

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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Dear Editor (and any potential reader),

I agree entirely with the author's response. Referees should follow certain rules when reviewing manuscripts. Equally incumbent, however, is that authors follow certain rules when writing manuscripts.

1. Pertinent literature should be read and referenced correctly;
2. Known problems should be presented and avoided;
3. Results should be discussed with comparison to available data;

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4. Interpretations should be made within the framework of these three points.

It is obvious from the figures alone that these were not followed in the present submission. These exact problems affect recent literature on the topic, including their published work (Marquardt et al., *Biogeosciences*, 2010; Burwicz et al., *GCA*, 2011) and past “initial” submissions (e.g., see comments on Marquardt et al., 2010).

Enough is enough. The community does not need any more ungrounded simulations for global gas hydrate distribution that have obvious problems and fail to explain basic observations, especially without acknowledging the discrepancies, or without discussing how various assumptions impact the conclusions. It seemed to me that a different style of review was on the menu. I apologize if the authors took offense or anyone thinks I was “out of line”. The authors are clever and smart; my main goal: make them wake up, think, rethink, and do things right (and submit future manuscripts accordingly). Should they adhere to this notion, I will give any such future submission that comes my way open, fair and honest commentary (as I have in multiple reviews of their work in the past).

Per request by the authors, here is a more formal and constructive review, after reading the text multiple times. They can complain about the messages; they can shoot the messenger: the primary criticisms of their work as noted in the previous review defy escape. Of course, should they want to change tack, and they have the ability to do so, the authors could also move the field forward with one or more new manuscripts along the general path they are chasing.

The current manuscript should be rejected outright (as clear from below). However, the appropriate recommendation, in this case and in my opinion, is to suggest to the authors that they parse components of the current manuscript, and go after individual problems correctly.

Sincerely,

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Gerald Dickens

**** Background: The amount and distribution of gas hydrate that occurs in sediment on present-day continental slopes is an important topic for a variety of reasons, as awkwardly introduced in the manuscript (p.583, Lines 1-5). Here, I state “awkwardly” for two reasons. First, this is stated as fact “. . .have been recognized. . .”, but the conclusions of the manuscript would generally imply otherwise. Second, large amounts of gas hydrate, if correct, force the Earth Science community to change perspectives on carbon cycling in the time domain (Dickens, EPSL, 2003; Clim. Past, 2011). This far more interesting aspect is omitted from the text.

Estimates for the total amount vary considerably. Circa 2000, several papers suggested that gas hydrates hold about 10,000 Gt of C. Several recent papers have indicated, instead, that it is less than <1500 Gt (Milkov, Earth Sci. Rev., 2004; Archer et al., PNAS, 2009; Burwicz et al., GCA, 2011). There are potential problems with the earlier estimates; there are also clear problems with the more recent estimates (Dickens, 2011). These problems and the range for gas hydrate abundance can be appreciated with an understanding of two parameters, potential volume and occupancy (Dickens, Org. Geochem., 2001).

The first is the amount of pore space that can host gas hydrates. We know its basic shape – a lens between the seafloor and a sub-seafloor depth that expands down the slope. However, the dimensions of this lens are complex because of variations in water depth and the geothermal gradient over space and time. It is probably between 4 and 24 million cubic kilometers (Dickens, 2001). A recurring issue with gas hydrate estimates is that the potential volume and associated error behind such estimates is never stated (Dickens, 2001).

The occupancy is the amount of gas hydrate within this volume. However, direct quantification of gas hydrate is not easy, so there is limited field data. Moreover, concentrations at locations with direct drilling are highly heterogeneous. The global average

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occupancy is probably between 0 and 4% (of pore space).

In theory, the potential volume times the occupancy gives the total amount of gas hydrate. The wide range in estimates occurs because of large errors in BOTH potential volume and occupancy (Dickens, 2001). A low potential volume and a low occupancy will render a low amount of gas hydrate, and vice versa.

A series of papers have tried to address the issue of global gas hydrate abundance and distribution through numerical modeling (e.g., Gornitz and Fung, Glob. Biogeo. Cycles, 1994; Archer et al., 2009, Burwicz et al., 2011). The basic idea here is to determine the potential volume of gas hydrate across continental margins, and then fill this volume with gridded inputs and outputs of methane. While seemingly straightforward, this approach is fraught with potential problems, especially including because it hinges on an accurate representation for how methane accumulates in marine sediment over time (discussed below). A recurring issue with such gas hydrate estimates is that calculated amounts for areas of the seafloor are not compared to field data (Dickens, 2011).

Pinero and colleagues have estimated the global amount of gas hydrate, following the general approach of previous work. They have made some changes (Line 25, p. 601), but without appreciating existing problems in such an exercise. They conclude there is about 400-1200 Gt C in gas hydrate for present-day marine sediment.

Such a low amount affects a range of concepts, those given in the introduction, although this is not really discussed.

Criticisms of the Work: Even assuming the conclusion to be correct, there are four basic criticisms:

- (1) The potential volume and its error are not presented (or assessed with field data). As such, the work cannot be compared to previous studies.
- (2) The simulations for methane inputs and outputs have known or potential errors, which impact the accumulation of gas hydrate. Some of these errors are presented or

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discussed; some are not. In the end, most are ignored.

(3) The results are not compared to field data. Such a comparison readily shows a significant discrepancy: the estimates for gas hydrate in some regions are far too low.

(4) The end of the discussion and the conclusions are made without considering the obvious: the modeling has major problems.

A more systematic critique can be offered as follows:

(A) The most fundamental problem with the manuscript concerns the end of the discussion (p.601, Line 23 onward), and ultimately the conclusions. It is stated (Line 602, Lines 18-21) "... our study provides an improved and well constrained estimate for the global inventory of GH in marine sediments of 400-1200 GtC". This conclusion, based on gas hydrate distributions shown in Figure 10, has no support.

(A1) Bottom simulating reflectors on seismic profiles are widely acknowledged to represent locations where gas hydrate overlies free gas (e.g., Korenaga et al., JGR, 1997, and numerous publications before and after). This has been confirmed by direct drilling in multiple locations.

It is also clear that gas hydrate and free gas should not contact one another at most theoretical locations with low methane concentrations and low gas hydrate contents (e.g., Bhatnagar et al., Am. J. Sci., 2007). This is largely because the dissolved gas-gas hydrate saturation curve increases with depth, whereas the dissolved gas-free gas saturation decreases with depth. Albeit without referencing, the concept is acknowledged in the current work (Fig. 7), as well in previous modeling (Marquardt et al., 2010), which forms the basis for the present work. How is it then that bottom simulating reflectors (BSRs) cover large areas along continental slopes of many margins, including especially the Atlantic, where the simulations (Figs. 7, 10) show little to no gas hydrate?

(A2) Measurements of gas hydrate abundance have been made at several locations

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through drilling (e.g., Blake Ridge, Hydrate Ridge, Cascadia Margin, Peru Margin, Gulf of Mexico, northern Indian Ocean, Japan). Various measurements do not always agree in detail, but multiple independent techniques generally converge on the amount and distribution for a drill site. These can be converted to the chosen units shown in the maps (gCH₄/cm² seafloor). For example, gas hydrate at Site 997, outer Blake Ridge, occupies, on average, about 4% of pore space (~50-60% porosity) between 190 and 450 mbsf. Thus, over the entire 450 m, it has about 40 gCH₄/cm² seafloor. At "low flux" (and low gas hydrate) sites on Hydrate Ridge, the average amounts are 1-2% of pore space over about 70 m above 120 mbsf, giving 10 gCH₄/cm² seafloor. At Cascadia Margin (Site U1326), gas hydrate occupies about 4% of pore space over 180 m above 230 mbsf, or about 36 gCH₄/cm² seafloor. How is it that quantification of gas hydrate through measurements gives much greater amounts than predicted by the simulations?

The above discrepancies are not acknowledged or explained in the text, even though they clearly demonstrate the modeling to be incorrect.

(B) One general possibility for the simulated low gas hydrate abundances concerns potential volume. Unfortunately, while shown (Fig. 5), it is only verified with data from a few chosen sites, and it is not compared to previous work from a global perspective.

For example, the base of the GHSZ at Site 685/1230 (Peru Margin) is about 600 mbsf, as can be determined from the measured geothermal gradient, and which they state in previous work (Marquardt et al., 2010). Their map (Fig. 5) shows this to be about 300 m. Such discrepancies may reflect the resolution of their grid cells, but this is not mentioned.

More importantly, and as noted above, the global potential volume has about a six-fold error with given presentation in the literature (Dickens, 2001; 2011). At least, this is as best as I can ascertain, because nobody seems willing to present and discuss this value. It is important, though: even a two-fold error changes estimates immensely,

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irrespective of how carbon/methane inputs and outputs to and from the seafloor are modeled. The present manuscript determines this volume by two approaches, and then only perpetuates the problem, stating (p.592, Lines 16-18), "... both approaches reveal very similar results in terms of GHSZ thickness for most parts of the global ocean". How similar are the volumes, especially along continental slopes? How similar are they to previous estimates? In particular, if the 90-95% of the ocean with no potential for gas hydrate gives very similar results, and the 5-10% of the ocean with potential for gas hydrates gives very different results, such analysis and commentary has zero meaning.

My suggestion would be to pull this section out of the current paper, and do a proper analysis with comparisons between approaches and comparisons to previous literature. It seems that they have already done much of the work, and this would make a very useful contribution to the broad community. They (and many others) can then reference this effort in attempts to model and constrain the amount of gas hydrate within this context.

(C) The much more likely possibility for the simulated low gas hydrate abundances concerns occupancy. Basically, the embedded modeling does not accumulate sufficient methane over time for a given grid cell.

In fact, but not stated in the current manuscript, the modeling behind the transfer function (Marquardt et al., 2010) does not accurately simulate gas hydrate inventories at multiple locations. For example, at Site 685/1230 (Peru Margin), it only matches some basic sediment and pore water data sets if large quantities of gas hydrate extend to the base of the GHSZ; this clearly does not occur at this location. At Site 995 (Blake Ridge), the modeling suggests about 3.0 gCH₄/cm²; the value determined through drilling is closer to 35 gCH₄/cm² (Paull and Matsumoto, Proc. ODP Sci. Res. 164, 2000).

The generalities for gas hydrate accumulation in marine sediment have been discussed

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in the literature. They are somewhat different than those stated in the text (p.585, Lines 6-9), as pointed out to the authors before (e.g., see review of Marquardt et al., 2010). The three key parameters are the thickness of the gas hydrate stability zone, the ratio of methanogenesis to methane diffusion, and the ratio of methane advection to methane diffusion (Bhatnagar et al., 2007); it is not, and should not be, the thickness of the gas hydrate stability zone and POCAr. This can be understood through simple examples, as also pointed out to the authors previously. Consider two sites with the same GHSZ thickness, the same POCAr and:

- the same POC reaction rate, but where one site has low POC and high sedimentation rate, and the other site has high POC and low sedimentation rate;
- the same POCAr, same sedimentation rate, but different POC reaction rates;
- same sedimentation rate, same POC reaction rates, but different fluid flow.

All these possibilities for the same GHSZ thickness and the same POCAr can and should give different gas hydrate distributions (Bhatnagar et al., 2007).

It is also clear, through basic stratigraphy, simple mass balance calculations, and numerical modeling of wide complexity, that the accumulation of gas hydrate at many present-day locations must involve carbon cycling on the million year time scale (e.g., many references; certainly, all pertinent papers for which I have been a co-author for at least 10 years). Lastly, as the manuscript nicely shows (Fig. 5), the geothermal gradient varies widely across continental slopes, but always increases. Take just one example, Site 995: the gas hydrate lies in sediment between about 3.5 and 5.0 Ma, and with temperatures between about 10 and 22°C, compared to bottom water of 3°C.

With that background, it is straightforward to understand how and why the original modeling, the transfer function, and the current effort will never "provide an improved and well constrained estimate for the global inventory of GH in marine sediments" (independent of any issues with the potential volume, as noted above).

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(C1) The input of POC at relevant locations (i.e., the continental slope) must represent the integrated supply over the last 1-10 millions of years. (The manuscript agrees, p. 586, Line 17-19, although with no reference to where this concept derives).

It is well known that the supply of sediment and organic carbon to continental slopes during the Plio-Pleistocene is generally reduced during sea-level highstands, particularly over the Holocene (e.g., see references in Dickens, 2011). Holocene (~last 10 kyr) inputs to models, which the manuscript ultimately selects for POCAr, mostly because this is convenient (p.592), will probably give much different gas hydrate distributions on margins than actually occur.

I would predict that, in general, such modeling will give a lower expected amount of gas hydrate (Dickens, 2011), but on any margin, this should depend on the basic parameters over time, especially relationships between long-term sedimentation rates and POC contents.

The manuscript begins to travel down this path by considering different possibilities for past sedimentation (as suggested in previous reviews and correspondence). However, for reasons unknown, the manuscript uses alternatives that make little sense. In particular, the extension of sedimentary sequences to basement after removing the top 1 million years (p. 589) lacks justification, because in many cases, the material deposited before 10-20 Ma has little relevance (and includes hiatuses, etc).

A reasonable input might be the “recalcitrant” amount of POC at sites over the last 10 million years (more on this notion below).

In the end, the manuscript presents the issue (albeit without referencing), then dismisses it because it cannot be constrained to some satisfactory level . . . and all is back to square one, where an illogical input is used.

To be constructive, the authors might take the general idea of comparing gas hydrate accumulation with Holocene versus Plio-Pleistocene inputs of sediment and POC on

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continental slopes and run with this. Even if the modeling for carbon/methane cycling in marine sediment were misguided (which I think is the case), this would be another really valuable contribution.

(C2) A change in sediment inputs to the slope from Holocene to average Plio-Pleistocene conditions will likely change the perspective on gas hydrate distribution significantly. However, it will not solve the order of magnitude discrepancies between the model simulations in the current paper and field observations at multiple locations.

Unfortunately, this will require a different model framework. The modeling in the present work hinges on multiple notions that make no sense within the context of available data. I have presented and articulated these in the previous comment, but stress one of these here.

We know that POC degradation decreases with depth in shallow sediment on the shelf (at relatively high temperature), or in deep-sea sediment at sites of very low sedimentation rate (as referenced, p. 584, Lines 5-9). So, why should POC degradation decrease with depth in rapidly buried sediment on the continental slope, where seafloor temperatures are cold? Such an extrapolation is not valid, but lies behind the modeling.

Consider multiple organic components landing on a cold seafloor with high sedimentation rates. Those with high reaction rates, degrade relatively fast and within the upper few meters; those with low reaction rates, and pertinent to methanogenesis, which is highly dependent on temperature, degrade along the geotherm (Burdige, EPSL, 2011; Gu et al., Nature Geosci., 2011).

A simple change in perspective may explain much of the discrepancy between modeling and data. According to the “conventional” view (i.e., that assumed “carte blanche” in the present work and its ancestors), the generation of methane (and ultimately the accumulation of gas hydrate) within the GHSZ will be too low.

Here again, the authors have a golden opportunity, should they switch their framework

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for modeling. How does the distribution of gas hydrate change if the reaction rate for methanogenesis changes along the geotherms for the grid cells?

I can point out numerous minor issues. The most egregious problems are when statements are made without appreciating concepts or without appropriate referencing.

For example: Page 583, Lines 5-10. What models? What framework for kinetics? And where does diffusion come to play? Page 584, Lines 4-9. Why is constant reactivity worse than assuming decreasing reactivity, which is not the case when the geotherm and T-dependent methanogenesis rates are incorporated for recalcitrant components? Page 586, Lines 16-19. And where does this idea come from? page 595, Line 19: This concept was clearly articulated in the literature before Tishchenko et al. (2005).

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