Control of sulphate and methane distributions in marine sediments by organic matter reactivity

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Abstract

The reactivity of organic matter serving as fuel for microbial activity in buried sedimentary layers imposes a strong control on the subsurface biogeochemical zonation and rates of metabolism. To understand the consequences of different organic matter degradation rates on subsurface microbial activity and sediment pore water chemistry, sulphate and methane concentration profiles were simulated using different organic matter decay models from the literature. Results show how the decay of a more reactive pool of organic matter results in a more curved sulphate profile and deeper sulphate methane transition (SMT) with decreasing apparent initial age of the organic matter. A minimum in SMT is reached if the initial age is intermediate, commonly in the order of 10^4–10^5 years. If the initial age is very large the sulphate profile is almost linear and the sulphate methane transition is located deeper with increasing apparent initial age of the organic matter. Curved versus linear shaped sulphate profiles reflect different relative contributions of organoclastic sulphate reduction versus anaerobic methane oxidation to the total consumption of sulphate. Our model results demonstrate that the SMT can move up or down depending on organic matter reactivity and its depth is not necessarily diagnostic of total organic carbon flux. The model provides a mechanistic understanding of how the shape of the sulphate profiles and the relative contributions of organoclastic sulphate reduction versus anaerobic oxidation of methane are controlled by the kinetics of organic matter degradation.
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1. INTRODUCTION

The consumption of sulphate is one of the most obvious features of subsurface metabolic activity in marine sediments. Sulphate is consumed at the end of a cascade of electron acceptors (Froehlich et al., 1979) and, once sulphate is depleted, methanogenesis remains the main terminal process of organic matter mineralization. Two different types of sulphate reduction occur. One is fuelled by degradation of organic matter (organoclastic sulphate reduction, OSR), the other by anaerobic oxidation of methane (AOM) diffusing upward from the methanogenic zone. Although it is obvious that both sulphate-reducing pathways are ultimately fuelled by degradation of buried organic matter, the factors that control their relative contributions to the total sulphate consumption and the depth where sulphate is depleted (the sulphate methane transition, SMT) remain poorly understood. Knowing these factors is essential to understand how the amount and composition of organic matter deposited in past oceans controls today's subsurface microbial activity and how this deep biosphere responds to changes in oceanographic conditions on geological timescales.

Many factors influence the subsurface distribution of sulphate, such as diffusivity, permeability, advective flow (Jørgensen and Kasten, 2006; Holstein and Wirtz, 2010),

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bioturbation and bio-irrigation (Fossing et al., 2000; Jørgensen and Parkes, 2010). Near the SMT, kinetics of the AOM reaction control the shape of the sulphate and methane profiles (Dale et al., 2008a; Knab et al., 2008). Recently, a cryptic sulphur cycle driven by reduction of solid phase ferric iron has been proposed by Holmkvist et al. (2011) to provide additional sulphate below the SMT. Additional methane may also be contributed from external sources (Burdige and Komada, 2011), such as the dissociation of gas hydrates (Borowski et al., 1999). Moreover, due to variation in sediment deposition at many sedimentary settings, the observed sulphate and methane profiles may not be in a steady state (Adler et al., 2000; Kasten et al., 2004; Arndt et al., 2006, 2009; Regnier et al., 2011). Nevertheless, in an ideal steady state case the subsurface reaction and transport of sulphate can be reduced to three main factors that are inherent to all natural marine sediments: (1) the total organic carbon (TOC) content of sediment deposited on the seafloor, (2) its reactivity, and (3) the burial rate.

It is observed that organic matter degradation rates generally decrease with age and depth in the sediment and several models have been formulated that describe organic matter degradation as a function of time and burial depth (i.e. depth below seafloor). Based on the assumption that a single organic compound decays according to first order kinetics, Berner (1964) suggested an exponential decay function. Jørgensen (1978) observed by means of radiotracer incubation experiments that microbial metabolic rates could be better described by a power-law function in marine sediments. Recent studies of microbial cell counts and metabolic rate measurements have confirmed this trend in a wide range of marine sediments (D'Hondt et al., 2003, 2004; Parkes et al., 2005; Jørgensen and Parkes, 2010). An apparent power function also resulted from the combination of multiple compounds with different exponential decay constants (multi-G model; Berner, 1980; Westrich and Berner, 1984). Middelburg (1989) used a power law relationship between the rate constant and the age of the organic matter to describe the observed decrease in organic matter degradation rates. Boudreau and Ruddick (1991) considered the entire pool of organic matter as the sum of an infinite number of differently reactive compounds: the "reactive continuum". Both model approaches, the power law model and the reactive continuum model, demonstrate that, although individual substances decay exponentially over time, a higher order decay function may simulate the combined decay due to a heterogeneous composition of the organic matter. However, a systematic study of how different organic decay functions affect subsurface activity and concentrations of sulphate and methane has not been presented yet. Regnier et al. (2011) display the depth of the SMT as a function of the age of organic matter during sedimentation (here called the initial age of organic matter) over a range of 2–20 years. Within this range the initial age is small relative to the burial age in the considered sedimentary interval. Accordingly, the reactivity of the organic matter is relatively high and may not represent the full range of reactivities of organic matter in different marine sediments.

Here we systematically evaluate the role of organic matter degradation kinetics on sulphate and methane profiles in marine sediments on the basis of a reactive transport model, in which the production and consumption of sulphate and methane are related to the organic decay function. The effects of organic carbon concentration, deposition rate and decay function on sulphate and methane profiles are tested for a general steady state case.

## 2. MODELLING APPROACH

2.1. Reactive transport model

In this study we compute sulphate and methane concentration profiles, the depth of the sulphate methane transition (z_{SMT}), and the rates of OSR and AOM as a function of sedimentation rate (ω), initial TOC content, and TOC reactivity (constrained by parameters in the decay function, see below and Table 1) using a transient reactive transport model. The following two equations were used for sulphate (Eq. (1)) and methane (Eq. (2)) as described in Arndt et al. (2006, 2009):

$$\frac{\partial[SO_4^{2-}]}{\partial t} = -w\frac{\partial[SO_4^{2-}]}{\partial z} + \frac{D_S}{\tau^2}\frac{\partial^2[SO_4^{2-}]}{\partial z^2} - \frac{1}{2}s_{TOC} - s_{AOM} \quad (1)$$

$$\frac{\partial[CH_4]}{\partial t} = -\omega\frac{\partial[CH_4]}{\partial z} + \frac{D_{CH_4}}{\tau^2}\frac{\partial^2[CH_4]}{\partial z^2} + \frac{1}{2}s_{TOC} - s_{AOM} + v_{CH_4}A\frac{\partial([CH_4]-[CH_4]_{sat})}{\partial z}, \quad (2)$$

where $[SO_4^{2-}]$ and $[CH_4]$ are the concentrations of sulphate and methane, respectively, t is time, ω is the sedimentation rate, z is the depth below seafloor, and D_S and D_{CH_4} are the effective diffusion constants for sulphate and methane. Diffusion constants are from Schulz and Zabel (2000) and are corrected for porosity (ϕ) and tortuosity (τ). A constant porosity of 0.7 was assumed and the tortuosity was calculated according to Boudreau (1997) as $\tau^2 = 1-2\ln\phi$. Furthermore, s_{TOC} and s_{AOM} are source or sink terms due to metabolic turnover (see below), v_{CH_4} is the rise velocity of methane gas and $[CH_4]_{sat}$ is the saturation concentration of methane. The factor $A = 1$ if $[CH_4] > [CH_4]_{sat}$ and $A = 0$ if $[CH_4] < [CH_4]_{sat}$. All parameters with values and units are listed in Table 1.

Different source and sink terms $s(x)$ are due to several metabolic processes. Sources and sinks of methane and sulphate are stoichiometrically coupled to rates of organic carbon decay via the following simplified reactions for sulphate reduction (Eq. (3)) and methanogenesis (Eq. (4)):

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + 2HCO_3^- + H^+ \quad (3)$$
$$2CH_2O \rightarrow CH_4 + CO_2 \quad (4)$$
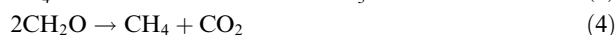
The sink of sulphate and source of methane, respectively, is calculated as ½ of the organic matter decay rate s_{TOC}, whereby s_{TOC} is calculated from the derivative of organic matter decay with time:

$$s_{TOC} = \partial\left(\frac{TOC\rho_S}{100\,M_C\phi}\right)\bigg/\partial t \quad (5)$$