

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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There are fundamental difference between our modeling approach and the approach developed by the reviewer and his co-workers. Most of the comments by Dickens are related to these differences. Our approach may be summarized as follows:

Step 1. We developed a kinetic model for organic matter degradation and methane formation within the gas hydrate stability zone and calibrated this model using pore water and solid phase data measured in marine sediments (MARQUARDT et al., 2010; WALLMANN et al., 2006). The major parameters that we used to calibrate the model are concentrations and depth profiles of dissolved sulfate and ammonium and depth

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profiles of particulate organic carbon (POC) and nitrogen (PON). If available we also apply dissolved bromide, iodide and alkalinity data. We used these parameters since they are not affected by sampling artifacts. Dissolved ammonium is the most important and robust parameter since the biogeochemistry of ammonium is very simple in anoxic sediments. It is released into the porewater by the microbial degradation of organic matter while a minor portion is adsorbed on the solid phase until an adsorption/desorption equilibrium is attained. The stoichiometry of ammonium release is constrained by field data (POC/PON ratios) while the adsorption constant has been defined experimentally (MACKIN and ALLER, 1984). The shape of the ammonium depth profile is thus giving us important constraints on the down-core change in organic matter reactivity. We did NOT use concentrations of gas hydrates to constrain our kinetic model since gas hydrates are in most cases NOT formed from methane being produced within the gas hydrate stability zone (GHSZ) but from methane migrating upwards into the GHSZ via fluid and gas flow.

Step 2. We used our calibrated model to predict gas hydrate formation from methane being generated within the global GHSZ (BURWICZ et al., 2011). We performed this exercise under both Holocene and Quaternary boundary conditions. Considering the down-slope transport of sediments during glacial sea-level stands, we obtained a global gas hydrate inventory of about 1000 Gt C formed by the microbial degradation of organic matter within the GHSZ. This inventory is just a fraction of the total since it does NOT include gas hydrates formed by the upward migration of dissolved and gaseous methane.

Step 3. In our submitted manuscript we use our model to simulate gas hydrate formation from methane being formed within the GHSZ and from methane transported into the GHSZ via upward fluid flow. The inventory that we get with this approach is larger than the inventory derived by (BURWICZ et al., 2011) since we consider the additional input of dissolved methane from below. However, also this inventory is just a fraction of the total since it does NOT include gas hydrates formed by the upward

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migration of gas. Our model does therefore not reproduce gas hydrate inventories at Blake Ridge, Hydrate Ridge and other sites where it is well-known that a large fraction of the hydrates has been formed by upward migration of gaseous methane (Haeckel et al., 2004; Torres et al., 2004; Wallmann et al., 2006).

Future steps. The next logical step is to include upward migration of gaseous methane using a more advanced multi-phase fluid flow model (see for example GARG et al., 2008). Since gas flow is focused to fractures and other high permeability pathways, this type of modeling should be performed in a 3-D mode. Moreover, it needs to be done using a non-steady state approach considering the local history of sediment and organic matter accumulation, the thermal evolution of the studied sedimentary basin and the history of fault emplacement. We are currently developing such a regional-scale basin modeling approach starting with the Alaska North Slope (PIÑERO et al., 2011). However, it will not be possible to apply this approach at global scale in the near future.

The reviewer and his research group use a very different approach. Their basic model (BHATNAGAR et al., 2007) assumes simplistic first order kinetics for organic matter degradation and considers upward flow of dissolved methane. It neglects sulfate reduction and AOM and assumes that methanogenesis starts already at the upper boundary of the model column. The upward flux of gaseous methane is not considered in their model. The model was tested and calibrated using gas hydrate abundances at Blake Ridge (ODP Site 997) and the Cascadia Margin (ODP Site 889). The model reproduced these field observations but the underlying kinetic model was not tested against geochemical data related to organic matter degradation, such as POC, PON, and dissolved ammonium concentrations.

The reviewer is convinced that our kinetic model is not valid since it does not reproduce observed gas hydrate abundances. We argue that a large fraction of the gas hydrate has been formed by gas ascent at those sites where our model underestimates gas hydrate concentrations. Moreover, the reviewer is convinced that the reactivity of or-

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ganic matter does not decrease with sediment depth. He and his group rather propose that the reactivity is constant (BHATNAGAR et al., 2007) or even increases with burial depth due the down-core increase in sediment temperature (GU et al., 2011).

To address and resolve these questions, we test the validity of the kinetic model developed by (BHATNAGAR et al., 2007) by integrating their kinetic equations into our transport-reaction model. ODP Site 799A was chosen to compare model profiles with observations since a comprehensive dataset constraining the down-core trends in organic matter degradation and temperature is available for this site (see also reply to the comments by D. Burdige for further information). Following (BHATNAGAR et al., 2007), the kinetic rate law for organic matter degradation was defined as:

$$R_{POC} = -\frac{dC_{POC-L}}{dt} = k \times C_{POC-L}$$

where C_{POC-L} is the concentration of labile particulate organic carbon and k is a first order kinetic constant. The kinetic constant was set to $k = 10^{-14}$ /s (BHATNAGAR et al., 2007; GU et al., 2011) and it was assumed that 75

The concentrations of particulate organic carbon (POC) and total nitrogen (N) retrieved at ODP Site 799A show no clear down-core trends (s. Fig. 1). The large scatter in these solid phase data can be ascribed to temporal changes in ambient export production, rain rate and burial efficiency. Dissolved ammonium concentrations nevertheless feature a regular increase with sediment depth (s. Fig. 1). Both, concentration gradients and curvature of the ammonium profile show a marked down-core decrease. The curvature in the ammonium profile is a good proxy for the degradation rate of organic matter. The data thus indicate a strong down-core decrease in the rate of organic matter degradation even though the organic matter concentrations are highly variable and significant. It is important to note that these trends are observed in most continental margin sediments sampled within the scientific drilling programs DSDP and ODP. They can only be explained by a strong down-core decrease in the reactivity of organic matter.

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As expected, the model introduced by (BHATNAGAR et al., 2007) severely overestimates the dissolved ammonium concentrations at large sediment depths since a constant reactivity of organic matter is assumed in the model. The model is not able to reproduce the marked down-core decrease in the curvature of the ammonium profile while our model is giving an almost perfect fit to the data (s. Fig. 1).

(GU et al., 2011) proposed that the reactivity of organic matter increases with sediment temperature and hence sediment depth. They propose the following rate law:

$$R_{POC} = -\frac{dC_{POC-L}}{dt} = k(T) \times C_{POC-L}$$

where the temperature dependent kinetic constant $k(T)$ is defined as:

$$k(T) = 10^{-14} \times \frac{\exp\left(-\frac{E_A}{R \times T}\right)}{\exp\left(-\frac{E_A}{R \times T_{BW}}\right)}$$

Here R is the gas constant, T is sediment temperature and T_{BW} is the temperature in the overlying bottom water. The activation energy was estimated as $E_A = 110 \text{ kJ/mol}$ (GU et al., 2011). For ODP Site 799A, the model predicts an exponential increase in organic matter reactivity from $k(T) = 10^{-14}/s$ at the upper boundary to $8.5 \times 10^{-12}/s$ at the base of the model column. (GU et al., 2011) further assume that only 40

We integrated this rate law into our transport-reaction model to simulate the degradation of organic matter at ODP Site 799A. The rate law produces dissolved ammonium profiles which are clearly not consistent with observations (s. Fig. 1). The entire pool of labile organic matter is consumed within the top 175 m of the sediment column. Dissolved ammonium concentrations thus increase rapidly to a depth of about 175 m and remain constant in the underlying section. The model of (GU et al., 2011) predicts lower ammonium concentrations than the model introduced by (BHATNAGAR et al., 2007) since only 40

It is important to understand that organic matter deposited in marine sediments is composed of a highly complex mixture of different organic compounds. The more labile

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ones are already consumed at shallow depths while the remaining more refractory compounds are slowly degraded in the deeper sections. The preferential and sequential loss of the more labile fractions induces the down-core decrease in reactivity observed in the data. In our model and in many previous models (BOUDREAU and RUDDICK, 1991; MIDDELBURG, 1989) sedimentary organic matter is thus treated as a complex mixture of different compounds having a continuous reactivity distribution. It is certainly not appropriate to arbitrarily divide sedimentary organic matter into one very labile and one totally inert fraction.

The models of (BHATNAGAR et al., 2007) and (GU et al., 2011) predict much higher dissolved methane concentrations than our model (s. Fig. 1). Pending on local pressure and temperature conditions, they also predict elevated gas hydrate inventories since they over-estimate the rates of methane formation within the GHSZ. We would thus urge G. Dickens and his research group to test their models against observations. Hundreds of sites have been sampled and characterized comprehensively within DSDP and ODP. All of these data are publically available and the reviewer and his co-workers should use this excellent data base to test their models against dissolved metabolite and solid phase profiles measured within the GHSZ.

We will not change the kinetic rate law used in our transport-reaction model since it is consistent with observations. However, Dickens raises two valid points in his review that we will consider in the revision of our manuscript.

He encourages us to use our model results to present new and better constrained estimates of the global pore volume within the GHSZ: Depending on the global heat flow data used and assuming our porosity-depth distribution, these amount to $4044 \times 10^6 \text{ km}^3$ with $7 - 7.8 \times 10^6 \text{ km}^3$ of it at the margins (active: $1.8 \times 10^6 \text{ km}^3$, passive: $6 \times 10^6 \text{ km}^3$); the numbers do not change significantly for Pleistocene sea level conditions (120 m lower than today). We will follow his advice and include these estimates in our revised version. Nevertheless, the average pore volume occupied by gas hydrates in the GHSZ only amount to a few percent (as also stated by Dickens in his papers, e.g. Dickens,

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2011). Hence, the global pore volume number is not a limiting factor for gas hydrate accumulations on a global scale and thus rather irrelevant for the discussion on global hydrate volumes. Moreover, Dickens argues that the accumulation rate of POC is not a valid master parameter since POC concentrations and burial velocities may have opposing effects on gas hydrate accumulation. This is a valid point. We will thus up-date our manuscript and use POC concentrations and burial velocities as independent parameters in our transfer function for the calculation of gas hydrate inventories. This will help to improve our global maps and estimates of gas hydrate abundance.

Elena Piñero,

on behalf of all co-authors.

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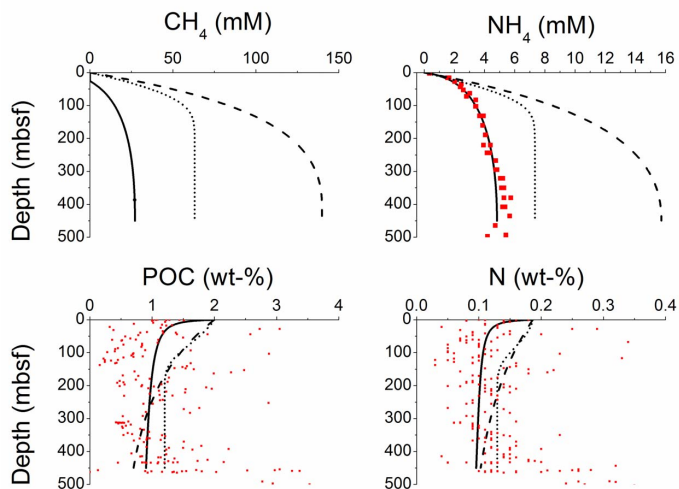


Figure 1: Model results for ODP site 799A. CH₄, NH₄, POC are the concentrations of dissolved inorganic carbon, ammonium, and particulate organic carbon, respectively. N concentrations are the sum of particulate organic nitrogen (PON) and adsorbed ammonium. Symbols indicate the data measured at ODP site 799A; solid lines indicate the results obtained with our model applying the parameter values listed in Tab. 1 (see reply to the comments by Burdige). Broken and dotted lines indicate the results obtained with the kinetic rate laws used by (BHATNAGAR et al., 2007) and (GU et al., 2011), respectively. Porosity, POC/PON ratios, burial velocity, and the geothermal gradient were set to the values listed in Table 1 for all simulations (see reply to comments by Burdige).

Fig. 1.