
<td>$\sum R_{CH_4}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>Sulfate reduction rate</td>
<td>$R_{SR}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>Methanogenesis rate</td>
<td>$R_{MET}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>AOM rate</td>
<td>$R_{AOM}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>Decay constant for particulate organic matter</td>
<td>$k_{f,g}$</td>
<td>a⁻¹</td>
</tr>
<tr>
<td>Rate constant for AOM</td>
<td>$k_{AOM}$</td>
<td>mM/a</td>
</tr>
<tr>
<td>Molar carbon transfer rate</td>
<td>$W_{CH_2O}$</td>
<td>mM/a</td>
</tr>
</tbody>
</table>

*grams of dry sediment

\[
\phi_a + \phi_s + \phi_g = 1 \tag{4}
\]

\[
\varphi = \phi_a + \phi_g \tag{5}
\]

where $\varphi$ is the non-solid volume fraction and is defined here as the porosity of the sediment, thus,

\[
1 - \varphi = \phi_s \tag{6}
\]

The fluid phase densities ($\rho_a, \rho_o, \rho_s$) depend on temperature ($T$), pore fluid pressure ($P$), and chemical composition of the pore water. In shallow marine sediments, the variation in $\rho_g$ and $\rho_s$ over the given ranges of $P$ and $T$ is small, so that zero compressibility for all three phases (that is, constant densities) is assumed here. Equations (1–6) can be combined and rearranged to describe the gradients of the aqueous and gaseous velocities relative to the velocity of the solid phase:

\[
- \frac{\partial v_s}{\partial z} = \frac{\partial (\phi_a v_a - \phi_g v_g)}{\partial z} + \frac{\partial (\phi_g v_g - \phi_s v_s)}{\partial z} \tag{7}
\]

In addition, combining equation (1) with equation (5) gives the following relationship for the porosity ($\varphi$):

\[
- \frac{\partial \varphi}{\partial t} = -(1 - \varphi) \frac{\partial v_s}{\partial z} + \sum R_i \tag{8}
\]

where the advective derivative defined with respect to the solid matrix velocity is given by:
To solve for the porosity profile, the momentum balance conservation equations (Darcy's law) for the aqueous and gaseous phases must be applied with respect to the solid phase:

\[
\frac{d\phi}{dt} = \frac{\phi}{\tau} + \nu_s \frac{\partial \phi}{\partial z}
\]

Transitory Porosity Profile

\[q_a = (\phi_a \nu_a - \phi_g \nu_g) = K_a \left(1 - \frac{1}{g \rho_a} \frac{\partial P}{\partial z}\right)\]  

\[q_g = (\phi_g \nu_g - \phi_g \nu_g) = K_g \left(1 - \frac{1}{g \rho_g} \frac{\partial P}{\partial z}\right)\]

where \(q_a\) and \(q_g\) are the aqueous and gaseous flows relative to the solid velocity. \(P\) and \(P_g\) are the pore fluid and the gas pressure, respectively, \(K\) is the hydraulic conductivity of the corresponding phase, and \(g\) is the acceleration due to gravity. \(K\) expresses the capacity of a fluid (aqueous or gaseous) to move through a porous medium (or resisting substance) and, thus, depends on the properties of both the fluid (density and viscosity) and the solid. The conductivities are defined as follows:

\[K_a = \frac{\rho_a g}{\eta_a} \kappa_{a/s}\]

\[K_g = \frac{\rho_g g}{\eta_g} \kappa_{g/s}\]

where \(\eta\) and \(\kappa\) are the dynamic viscosity and permeability for the respective phases.

Many theoretical expressions for the permeability exist in the literature (Siminek and others, 2003; MacQuarrie and Mayer, 2005), and it is beyond the scope of this work to detail the strengths and weaknesses of each approach. Rather, \(\kappa\) is described by the Carman-Kozeny equation, whose applicability has been proven for muddy sediments (Heij and Lowe, 1995):

\[\kappa_{a/s} = \frac{\varepsilon d^2 \phi_a}{\phi_a^3}\]

\[\kappa_{g/s} = \frac{\varepsilon d^2 \phi_g}{\phi_g^3}\]

where \(\varepsilon\) is a dimensionless proportionality constant related to the characteristics of the porous media, and \(d\) is the average grain-size diameter.

Combining the definition for \(\frac{\partial \phi}{\partial z}\) given by equation (7) and equation (8), and taking into account equations (9, 12-15), an expression for porosity in terms of the pressure gradients can be obtained:

\[\frac{\partial}{\partial z} \left( K_a - \frac{\varepsilon d^2 \phi_a^3}{\eta_a(1 - \phi)} \frac{\partial P}{\partial z} \right) + \frac{\partial}{\partial z} \left( K_g - \frac{\varepsilon d^2 \phi_g^3}{(1 - \phi) \eta_g} \frac{\partial P}{\partial z} \right) = \frac{(d\phi/dt + \Sigma R)}{1 - \phi}\]

The pore fluid pressure gradient \((\partial P/\partial z)\) can be expressed in terms of the mechanical response proposed by Hubbert and Rubey (1959) with a correction for the
presence of a gas phase. This is first performed by defining the total stress ($\Omega$) or total weight per surface area of the system which, assuming no inertial terms, is:

$$\Omega = P + \sigma$$  \hspace{1cm} (17)

where $\sigma$ is the effective stress and $\Omega$ is given by (assuming $z = 0$ to be the SWI):

$$\Omega = g \int_{0}^{z} [\rho_{s}(1 - \varphi) + \rho_{f} \phi_{a} + \phi_{g} \rho_{g}] \, dz + P_{I_{0}}$$  \hspace{1cm} (18)

where $P_{I_{0}}$ is the pressure at the SWI (see § Model Parameters and Boundary Conditions).

Differentiating equation (17) with respect to the depth ($z$), and applying equation (18) gives the pressure gradient:

$$\frac{\partial P}{\partial z} = g[\rho_{s}(1 - \varphi) + \rho_{f} \phi_{a} + \phi_{g} \rho_{g}] - \frac{\partial \sigma}{\partial z}$$  \hspace{1cm} (19)

Hubbert and Rubey (1959) assumed that the effective stress can be expressed as a single function of porosity, so that:

$$\frac{\partial \sigma}{\partial z} = \frac{\partial \sigma}{\partial \varphi} \frac{\partial \varphi}{\partial z}$$  \hspace{1cm} (20)

The quantity $\partial \sigma/\partial z$ is termed the "differential mechanical response" in L’Heureux and Fowler (2000), where this concept was used to investigate compaction in overpressured thick sediments. When characterizing a gas phase as an aggregate of individual bubbles, the gas pressure is equal to the pore fluid pressure corrected for the surface tension ($\gamma$) exerted on a gas bubble and, thus, the gas pressure gradient can be written in terms of the fluid phase pressure gradient (Rosner and Epstein, 1972):

$$P_{g} = P + \frac{2\gamma}{r}$$  \hspace{1cm} (21)

where $r$ is the average equivalent gas bubble radius, or bubble radius for short.

With these pressure relations established, equation (16) can be rearranged into an expression which defines the time-dependent vertical porosity profile:

$$(1 - \varphi)^{-1} \frac{d\varphi}{dt} = -z \frac{d}{dz} \left[ \frac{B - D}{(1 - \varphi)^{2}} + \frac{(\phi_{a}^{3}/\eta_{a} + \phi_{g}^{3}/\eta_{g}) \, \partial \sigma \, \partial \varphi}{(1 - \varphi)^{2} \, \partial \varphi \, \partial z} - \frac{\Sigma R_{i}}{(1 - \varphi)} \right]$$  \hspace{1cm} (22)

where

$$B = \phi_{a}^{3} \frac{\rho_{a} \phi_{a}}{\eta_{a}} + \phi_{g}^{3} \frac{\rho_{g} \phi_{g}}{\eta_{g}} + \frac{2\gamma \phi_{a}^{3}}{\eta_{a}^{2}} \, \partial \varphi \, \partial z$$  \hspace{1cm} (23)

$$D = g \left[ \frac{\phi_{a}^{3}}{\eta_{a}} + \frac{\phi_{g}^{3}}{\eta_{g}} \right] (\rho_{s} \phi_{a} + \rho_{g} \phi_{g} + \rho_{f}(1 - \varphi))$$  \hspace{1cm} (24)

Equation (22) can be further simplified by assuming that the solid volume fraction within a fluid medium undergoes steady-state compaction.

**Steady-State Compaction**

By assuming steady-state compaction ($d\varphi/dt = 0$), and that any temporal change in the gas volume fraction ($\phi_{g}$) is compensated by a change in the aqueous volume
fraction ($\phi_s$), a simple algebraic relationship between the solid phase velocity ($v_s$) and the porosity ($\varphi$) can be established by integrating equation (1) under steady state and applying appropriate boundary conditions at the SWI:

$$v_s = \frac{1 - \varphi_0}{1 - \varphi} + \frac{\int^z_0 \Sigma R_d dz}{(1 - \varphi)}$$  \hspace{1cm} (25)

where $\varphi_0$ is the porosity at the SWI and $\omega = \varphi_0$ is the imposed sediment accumulation rate.

With the solid advective velocity ($v_s$) defined, equation (22) can be transformed into a relation which is amenable to a numerical solution by finding a link between the effective stress ($\sigma$) and the solid volume fraction ($\phi_s$). Boudreau and Bennett (1999) explored this correlation under conditions of steady-state compaction. Here we define a similar relationship in terms of porosity:

$$\varphi = \varphi_w + (\varphi_w - \varphi_0)e^{-ab}$$  \hspace{1cm} (26)

where $\varphi_w$ is the porosity at sufficiently large depth for the effective stress to be constant and $b$ is an effective elastic response coefficient termed the “compaction coefficient” by Hart and others (1995) or “sediment compressibility” by Gordon and Flemings (1998). Consequently,

$$\frac{d\sigma}{d\varphi} = \frac{1}{b(\varphi - \varphi_w)}$$  \hspace{1cm} (27)

Substituting equation (25) and equation (27) into the steady-state form ($\partial/\partial t = 0$) of equation (22) gives the following expression:

$$(1 - \varphi_0)\frac{\partial(1 - \varphi)^{-1}}{\partial z} \frac{\partial v_s}{\partial z} = -\frac{\partial(1 - \varphi)^{-1}}{\partial z} \int^z_0 \Sigma R_d dz$$  \hspace{1cm} (28)

where,

$$-\frac{\partial v_s}{\partial z} = ed^2 \frac{\partial}{\partial z} \left( \frac{B - D}{(1 - \varphi)^2} \right) \frac{\partial(1 - \varphi)^{-1}}{\partial z}$$  \hspace{1cm} (29)

If flows for the aqueous phase ($q_a$) and the gaseous ($q_g$) phase with respect to the solid phase are imposed at the lower boundary of the system ($z = L$) so that $q_{al} = (\phi_s v_s - \phi_a v_a)|_L$ and $q_{gL} = (\phi_g v_g - \phi_g v_g)|_L$ respectively, equation (28) can be integrated:

$$\frac{\partial\varphi}{\partial z} = \frac{-b(\varphi - \varphi_w)(1 - \varphi)^2}{ed^2} \left[ \frac{(1 - \varphi)^{-1}}{A - \omega(1 - \varphi)} \right] \left[ \int^z_0 \Sigma R_d dz \right]$$  \hspace{1cm} (30)

where $A$ is the integration constant.
and \( \phi_L \) is the porosity at \( z = L \).

To derive the aqueous phase velocity, steady-state compaction is assumed \( (\partial \phi / \partial t = 0) \) and the resulting phase conservations (eqs 1–3) are summed:

\[
\int_{\phi_a}^{L} d(\phi_a v_a) + \int_{\phi_p}^{L} d(\phi_p v_p) + \int_{\phi_g}^{L} d(\phi_g v_g) = 0
\]

Upon solving and rearranging,

\[
v_a = \frac{q_{dL} + q_{gL} + v_{aL} - (1 - \phi) v_{g} - \phi_a v_g}{\phi_a}
\]  

(33)

Summarizing the results, equation (30) formally solves for the porosity \( \phi \) as a function of the gas phase volume fraction \( \phi_g \) through equation (5); equation (25) expresses the solid matrix velocity once \( \phi_a \) is known, whereas equation (33) gives the aqueous phase velocity \( v_a \) as a function of the gas phase properties \( v_g \) and \( \phi_g \). The following sections give expressions for \( v_a \) and \( \phi_g \).

**Gas Volume Fraction**

For single component gas phase systems, the gas volume fraction \( \phi_g \) can be represented as the product of the bubble number density in the pore water \( n \) and the characteristic bubble volume \( (\frac{4}{3} \pi r^3) \), where \( r \) is the characteristic (equivalent) bubble radius. Here we assume nucleation is negligible throughout the profile (nucleation is not rate limiting). Therefore, gas generation and consumption are considered to be solely due to radius growth and shrinkage. Assuming the bubbles can be characterized through an equivalent radius for spherical bubbles, \( \phi_g \) is equal to:

\[
\phi_g = \frac{4}{3} \pi r^3 n 
\]

(34)

and the mass transfer between the aqueous and the gas phase can be expressed as:

\[
R_g = \frac{4 \pi r^2 \psi_n}{v} \psi \phi_a
\]

(35)

where \( \psi \) is the bubble radius growth rate that expresses the aqueous-gas phase mass transfer rate as a function of the deviation from saturation. The gas-aqueous transfer rate during bubble growth is assumed to be governed by diffusion \( (\psi_D) \) or interface controlled \( (\psi_{IC}) \) kinetics (Rosner and Epstein, 1972). Bubble dissolution is assumed to be a process strictly controlled by interface kinetics since the bubble is assumed to be composed of a single gas component and thus diffusive processes within the bubble are negligible (see § Methane Saturation and Phase Transfer):

\[
\psi = \begin{cases} 
\psi_D & \text{if } (C_i \geq C_i^*) \\
\psi_{IC} & \text{otherwise}
\end{cases}
\]

(36)

\[
\psi_{IC} = \beta \left( \frac{C_i - C_i^*}{C_i}ight)
\]

(37)
where $\Psi_d = \frac{D_d}{\lambda} (C_i - C^s_i)$

\begin{equation}
\Psi_d = \frac{D_d}{\lambda} (C_i - C^s_i)
\end{equation}

The gas phase velocity is strictly dependent on the characteristics of the gas phase and the media through which it moves. In the water-saturated deep subsurface (oil reservoirs), the free-gas phase has been characterized as a continuous phase with buoyancy and capillary pressure acting as the main forces driving and resisting migration respectively (Schowalter, 1979). In sandy soils and aquifers, both the gas and aqueous phases have been described as continuous phases governed by Darcian flow, each one inhibiting the movement of the other phase, a process that is captured through the concept of relative permeability (van Genuchten, 1980). In both of the above cases entry pressures are required to initiate movement of the non-wetting phase (the free gas), leading to the conclusion that gas migration only occurs above specific gas saturations. However, in muddy sediments where the gas phase has been observed to occur as bubbles forming in areas where supersaturation takes place (Martens and Klump, 1980; Anderson and others, 1998), the movement of the gas phase has been proposed to occur due to fracture propagation and to take place even at the level of a single bubble (Boudreau and others, 2005). Unfortunately, the physics for this process (particularly for a 1-D sediment) have yet to be developed. Thus, in this study, we derive the gas phase velocity according to density differences and the relative movement amongst the solid, aqueous, and gas phases, which incorporates the general ideas mentioned above and is able to describe the velocity for each phase individually. We do not take into account random and episodic ebullition since it appears to constitute a small fraction of the free gas being generated (Martens and others, 1999). Rather, we concentrate on elucidating the essential question of the behavior of gas within the sediment column.

In a three phase system, a volume-averaged momentum balance for the gas phase can be used to derive the gas phase velocity (Whitaker, 1999). This gas phase velocity is based on the following assumptions: (1) the gas phase only forms and is transported within the aqueous phase, (2) a gas phase made of a large number of discrete bubbles can be simulated as a continuous phase and, (3) steady-state compaction will not be affected by the presence of a gas phase, such that changes in $\phi_s$ are accounted for by changes in $\Phi$. Following Whitaker (1999), we obtain

\begin{equation}
0 = -\eta_g \kappa_g^{-1} \phi_g (v_g - v_i) - \eta_g \kappa_g^{-1} \phi_g (v_g - v_a) + \rho_g g - \frac{\partial P}{\partial z}
\end{equation}

where $\kappa_g$ and $\kappa_g^{-1}$ are the inverse of the gas permeability with respect to the solid and aqueous phase, respectively. The first two terms in equation (39) represent the resistance due to the other phases with respect to the movement of the gas phase. The third term represents the force density exerted on the gas bubbles due to their weight, and the last term expresses the force density due to the pressure gradient exerted on the gas phase.

Solving for the gas phase velocity and applying equation (21) gives the following expression for the gas velocity in terms of the gas permeability:

\begin{equation}
v_g = \left( -\frac{\partial P}{\partial z} + \frac{2\gamma}{\eta_g} \frac{\partial \gamma}{\partial z} + \frac{\rho_g g}{\eta_g} \right) \frac{(\kappa_g^{-1} + \kappa_g^{-1} a)^{-1}}{(\kappa_g^{-1} a v_a + \kappa_g^{-1} v_a)} + \frac{(\kappa_g^{-1} a v_a + \kappa_g^{-1} v_a)}{(\kappa_g^{-1} + \kappa_g^{-1} a)}
\end{equation}
where $\gamma$ is the bubble surface tension. The term on the right-hand-side depending on the radius gradient is only important at very small gas bubble radii. Using the permeability expression defined in equation (15), the gas phase velocity now reads:

$$
\nu_g = \frac{\epsilon_d^2 \phi_g^3}{(\phi_s^3 + \phi_a^3) \eta_s} \left( -\frac{\partial P}{\partial z} + \frac{2\gamma}{r^2} \frac{\partial r}{\partial z} + \rho_g g \right) + \frac{\phi_g^2 \nu_a}{(\phi_s^3 + \phi_a^3)} + \frac{\phi_g^2 \nu_a}{(\phi_s^3 + \phi_a^3)}
$$  \hspace{0.5cm} (41)

Note that in equation (41), a Carman-Kozeny expression for the permeability of the gas phase with respect to the aqueous phase has been adopted. For this relationship to be valid, the pore size is assumed to be comparable to the average grain-size diameter:

$$
\kappa_{g/a} = \frac{\epsilon_d^2 \phi_g^3}{\phi_s^3}
$$  \hspace{0.5cm} (42)

The gas phase dynamics is governed by two processes, nucleation and growth (or dissolution). In terms of nucleation, the number of bubble nuclei present in the system must be conserved, and thus, the bubble density will be determined by transport and reaction processes through:

$$
\frac{\partial \phi_{a,n}}{\partial t} = -\frac{\partial (v_g \phi_a \eta)}{\partial z} + J \phi_a
$$  \hspace{0.5cm} (43)

where $J$ is the methane bubble nucleation rate. Nevertheless, for the simulations in this paper, we assume that no nucleation is taking place ($J = 0$) and therefore all mass transfer is channeled towards bubble growth.

Growth is described by combining equation (43) with the continuity equation for the gas phase (eq 3) (assuming constant gas density) and implementing the definitions for $R_g$ (eq 35) and $\phi_s^a$ (eq 34), which results in the following expression for the propagation of the bubble radius ($r$) through the sediment:

$$
\frac{\partial r^3}{\partial t} = -\frac{\partial (v_g r^3)}{\partial z} + 3r^2 \psi
$$  \hspace{0.5cm} (44)

The bubble radius is thus an explicit function of the gas advection ($v_g$) and the phase transfer rate ($\psi$) for any substance present in both the gas and the aqueous phase.

A conceptual sketch summarizing the main properties of the three-phase model is shown in figure 1, with specific reference to a highly-porous marine sediment with and without imposed aqueous basin flow. The panels depict different characterizations for the gas phase and aqueous phase velocities.

**Numerical Solution**

The numerical procedure employed to solve the set of coupled non linear equations begins with determining the porosity profile from equation (30) and equation (31). First, since all gas is generated within the model boundaries, the porosity at the model limit ($\phi_g$) can be estimated iteratively using a shooting method coupled with a 4th order Runge-Kutta scheme and assuming no gas phase. Then, using the initial conditions for the radius ($r$), [and consequently an initial guess for the gas volume fraction ($\phi_g$)], the aqueous and solid volume fraction profiles ($\phi_a^s, \phi_s$) are calculated, again applying a Runge-Kutta algorithm to equation (30). This process is repeated until all three volume fractions converge. Furthermore, this solution provides the pore fluid pressure and the effective stress as well as their respective gradients (eqs 19 and 20). Subsequently, equation (25) is used to calculate the solid phase velocity.
Fig 1. (A) Schematic representation of physical processes during steady-state compaction of the three-phase (gaseous, aqueous and solid) model indicating the depth at which methane goes from undersaturation to supersaturation (horizontal dashed line). Compaction leads to an increase in the solid volume fraction (SVF) with sediment depth (arbitrary scaling). Gas transport is described as a propagation of the average bubble radius, shown by the gas volume fraction (GVF) which transports gas above the saturation depth. A decrease in bubble radius, which represents gas dissolution, occurs above this saturation horizon and leads to a decrease in GVF. The aqueous volume fraction (AVF) compensates for both compaction and variations in the GVF. (B) During steady burial and compaction, and assuming no independent gas phase movement, all phases advect downwards as indicated by the arrows. (C) Assuming buoyancy of the gas phase, the gas is now transported upwards. (D) Assuming an externally-impressed flow which is greater than the downwards velocity of the aqueous phase due to burial, both the gas and aqueous phase are transported upwards. Note that in the convention used here, negative velocities represent migration towards the SWI.
Finally, the gas velocity \((v_g)\) and the aqueous phase velocity \((v_a)\) are solved simultaneously using equation (33) and equation (41). The chemistry of the system is described using separate mass conservation equations for each solute or solid species (§ Mass Conservation Equation for Individual Species). Once all profiles are determined, the bubble radius and the concentrations are updated at the next time step and the whole process is repeated. Note that the gas phase can be expanded to include more than one component. In such an instance, \(R_g\) in equation (2) and equation (3) would become a summation term similar to \(\sum R_s\) in equation (1) and equation (2), which implies that the constant gas phase density assumption might no longer be valid.

**Methane Gas Dynamics in Marine Sediments**

**Mass Conservation Equation for Individual Species**

The three-phase model is applied to the methane cycle in marine sediments (see table 1 and table 2 for a summary of all variables and parameters). In addition to solving for the total solid, aqueous, and gaseous phase dynamics, mass conservation is also imposed for each chemical species present in the system. In non-bioturbated sediments, the 1-D mass conservation equation for each solute \(i\) of concentration \(C_i\) is given by (Berner, 1980):

\[
\frac{\partial \phi_a C_i}{\partial t} = - \frac{\partial(v_a \phi_a C_i)}{\partial z} + \frac{\partial}{\partial z} \left( D_i^a \frac{\partial C_i}{\partial z} \right) + \phi_a \sum_i R_s
\]  

(45)

where \(D_i^a\) is the effective hydrodynamic dispersion coefficient for the solute. The solid species \((j)\) are not subject to diffusion and, therefore, the continuity equation for solid species depends only on burial and reactions:

\[
\frac{\partial (1 - \phi) C_j}{\partial t} = - \frac{\partial[v_a(1 - \phi) C_j]}{\partial z} + (1 - \phi) \sum_j R_s
\]  

(46)

\(R_s\) and \(R_f\) are the changes in concentration of the solute and solid species, respectively, due to production \((>0)\) and/or consumption \((<0)\) processes. In sediments subject to externally impressed flow, \(D_{i}^f\) is calculated from the tortuosity \((\theta)\) of the sediment (Boudreau, 1997) and the advection velocity of the aqueous phase:

\[
D_i^f = \alpha v_a + \frac{D_i}{\theta^2}
\]  

(47)

where \(\alpha\) is the dispersivity and \(D_i\) is the molecular diffusion coefficient and

\[
\theta^2 = 1 - 2 \ln (\phi_a)
\]  

(48)

Since the gas phase is comprised of methane only, phase conservation is used to describe the depth distribution of \(CH_4(\theta)\) (eqs 43 and 44).

**Biogeochemical Reaction Network**

The species considered here include a single methane gas phase, two dissolved species (methane and sulfate), one reactive solid species (particulate organic carbon, POC), and one non-reactive solid species (sediment grains, SG). The non-reactive solid species behave according to the solid phase conservation equations (§ Phase Conservation Equations), whereas the POC behaves according to equation (46). Volume conservation of the solid phase is maintained through \(\phi_s = \phi_{POC} + \phi_{SG}\) where \(\phi_{POC}\) is the volume fraction occupied by the POC and \(\phi_{SG}\) is the volume fraction occupied by the sediment grains. The reaction network consists of three microbially-mediated...
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pathways: sulfate reduction (SR), methanogenesis (MET), and anaerobic oxidation of methane (AOM), in addition to the mass transfer involved in gas formation/dissolution (F/D):

\[
\text{SR:} \quad \text{CH}_4 + \frac{1}{2} \text{SO}^{2-}_{4(aq)} + H^+ \rightarrow H_2O + \text{CO}_2(aq) + \frac{1}{2} \text{H}_2S(aq) \tag{49}
\]

\[
\text{MET:} \quad \text{CH}_4 \rightarrow \frac{1}{2} \text{CH}_4(aq) + \frac{1}{2} \text{CO}_2(aq) \tag{50}
\]

\[
\text{AOM:} \quad \text{CH}_4(aq) + \text{SO}^{2-}_{4(aq)} + 2H^+ \rightarrow 2H_2O + \text{H}_2S(aq) + \text{CO}_2(aq) \tag{51}
\]

\[
\text{F/D:} \quad \text{CH}_4(aq) \leftrightarrow \text{CH}_4(g) \tag{52}
\]

where \( \text{CH}_4 \) is the organic matter substrate (or POC) oxidized by the sulfate reducing and methanogenic microorganisms. The sum of rate terms in equation (45) and equation (46) are defined as the net production or consumption by all biotic, abiotic and physical processes. Organic matter decomposition follows a first-order rate expression which describes the extracellular hydrolysis of macromolecular organic compounds (units for the rates are given in table 2):

\[
\sum R_{\text{CH}_4O} = \frac{W_{\text{CH}_4O}}{\rho_{\text{CH}_4O}} = -k_{\text{pm}} C_{\text{CH}_4O} \tag{53}
\]

where \( W_{\text{CH}_4O} \) is the molar rate of carbon transfer from the aqueous to the solid phase (more importantly, \( -W_{\text{CH}_4O} \) represents the molar rate of carbon transfer from the solid to the aqueous phase) reported per total volume.

Since the sediment grains are inert in the model, the reaction term in equation (1), can be defined solely in terms of the POC:

\[
\sum R_i = W_{\text{CH}_4O} \frac{m_{\text{CH}_4O}}{\rho_{\text{CH}_4O}} \tag{54}
\]

where \( \rho_{\text{CH}_4O} \), \( m_{\text{CH}_4O} \) are the POC density and the molar weight, respectively.

Sulfate is consumed by both AOM and SR:

\[
\sum R_{\text{SO}_4^{2-}} = R_{\text{AOM}} + R_{\text{SR}} \tag{55}
\]

The AOM rate is given by:

\[
R_{\text{AOM}} = -k_{\text{AOM}} \frac{C_{\text{CH}_4}}{C_{\text{CH}_4} + H_{\text{CH}_4} + H_{\text{SO}_4^{2-}}} \tag{56}
\]

where \( k_{\text{AOM}} \) is the rate constant, \( H_{\text{CH}_4} \) and \( H_{\text{SO}_4^{2-}} \) are the half-saturation constants with respect to methane and sulfate respectively.

The SR rate follows from equation (58):

\[
R_{\text{SR}} = -f_{\text{SO}_4^{2-}} \frac{1}{2} k_{\text{pm}} C_{\text{CH}_4O} \phi \frac{(1 - \varphi)}{\phi_a} \tag{57}
\]

where \( f_{\text{SO}_4^{2-}} \) is a function which accounts for the limiting effect of low sulfate concentrations:
The half-saturation constant for sulfate-reducing bacteria \((H_{SO_4^-})\) can vary over several orders of magnitude (Pallud and Van Cappellen, 2006) and a value of 0.1 mM is selected here. However, a value of 1.0 mM, which shifts the profiles towards the SW, was used for the sensitivity analysis.

The half-saturation constant for methane oxidizers \((H_{CH_4})\) is also poorly constrained. A value of 1.0 mM is used in the model based on the results of Nauhaus and others (2002). The model is essentially insensitive to reasonable variations in the value of the half-saturation constant for methane oxidizers.

Aqueous methane is produced below the sulfate reduction zone by MET, and is consumed by AOM. Furthermore, the phase transfer will vary according to the \textit{in situ} methane saturation concentration: if oversaturated, \(CH_4(g)\) represents a methane sink and if undersaturated, \(CH_4(g)\) (if present) represents a methane source for the aqueous phase:

\[
\sum R_{CH_4} = R_{AOM} + R_{MET} - R_g / \phi_a
\]  
(59)

where \(R_g\) is described by equation (35), and the rate of MET is analogous to SR:

\[
R_{MET} = (1 - f_{SO_4^2}) \frac{1}{2} k_{CH_4} C_{CH_4} \phi_a \frac{(1 - \varphi)}{\phi_a},
\]  
(60)

\textbf{Methane Saturation and Phase Transfer}

The rate of methane transfer depends on the deviation of the aqueous phase concentration from the \textit{in situ} saturation concentration. Methane saturation is a function of temperature \((T)\), salinity \((S)\), and pore fluid pressure \((P)\) (Abegg and Anderson, 1997), and several approaches to calculating methane saturation have been described in the literature (Yamamoto and others, 1976; Abegg and Anderson, 1997; Duan and Mao, 2006). Here we employ a third-order polynomial to calculate methane solubility \((C^e_{CH_4})\) as a function of \(T, P,\) and \(S\) based on Dale and others (2008):

\[
C^e_{CH_4} = a_1 PT + a_2 PT + a_3 PS + a_4 TS + a_5 P + a_6 T + a_7 S + a_8
\]  
(61)

where the coefficients \((a_i - a_8)\) (table 3) were calibrated against the values from Duan and Mao (2006) for the range of \(P, T, S\) values found in shallow brackish marine sediments (3–5 bar, 275.15–285.15 K, 22–25 salinity).

The methane solubilities calculated using equation (61) as well as values obtained from Duan and Mao (2006) are compared to those predicted by Abegg and Anderson (1997) in figure 2. Our model, using the third-order polynomial deviates from the latter and may therefore predict different rates of methane gas generation with respect to studies (for example, Martens and others, 1998) that have used the curve proposed by Abegg and Anderson (1997). The temperature in the sediment is modeled using a heat transport equation following Dale and others (2008) under the assumption of no bioirrigation/bioturbation (Nitrourer and others, 1998). The pore fluid pressure in the sediment is calculated by integrating equation (19), whereas the salinity is imposed from the measured data reported by Albert and others (1998).

The mass transfer rate between the aqueous and gas phases \((\psi)\) has a kinetic (interface controlled) component \((\psi_{KC})\) and a diffusive component \((\psi_D)\) (eq 36). Both the thickness of the diffusive boundary layer over which the molecules transfer \((\lambda)\) and the mass transfer velocity coefficient \((\beta)\) are poorly constrained parameters. However,
based on previous studies (Boudreau and others, 2001; Gardiner and others, 2003), the diffusive phase transfer was assumed to be the limiting growth mechanism for bubble radiiues in the sub-cm range. The diffusive boundary layer is assumed to be linearly dependent on the radius of the bubble \( \lambda = \rho_r \). By comparison with previously modeled data (Gardiner and others, 2003) the constant \( \rho_r \) was determined to have a value of 2.3 (fig. 3). Bubble dissolution, however, remains poorly constrained. In previous studies dissolution rates were orders of magnitude higher than the ones reported here: (1) Fast dissolution rates resulted for fast rising bubbles in the water column according to empirical equations (McGinnis and others, 2006); and (2) in sediments, based on a first order dependence to the departure from saturation, fast dissolution rates were also required when performing a least-squares fit regression to measured data (Haeckel and others, 2004). In any case, for steady-state simulations, dissolution rates could be increased over several orders of magnitude without any

![Figure 2](image-url)

**Table 3**

**Third-order polynomial solubility constants**

<table>
<thead>
<tr>
<th>( a_i )</th>
<th>Value (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1 )</td>
<td>1.4387E-04</td>
</tr>
<tr>
<td>( a_2 )</td>
<td>-4.1222E-02</td>
</tr>
<tr>
<td>( a_3 )</td>
<td>-4.6842E-02</td>
</tr>
<tr>
<td>( a_4 )</td>
<td>4.1290E-06</td>
</tr>
<tr>
<td>( a_5 )</td>
<td>1.4346E+01</td>
</tr>
<tr>
<td>( a_6 )</td>
<td>-1.6022E-03</td>
</tr>
<tr>
<td>( a_7 )</td>
<td>-1.2680E-03</td>
</tr>
<tr>
<td>( a_8 )</td>
<td>2.7000E-01</td>
</tr>
</tbody>
</table>

Fig. 2. Methane solubility concentration profile calculated for the conditions of \( T, S, \) and \( P \) of Eckernförde Bay.
meaningful change in the free-gas and dissolved methane profiles since free-gas dissolution in methane depleted regions becomes transport limited (data not shown). Further constraints on free-gas dissolution rates may be obtained based on model calibrations using transient field data.

Model Parameters and Boundary Conditions

The selected model parameters (table 4) and the boundary conditions (table 5) correspond to the environmental conditions of Eckernförde Bay (Germany), a shallow marine environment (<30m water depth) characterized by high sedimentation rates (0.5–1.1 cm/a) (Martens and others, 1998, 1999; Nittrouer and others, 1998), up to 12 percent (by dry weight) POC concentration (Silva and Brandes, 1998; Whiticar, 2002) and perennial bottom water anoxia. These conditions favor sulfate reduction just below the SWI [in the central basin they also lead to insignificant bioirrigation and bioturbation, as observed by the extensive preservation of laminae (Nittrouer and others, 1998)], and high rates of methanogenesis in the underlying sediments. In situ dissolved methane concentrations frequently exceed the solubility concentration (Martens and others, 1999) leading to the formation of CH₄(g). Yet experimental evidence reveals no or limited free-gas escape to the water column (Martens and others, 1999).

The model is primarily calibrated using the physical and geochemical data reported in Martens and others (1999). Gravimetric water content and grain-size diameter measurements taken from Silva and Brandes (1998) were used to determine the aqueous porosity profile. Assuming a constant sediment density, the parameter b in equation (27) was varied in accordance with the imposed sediment accumulation rate of 0.6 cm/a (Martens and others, 1999). In addition, an upward aqueous flow of 1 cm/a was imposed at the lower model boundary to account for the freshwater advection introduced from the underlying Holocene glacial tills (Albert and others, 1998).

Due to complete consumption of all labile POC at the lower boundary (refractory POC was assumed to be inert at sulfate-reducing time scales), gas production and gas fluxes are assumed to be absent at the lower model boundary (400 cm). Accordingly,
the bubble radius is assigned a value equal to the critical radius of nucleation and a zero gas flux \( q_j = 0 \) is assumed. The boundary conditions for temperature at the top and bottom of the model were estimated from the average temperatures for Eckernförde Bay sediments from Wever and others (1998), whereas the boundary condition for the pore fluid pressure imposed at the SWI depends on the atmospheric pressure \( P_{\text{atm}} \), the aqueous density \( \rho_a \), gravity \( g \), and the height of the water column above the SWI \( h \).
For the dissolved species, a Dirichlet boundary condition is applied at the SWI, while a zero-gradient boundary condition is imposed at the lower model boundary. For POC at the SWI, the imposed boundary concentration is calculated from the POC flux ($F_{CH_4O}$) according to:

$$C_{CH_4|0} = \frac{F_{CH_4O}}{\omega \rho \phi_s}$$  \hfill (63)

Because no measurements are available to constrain the labile POC flux, it is determined from the observed sulfate and methane concentration profiles through model calibration exercises.

**Mass Balance**

Mass balance in the system was verified by establishing a budget for the gas phase, the POC, and the aqueous methane over the range of model forecasts investigated in
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Fig. 4. Simulated aqueous methane, sulfate and methane gas volume fraction as well as methane saturation profiles (lines) in Eckernförde Bay. Measured data from Martens and others (1998, 1999) are also shown (points).

this study. Firstly, the depth-integrated gas formation and dissolution rates agreed to within 1 percent. Secondly, the POC flux deposited at the SWI balanced the sum of the integrated (and stoichiometrically corrected) MET and SR rates to within 0.1 percent. Thirdly, the difference between the sum of the aqueous methane flux at the model boundaries plus the integrated MET and the integrated AOM rate never exceeded 1 percent.

BASELINE SIMULATION

The baseline simulation used for this study was the NRL site described and modeled in Martens and others (1999) and Albert and others (1998). The steady-state concentration and rate profiles simulated with the three-phase, gas-explicit RTM for methane cycling are shown in figures 4 and 5, respectively. Based on the calibration performed on the sulfate and methane profiles (fig. 4), the steady-state POC profile (fig. 5) decreases exponentially with depth from approximately 0.433 mmol C/g dry sediment (roughly 0.5% by weight) at the SWI, which is consistent with the first-order decay imposed in the model. Field measurements reveal, however, much larger superficial POC concentrations in Eckernförde Bay (Silva and Brandes, 1998), implying that the majority of this organic matter is unreactive within the first three meters of the sediment core.

The depth distribution of sulfate in Eckernförde Bay (fig. 4) is controlled by sulfate diffusion into the sediment and controlled by the in situ biogeochemical processes. The relative rates of sulfate reduction (due to both POC degradation and AOM) as well as the upward advection of pore water, diminish the sulfate penetration into the sediment leading to complete consumption by 35 cm. Organoclastic sulfate reduction measurements at this site are lacking, but the model predicts that in the first 25 cm sulfate is consumed only through the degradation of POC (fig. 5), and then by AOM in the underlying Sulfate-Methane Transition Zone (SMTZ).

Similarly, the aqueous methane profile (fig. 4) is controlled by the main biological (methanogenesis and AOM) and physical (advective, diffusive and gaseous transport) processes of the methane cycle. Methanogenesis begins when sulfate concentrations
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Figure 5. Simulated POC profile and rates for methanogenesis (MET), total sulfate reduction and AOM (lines). The (maximum) AOM rates measured by Martens and others (1998, 1999) are also shown (points).

Decrease to low values (fig. 5), and leads to the formation of CH$_{4(g)}$ approximately 100 cm below the SWI, where $C_{CH_4}$ exceeds the in situ solubility concentration (fig. 4). Under the steady-state conditions assumed here, the down-core temperature and salinity decrease of 2 to 3 °C (Wever and Fiedler, 1995) and 0.15 respectively compensates for the down-core increasing pressure in the system and leads to a relatively minor increase in the methane solubility concentration with depth. This slight increase has little effect on the spatial distribution of the CH$_{4(g)}$ production. Note however, that transient conditions induced by sea level changes due to winds and tides, and atmospheric pressure variations could have a significantly larger effect on the dissolution and formation of CH$_{4(g)}$ at this site (Wever and others, 2006).

Because methane is the only gas component considered, CH$_{4(g)}$ can be characterized through the gas volume fraction ($\phi_g$, eq 34) and thus the bubble density (eq 43) and the bubble radius (eq 44). The initial value for the bubble density ($n = 0.01 \text{ cm}^{-3}$) is a rough approximation based on the observations in Anderson and others (1998) and a sensitivity analysis of the model results with respect to n is performed below (see § Bubble Density).

The model-predicted $C_{CH_4}$ and gas volume fractions (fig. 4) agree with previous results reported by Martens and others (1999), and Anderson and others (1998). In the present study, however, CH$_{4(g)}$ generation, dissolution and transport are also included in the simulation. In addition, compaction is explicitly accounted for in the constitutive volume conservation equations, implying that, along with the CH$_{4(g)}$ formation and transport, it may also affect the spatial distribution of solutes. The sediment compaction algorithm predicts the typical exponential-type decrease of pore space with depth and is consistent with the data from Silva and Brandes (1998) (not shown).

Eckernförde Bay is a unique site since, despite high sedimentation rates, it is dominated by freshwater seepage from the underlying glacial till sediments (Schlüter and others, 2004). Consequently, an imposed basinal-upward aqueous flow of 1 cm a$^{-1}$ (Albert and others, 1998) generates a net aqueous flow towards the SWI relative to the solid matrix. Furthermore, the gas bubbles also have a strong tendency to move towards the SWI, since the combination of forces described in equation (39) are
dominated by buoyancy and the advective term of the aqueous phase. Mass conservation for the aqueous and gas phases predicts opposite fluxes between these two phases (eq 33) and therefore, the aqueous phase should compensate for the gas flow by moving in the opposite relative direction. At the imposed aqueous advective velocities, however, a total net fluid movement is still maintained towards the SWI, and the gas phase merely inhibits the aqueous phase flow (fig. 6). With higher gas fluxes, a change in the direction of the aqueous flow (away from the SWI) is possible, a situation further discussed in § Transport and Dissolution.

As CH$_4$(g) begins to accumulate in the sediment, it is transported upwards by advection until complete dissolution or ebullition from the sediment takes place. Haeckel and others (2004) reported the terminal speed of rising bubbles at Hydrate Ridge (an active seep) to be 4 to 46 cm/min based on calculations in locations of clathrate formation and active channel flow. Boudreau and others (2005) describe the rise velocity of single bubbles in gels mimicking muddy sediments to also be in the cm/min range. In this paper we do not consider fast bubble rise due to channel flow or fracture propagation, since reported ebullition rates in Eckernförde Bay are low and several orders of magnitude less than the estimated gas production rate (Jackson and others, 1998; Wilkens and Richardson, 1998), and in many cases not even detected (Martens and others, 1999). Rather, our model suggests that what appears to be a "static" acoustic gas layer actually has a small creep-like movement due to buoyancy and the upwards aqueous advection found in Eckernförde Bay. These gas velocities (fig. 7), which are about an order of magnitude higher than the aqueous phase velocities and 4 to 5 orders of magnitude lower than the velocities found in channels/tubes (Haeckel and others, 2004, 2007) and fracture propagation in gels (Boudreau and others, 2005), can become an effective mechanism for methane delivery to sediment depths which are undersaturated with respect to the in situ methane solubility.

At the site simulated here, methane transfer from the aqueous phase to the gas phase occurs between 95 and 240 cm depth (fig. 7). This process successfully removes most supersaturated methane, which maintains relatively low degrees of supersaturation and gas formation, and allows for slow buildup and movement of a gas phase.

---

**Fig. 6.** Aqueous volume fraction and aqueous velocity. Negative velocities indicate movement towards the SWI.
Bubble dissolution takes place between 65 and 95 cm depth where \( C_{CH_4} \) consumption driven by AOM in the SMTZ leads to undersaturated conditions with respect to the local methane solubility. Unlike the slow but widespread gas formation rate, dissolution rates are fast and occur over a sharp, narrow interval due to the fast decline in \( C_{CH_4} \) concentrations, and consequently, large departures from the *in situ* saturation concentration (fig. 4). Dissolution rates could diminish due to the presence of protective coatings surrounding individual methane bubbles (Rehder and others, 2002), a process observed in bubbles originating from clathrate dissolution and not included here. In this study, the growth rates were calibrated to the observed and modeled results of Gardiner and others (2003), whereas the dissolution rates were assumed to be kinetically dominated (eq 36). Both processes are first order dependent with respect to the departure from the saturation concentration, which is an analogous formulation to the transfer rates used by Davie and Buffet (2001) and Haeckel and others (2004).

Depth-integrated rates for the main biogeochemical processes in the baseline simulation are listed in table 6 and compared to those of Martens and others (1998). The values in table 6 differ due to the distinct formulations used for the AOM rate and the switch function implemented for simulating the organoclastic sulfate reduction-methane generation transition. In particular, the present model uses double (methane and sulfate) Michaelis-Menten kinetics instead of a first order rate law with respect to

### Table 6

*Integrated rates obtained in this study and in Martens and others (1998)*

<table>
<thead>
<tr>
<th>Baseline simulation results</th>
<th>This Model</th>
<th>Martens</th>
<th>Unit$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated AOM</td>
<td>0.280</td>
<td>0.426</td>
<td>mol/(m$^2$ a)</td>
</tr>
<tr>
<td>Integrated SR</td>
<td>0.408</td>
<td>0.98</td>
<td>mol/(m$^2$ a)</td>
</tr>
<tr>
<td>Integrated total SR</td>
<td>0.688</td>
<td>1.14</td>
<td>mol/(m$^2$ a)</td>
</tr>
<tr>
<td>Integrated MET</td>
<td>0.285</td>
<td>0.436</td>
<td>mol/(m$^2$ a)</td>
</tr>
</tbody>
</table>

$^a$ Values reported per m$^2$ porewater.
methane as in Martens and others (1998), and hence, predicts a different AOM zone thickness. Michaelis-Menten kinetics do not portray the tailing observed in the measured methane and sulfate profiles (Martens and others, 1999). This lack of tailing narrows the SMTZ and predicts slightly deeper (roughly 10 cm) maximum AOM rates than those actually observed (fig. 5). The incorporation of the complex interplay of microbial activity involved in the intermediate pathways of AOM and SR (such as acetogenesis and fermentation) could provide a more accurate description of methane and sulfate cycling in the AOM zone (Dale and others, 2006, 2008). Most importantly, the majority of the discrepancy between the depth-integrated rates in this study and those of Martens and others (1998) results from the lower first order organic degradation constant and POC flux used in this study. In both studies, these values were determined by calibration against the measured data. However, the lower values selected here reflect the effects of upwards advecting CH₄(,) dissolving in the methane-depleted areas, fueling the AOM, shallowing the SMTZ and hence requiring less POC to fit the data. These results emphasize the possible influence of a gas phase in the biogeochemistry of shallow marine sediments. The impact of gas generation, transport and dissolution on the methane cycling in marine sediments over a range of POC deposition fluxes is investigated in further detail in § Transport and Dissolution and § Integrated Rates.

**Sensitivity Analysis**

In what follows, the sensitivity of the gas phase model to variations in the bubble density and the Carman-Kozeny parameter is investigated. Note that for these simulations $H_{SO_4}^?$ = 1.0 mM, which produces a shallower SMTZ with respect to the baseline simulation.

**Bubble Density**

The density of bubble nuclei $n$ is a parameter that is very difficult to constrain experimentally since geophysical techniques for characterizing the in situ gas phase (such as CT scans and sonar) have minimum bubble radius detection limits, (Anderson and others, 1998). In this study, based on a rough estimate of the CT scans from Anderson and others, 1998, we assumed an initial bubble density of 0.01 cm⁻³ porewater. Initial values for $n$ were then varied by one order of magnitude and results reveal that over these range of values, the bubble density has a very limited impact on the steady-state simulations (fig. 8). This parameter exerts a minor effect on the CH₄(g) volume fraction profiles since variations in the bubble density have a partially compensating, opposite effect on the bubble radius.

**Carman-Kozeny Parameter Variations**

The value for the Carman-Kozeny parameter $\varepsilon$ in a porous medium consisting of perfectly packed spheres is 1/180. However, for real soils and sediments, most $\varepsilon$ values depart from this hypothetical value (Heijjs and Lowe, 1995). To account for the fact that the porous medium is not perfectly packed (porosity values exceed perfect packing) and silt and clay particles are not spherical, $\varepsilon$ was varied over two orders of magnitude. The results reveal that increasing $\varepsilon$ leads to higher gas velocities, and as a result, the $\phi_g$ profile shifts towards the SMTZ (fig. 9). Here methane undersaturation dissolves the gas before $\phi_g$ can build up to the peak values obtained with a higher $\varepsilon$, thus resulting in lower depth-integrated mass transfer rates. The converse situation occurs for lower $\varepsilon$ values (fig. 9).

**Importance of the Gas Phase in Methane Cycling**

In this section, the controls of the gas phase on methane cycling are explored for a range of POC fluxes. At the high end, methane gas formation rates are not large
Fig. 8. Model sensitivity to the \( n \) parameter at a POC flux of 1.025 mol C/(m\(^2\)a). Solid lines indicate \( n = 0.01 \). Dotted lines represent \( n = 0.001 \) whereas dashed lines represent a value of \( n = 0.1 \).

Fig. 9. Model sensitivity to the \( \varepsilon \) parameter at a POC flux of 1.025 mol C/g sed. Solid lines indicate \( \varepsilon = 1/180 \). Dash-dot lines represent \( \varepsilon = 1/1800 \) and dashed lines represent a value of \( \varepsilon = 1/18 \).
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Fig. 10. (A) Aqueous methane profiles for both the implicit (imp) and the explicit (exp) model. (B) Gas volume fraction profiles using the explicit model (top 100 cm). POC flux values are expressed in mol C/(m² a).

Transport and Dissolution

The $C_{CH_4}$ profiles and the accumulated methane gas content show significant variations over the array of POC fluxes (fig. 10). The results reveal that as the POC loading increases, the aqueous methane front moves towards the SWI and the concentration gradient becomes progressively sharper (fig. 10). Similar variations are observed for $C_{CH_4}$ in the case of the implicit model, yet the generation, transport, and dissolution of the gas phase causes a more pronounced methane front. As the POC flux increases, more methane gas is also generated and subsequently transported towards the methane starved zones, fueling the AOM, and therefore pushing further upwards the methane front and SMTZ. For the explicit model, figure 11 shows that with low POC fluxes, methane is primarily transported towards the AOM zone by solute diffusion. As more gaseous methane is generated with higher POC fluxes, the methane gas flux can reach a magnitude comparable to that of the diffusive flux. Consequently, a significant underestimation of the methane delivery to depleted areas like the SMTZ is likely in the case of an implicit gas phase model. Accordingly, all other model parameters being equal, a higher POC flux at the SWI will be required to fit the measured methane and sulfate profiles with the implicit model. The formation of a gas phase also has implications for the aqueous phase flow. As already observed in the baseline simulation, if a significantly upward aqueous flux is imposed at the lower model boundary, the movement of both the aqueous and gaseous phase will be towards the SWI because the inhibition of the gas phase on the aqueous flow is not large enough to overcome the externally impressed flow. Figure 11 shows that in the system with lower POC flux (thus lower $CH_4^{(aq)}$ content), the gas phase flux only hinders the upward aqueous advective flux. In contrast, in the system with the larger POC flux, where the $CH_4^{(aq)}$ content is somewhat larger, the direction of the aqueous advective flux reverses (around 30 cm depth), flowing away from the SWI, compensating the gas phase movement towards the SWI in such a way that the total volume (mass) is conserved. Note however, that for the transport regime investigated here, the aqueous advective methane flux remains always roughly one order of magnitude smaller than the diffusive methane flux.
Integrated Rates

The feedbacks of the gas phase on the biogeochemical dynamics can be examined by comparing the depth-integrated SR, MET, and AOM rates calculated with the explicit and implicit models, respectively. Figure 12 shows that substantial discrepancies occur between the results of both models, and that these differences escalate with increasing POC fluxes. As stated in the previous subsection, the methane fraction lost in the implicit model is primarily transported and delivered to the SMTZ in the explicit model. This methane transfer stimulates AOM and leads to higher integrated AOM rates with the gas explicit model (fig. 12C). Furthermore, higher AOM rates push the SMTZ towards the SWI, decreasing the sulfate penetration into the sediment and, consequently, the integrated organoclastic SR rates (fig. 12A). Since less POC is consumed in SR, more is available for MET, and thus, higher integrated MET rates are predicted with the explicit gas model (fig. 12B). In both the implicit and explicit models, the AOM rates dominate over the SR rates; hence, the total integrated SR reduction rate is also higher for the explicit gas phase model (fig. 12D), as opposed to those for the integrated organoclastic SR rates. In summary, a positive feedback takes place in the explicit model: the larger the gas phase, the larger the MET, free-gas formation/dissolution and AOM. Thus increasing the POC fluxes results in the increase of the divergence between the simulated integrated rates of the two models. Note that in the implicit gas phase simulations, upwards methane diffusion and advection become limiting for the AOM rate when the POC flux is large, leading to the asymptotic behavior shown in figures 12C and 12D. Such transport limitation does not occur in the explicit gas phase model, indicating that the generation, transport and dissolution of CH$_4$(g) could be important processes for sustaining high AOM rates. The results reveal that, in the absence of channel vents, AOM acts as an efficient subsurface methane barrier.

CONCLUSIONS

A 1-D model has been developed to describe the steady-state phase behavior of unconsolidated marine sediments characterized by the presence of free (methane) gas. The model explicitly includes the depth distributions of the gaseous, aqueous and...
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solid fractions, which are defined from fundamental laws of mass and momentum conservation. In contrast to other previous 1-D representations of gassy marine sediments, our approach allows to investigate the effects of gas formation, transport and dissolution on the dynamics of the aqueous and solid fractions as well as on the biogeochemistry of anaerobic sediments. This approach reveals that the gas phase dynamics are instrumental in determining the position and shape of the methane front as well as the magnitude of the AOM rate, which may function as an efficient sink term not only for aqueous methane, but also for methane gas. The model is applied to a comprehensive set of benthic data collected in Eckernförde Bay (Germany), which is a shallow-water environment with a low gas content (<1%). The model results support independent observations in the literature in that relatively slow gas migration prevails over rapid loss of the gas phase through ebullition in Eckernförde Bay. This prevents methane gas escape from the sediment by allowing sufficient time for gas dissolution in unsaturated pore water and further consumption by anaerobic microorganisms to take

Fig. 12. Depth-integrated organoelastic SR (A), methanogenesis (B), AOM (C), and total SR (D) rates over a range of POC flux values. Integrated rates expressed per m² sediment.
place. Further research is needed to determine the wider importance of this type of gas transport mechanism in other organic-rich marine sediments, and also whether gaseous methane could escape to the water column under the transient regime, when short-term changes in gas solubility through variations in water temperature and pressure occur.

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REFERENCES


Hart, B. S., Flemings, P. B., and Deshpande, A., 1995, Porosity and pressure: Role of compaction
Methane gas-phase dynamics in marine sediments: A model study


oxidation of methane in the gassy sediments of Eckernförde Bay (German Baltic): Limnology and Oceanography, v. 50, p. 1771–1786.


