

## ***Interactive comment on “Estimation of the global inventory of methane hydrates in marine sediments using transfer functions” by E. Piñero et al.***

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D. Burdige questions the validity of our kinetic model for microbial organic matter degradation and methane formation (WALLMANN et al., 2006) and urges us to look at the new paper on organic matter degradation kinetics recently published by the reviewer (BURDIGE, 2011). We would like to emphasize that our model has been calibrated more comprehensively by field observations at various ODP sites (MARQUARDT et al., 2010; WALLMANN et al., 2006) than any other model currently used to simulate microbial methane formation within the gas hydrate stability zone. However, below we present additional data and model results to further test our model and the new

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approach proposed by the reviewer. We chose an OPD site featuring a strong geothermal gradient and high-quality dissolved ammonium data to test our model at elevated temperatures of up to 50°C and to investigate the possible temperature effects on POC degradation kinetics proposed by the reviewer (BURDIGE, 2011).

Pore water and sediment data from ODP Leg 128, Site 799, Hole A were used for this exercise [1]. This Site is located in the Japan Sea, a marginal sea in a continental arc setting (INGLE et al., 1990). Sediments were taken at about 2000 m water depth from the Kita-Yamato Trough, a narrow graben structure filled with sediments featuring a very high geothermal gradient of about 100°C /km [2]. Sediments cored in Hole 799A include biosiliceous sediments and fine-grained detrital sediments intercalated with carbonate-rich intervals and numerous ash layers [3]. They accumulate at an average rate of about 70 m /Myr and contain abundant organic matter of mostly marine origin with particulate organic carbon values (POC) ranging from 0.24

Our transport-reaction model (WALLMANN et al., 2006) was applied to site 799A to simulate the microbial degradation of POC and particulate organic nitrogen (PON) and the turnover of ammonium. The reaction network of the model includes degradation of particulate organic matter via sulfate reduction and methanogenesis, anaerobic oxidation of methane, the release of dissolved ammonium from degrading PON, and ammonium adsorption. The effects of porosity, tortuosity and temperature on diffusion coefficients of dissolved sulfate, methane, ammonium and dissolved inorganic carbon (DIC) were considered in the model applying appropriate empirical equations (BOUDREAU, 1996; BOUDREAU, 1997). Constant concentrations were applied at the upper boundary of the model column while zero gradients were used as lower boundary condition. Some of the parameters applied in the modeling were adjusted to observations (porosity, POC/PON ratios, burial velocity, geothermal gradient, s. Table below) while other values (inhibition constant for POC degradation, initial age of POC, adsorption constant for ammonium) were taken from the literature (MARQUARDT et al., 2010; WALLMANN et al., 2006).

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Parameter	Value
Porosity (constant over depth)	0.75
Geothermal gradient	100°C km <sup>-1</sup>
Burial velocity	70 m Myr <sup>-1</sup>
PON/POC ratio	0.08 mol/mol
Initial age of POC	40 kyr
Inhibition constant for POC degradation	40 mM
Adsorption constant for ammonium	1.7 cm <sup>3</sup> g <sup>-1</sup>

Table 1: Parameter values applied in the simulation of organic matter degradation and ammonium turnover at Site 799A (Japan Sea)

The model results clearly show that the kinetic model for POC degradation introduced by (WALLMANN et al., 2006) is able to reproduce the data (s. Figure 1). The ammonium and sulfate profiles calculated by the model applying the parameter values listed in Table 1 are very close to observations and the model results are also consistent with the solid phase data (POC and total N). The model considers the down-core decrease in POC reactivity as previously introduced by (MIDDELBURG, 1989) and an additional inhibition term suppressing the rate of POC degradation at high metabolite concentrations:

$$R_{POC} = -dC_{POC}/dt = \frac{K_c}{C_{CH_4} + C_{DIC} + K_c} \times k_{age} \times C_{POC} (Eq.1)$$

where KC is the inhibition constant for POC degradation (40 mM), CH<sub>4</sub> and CDIC are the concentrations of dissolved methane and dissolved inorganic carbon (in mM) and k<sub>age</sub> is the age-dependent kinetic constant defined as (MIDDELBURG, 1989):

$$k_{age} = 0.16 \times (age_0 + age)^{-0.95} (Eq.2)$$

where age<sub>0</sub> is the initial age of POC (here, 40 kyr) and age is sediment age as calculated from burial velocity and sediment depth.

ODP site 799A was also simulated applying the original Middleburg model without C1673

inhibition term. The following kinetic equation was applied in this model run:

$$R_{POC} = -\frac{dC_{POC}}{dt} = k_{age} \times C_{POC} (Eq.3)$$

using the parameter values listed in Table 1. The model results shown in Figure 1 suggest that the original Middelburg model tends to overestimate the rate of organic matter degradation at large sediment depths since the predicted ammonium concentrations clearly exceed the measured values. The Middelburg model was calibrated using mostly shallow sediment cores which are apparently not representative for the gas hydrate stability zone typically extending several 100 m into the subsurface. Our model clearly gives a better approximation of the down-core change in organic matter reactivity than the original Middelburg model (s. Figure 1).

A new kinetic rate law for POC degradation was recently introduced by (BURDIGE, 2011). Burdige proposed that microbial POC degradation rates increase with sediment temperature and that this increase can be described by a simple Arrhenius equation:

$$k(T) = A \times \exp\left[-\frac{E_a}{R \times T}\right] (Eq.4)$$

where k(T) is a temperature-dependent kinetic constant, E<sub>a</sub> is the activation energy, T is sediment temperature and R is the gas constant (R = 8.314472 J/mol/K). The corresponding non-dimensional constant describing the down-core increase in reactivity is defined as:

$$k_t = \frac{\exp\left(-\frac{E_a}{R \times T}\right)}{\exp\left(-\frac{E_a}{R \times T_{BW}}\right)} (Eq.5)$$

where TBW is bottom water temperature. We introduced this constant into the Middelburg rate law to simulate OPD site 799A considering the effects of temperature on POC degradation:

$$R_{POC} = -\frac{dC_{POC}}{dt} = k_{age} \times k_t \times C_{POC} (Eq.6)$$

Applying an activation energy of E<sub>a</sub> = 200 kJ/mol (BURDIGE, 2011), a bottom water temperature of 2°C and a geothermal gradient of 100°C/km, the value of the kinetic

constant  $kT$  increases exponentially from 1 at the sediment surface to  $2 \times 10^5$  at the base of the sediment column. The rates of POC degradation are thus strongly enhanced such that POC is almost completely consumed at a sediment depth of about 100 m (s. Figure 1). Ammonium concentrations sharply increase at shallow sediment depth due to the enhanced rate of organic matter degradation. Both, the complete consumption of POC at about 100 mbsf and the elevated ammonium concentrations are clearly not consistent with observations (s. Figure 1). It should be noted that ODP cores taken at continental margins usually feature highly variable POC concentrations and no pronounced down-core decrease in POC. A model predicting an almost complete consumption of POC within a few hundred meters burial depth is thus certainly not consistent with observations. It thus seems that the model proposed by (BURDIGE, 2011) strongly overestimates the effect of temperature on rates of organic matter degradation in the deep biosphere.

Microbial organic matter degradation in the deep biosphere is certainly a very complex and poorly understood process. Nevertheless, our model is clearly giving a good approximation to the general trends observed in geochemical ODP data and can thus be used to predict organic matter degradation and microbial methane formation in anoxic marine sediments to sediment temperatures of up to  $50^\circ\text{C}$ . The good correspondence between observations and model results is very encouraging but also surprising. Our model was originally developed using pore water data from sediment cores retrieved at the slope of Sakhalin Island where sediment temperatures are close to  $2^\circ\text{C}$ . Moreover, our model does not explicitly consider effects of temperature on microbial degradation rates even though several studies have shown that the microbial degradation of labile organic matter in marine surface sediments and shallow terrestrial environments is promoted under high temperatures (BURDIGE, 2011; GU et al., 2011). A weak temperature effect is implicitly considered in our model: Rates are suppressed by the built-up of high metabolite concentrations in ambient pore fluids which is partly controlled by the diffusive flux of these species towards the sediment surface. Since diffusion coefficients increase with temperature, elevated temperatures promote the diffusive loss of

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metabolites and thereby the rate of organic matter degradation. Thus, the rate of POC degradation amounts to  $1.01 \times 10^{-8}$  mmol/cm<sup>3</sup>/yr at the base of the model column (450 mbsf) in the model run depicted in Fig. 1 and decreases to  $0.93 \times 10^{-8}$  mmol/cm<sup>3</sup>/yr when the sediment temperature is kept at a constant value of  $2^\circ\text{C}$  throughout the model column. Considering this very modest temperature sensitivity, our model should significantly underestimate degradation rates at about  $50^\circ\text{C}$  if microbial turnover rates in the deep biosphere would strongly respond to temperature. It thus seems that temperature is not having a strong effect on the kinetics of refractory organic matter degradation in the deep biosphere. Rates are rather controlled by the strong down-core decrease in reactivity induced by the preferential degradation of labile organic matter at shallow depth levels and the inhibition of degradation processes by the accumulation of dissolved metabolites. Considering the long time periods available for adaptation in slowly accumulating sediments, it might be possible that each sediment level is harboring microorganisms being adapted to ambient temperature. This would suggest a down-core succession of microbial communities along the geothermal gradient with each community operating close to its temperature optimum. In this scenario, ambient temperature would have a negligible effect on the microbial degradation of refractory organic matter in the deep biosphere. However, much more fundamental research on microbial processes, diversity, and adaption in the deep biosphere is needed to test this hypothesis.

Burdige also raises a number of questions on our procedures to calculate accumulation rates of particulate organic matter in marine sediments (POCar). We would like to emphasize that our POCar calculations are in fact correct and internally consistent. However, POCar is probably not a useful master parameter for our transfer function since POC concentrations and burial velocities may have opposing effects on gas hydrate accumulation (see review by Dickens). We will thus not address the detailed questions on POCar posed by Burdige since POCar values will no longer be used in our revised manuscript (see our reply to Dickens' comments).

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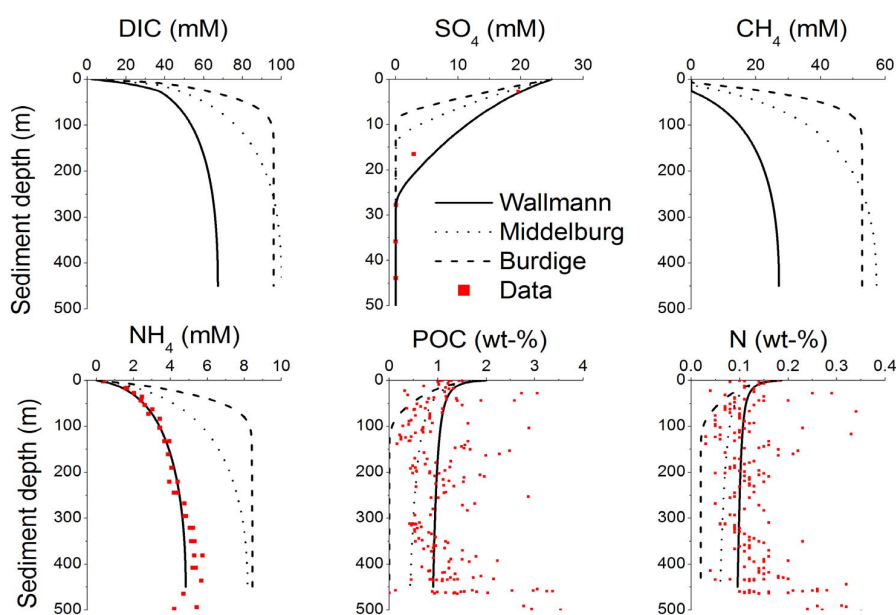
[1] <http://iodp.tamu.edu/janusweb/chemistry/chemiw.cgi>

[2] <http://iodp.tamu.edu/janusweb/physprops/adara.cgi>

[3] <http://www-odp.tamu.edu/publications/prelim/128PREL.PDF>

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**Figure 1:** Model results for ODP site 799A. DIC, SO<sub>4</sub>, CH<sub>4</sub>, NH<sub>4</sub>, POC are the concentrations of dissolved inorganic carbon, sulfate, methane, ammonium, and particulate organic carbon, respectively. N concentrations are the sum of particulate organic nitrogen (PON) and adsorbed ammonium. Symbols indicate the data measured at ODP site 799A while lines indicate model results obtained applying the kinetic rate laws introduced by Wallmann (Eq. 1), Middelburg (Eq. 3), and Burdige (Eq. 6) and the parameter values listed in Table 1. Please note the different depth scale for dissolved sulfate concentrations.

**Fig. 1.**

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