**Biogeosciences
Discussions**

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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I decided 20 years ago to sign all my reviews irrespective of my thoughts on scientific content or on authorship. I mostly have tried being polite and constructive through about 600 reviews. The present manuscript tests my resolve, especially given recent commentary and discussions on the topic in the literature, as well as open correspondence with the senior author. The only means to stay true to character appears a different style of review . . .

Last year, the senior author published a manuscript concerning the global inventory of gas hydrate in marine sediment (Burwicz et al., GCA, 2011). The overarching frame-

work stemmed from previous work (e.g., Gornitz and Fung, GBC, 1994; Dickens, Org. Geochem., 2001; Archer, Biogeosci., 2007): determine the potential volume for gas hydrate across the oceans; fill this volume over space and time with inputs and outputs of carbon (and methane). The potential volume was never stated, despite advocacy for such numbers (Dickens, 2001; Dickens, Clim. Past., 2011). The carbon/methane flux model contained multiple problems, generally ignoring papers that articulated these issues (see below). They presented maps showing the distribution of gas hydrate in marine sediment, and concluded that modern marine sediment hosts between 4 and 995 Gt C. This came with little appreciation as to why this range varied from other efforts. Most crucially, the authors never compared their modeling results to field data (even though they were informed of this disconnect in reviews). In the end, they produced some very nice maps that clearly demonstrate that no gas hydrate exists at numerous locations where it has been recovered or inferred from geophysics. The current effort is no different.

The senior author is well aware of these criticisms; the broad marine geoscience community also seems perfectly happy with their revelations.

So, I have no problem with publishing the current paper, whatever its contents. It seems to be "en vogue" to discuss gas hydrate distribution with no understanding as to how these systems work over space and time, no appreciation of field data, and no referencing to relevant work (Dickens, 2011). I might as well become a derelict and stop writing and reviewing papers . . . clearly many of my colleagues do not read or cannot understand my commentary. Of course, for those that still value critical reviews, you're welcome to read below. It remains constructive, but the usual politeness needs some polishing.

My only request: should this paper be published, the authors need to explain and justify their figures.

Sincerely,

Jerry Dickens

To any and all reading this review, we need two initial agreements: 1/ bring no anti-quated, ill-conceived concepts to this table; 2/ accept that recent works concerning the mass and distribution of marine gas hydrate (Archer, 2007; Burwicz et al., 2011) are demonstrably wrong. Both these efforts determined the potential volume for gas hydrate and filled this volume using models for the cycling of organic carbon and methane over time. Both efforts rendered simulations with far too little methane on continental slopes compared to field observations. For example, numerous lines of evidence arising from direct drilling shows that outer Blake Ridge off the southeast USA coast hosts about 400 kg C/ m2 of seafloor as methane. Simulations by Archer (2007) predict this to be <100 kg C/ m2; those by Burwicz et al. (2011) predict this be 0 g C/ m2.

Houston (moi), we have a problem.

Why is this relevant to the present submission? The work under review directly stems from these previous efforts, both which completely failed to acknowledge, let alone address, the discrepancy between modeling and observations. Moreover, both these works conveniently omitted theory, data and previous discussions for why such a discrepancy should arise in the first place.

I think some sub-section of the community knows the basics for how carbon and methane cycles in sediment on continental slopes – locations typically marked by cold seafloor temperatures and relatively high long-term sedimentation rates. (Should one want to understand things more fully regarding carbon/methane cycling in these environments, read recent papers – e.g., Burdige, EPSL, 2011; Chatterjee et al., JGR, 2011; Dickens, 2011 – and migrate back through references and concepts ...)

There are at least five obvious problems in recent works regarding the global inventory of gas hydrate. Most have been articulated in the literature for several years or more (and most have been presented to authors of these works in previous reviews and correspondence). These problems can be understood with a combined appreciation of

basic chemistry, physics, geology and oceanography:

1/ Carbon and methane cycling in gas hydrate systems on continental slopes occurs on the Myr time scale. This means that modern (Holocene) organic carbon inputs to the slope are largely irrelevant, because the present-day – with high sea level and significant organic carbon accumulation on the shelf – is an anomaly. Organic carbon accumulation on slopes was much greater during prevailing low-stand conditions. Any modeling exercise for the modern global distribution should begin with organic carbon inputs for "average" Pliocene-Quaternary conditions to slopes (Dickens, 2011).

2/ Degradation of organic carbon toward methanogenesis happens well below the seafloor. This is important because it signals that recalcitrant compounds degrade along the geotherm in environments with low seafloor temperature and high sedimentation rate. The commonly assumed decrease in bulk organic carbon reaction rates (e.g., Middelburg, GCA, 1989) does not apply to the slope. Instead, the reaction rate for individual compounds (obviously) and for bulk organic carbon increases significantly with depth below X number of meters on the slope (Burdige, 2011). This is important to the problem because an incorrect (and decreasing) reaction rate will drop methanogenesis over the upper few hundred meters considerably.

3/ Organic carbon contents and sedimentation rates need to be disentangled (Bhatnagar et al., AJS, 2007). When sedimentation is too high and the fraction of TOC available for methanogeneis is too low, organic carbon dilution occurs, which pushes organic carbon through the GHSZ too fast; alternatively, the opposite end-member can lead to consumption of organic carbon near the seafloor by reactions other than methanogenesis. Models with Holocene organic carbon contents and Pliocene-Quaternary sedimentation rates will lead to low methane contents.

4/ All data (and, in my opinion, all good interpretations of such data) suggest that AOM dominates net consumption of pore water sulfate in shallow sediment above gas hydrate systems (e.g., Chatterjee et al., 2011). This is important to the problem because,

if not balanced correctly in diagenetic models, too much organic carbon is consumed by SO_4^{2-} in very shallow sediment and too little organic carbon passes into deep sediment for methanogenesis. Most diagenetic modeling efforts have not overcome this conceptual hurdle, despite overwhelming evidence indicating that alternative modeling is wrong.

5/ Pore fluid components derived from methanogenesis, especially methane but also DIC, NH_4^+, etc, need to migrate upward over time (Bhatnagar et al., 2007; Chatterjee et al., 2011). Models that do not include upward vertical movement of these components will grossly underestimate methane production and methane amounts in shallow sediment.

All these problems plague the previous modeling exercise by Burwicz et al. (2011). So, let's take a look at how things have progressed since . . .

Always fun to start with the figures and ignore the text . . .

Figure 1 is misleading, especially with the current caption. Many of the estimates should be expressed as ranges, following their presentation in the literature. More interestingly, Dickens (2001) does not give a single value; instead, this paper focuses on why such a range in estimates exists. The key point made by Dickens (2001) is that everything boils down to the potential volume of pore space where gas hydrates can occur and the occupancy, and that both these parameters have major uncertainty.

Figure 2 is absolutely ridiculous with the current caption. As best as I can tell, it is a map of bathymetry NOT sedimentation rates! Hmmm . . . already I have to cheat and look at the text, because the only clue is "Eq. 2". Equation 2 suggests that Holocene sedimentation rates are directly linked to water depth. What? This is so demonstrably wrong with countless observations I am at a loss for words.

I'll just bypass for now the crucial issue missing in much of the literature, namely that Holocene sedimentation rates (and organic carbon inputs) are mostly irrelevant to un-

derstanding gas hydrate systems in marine sediment (Dickens, 2011). Presumably, these past rates also have little relationship to modern (or past) water depth.

I'm already predicting, irrespective of how they model organic carbon accumulation and methane cycling, that there's no way they can explain high methane (and gas hydrate) concentrations at deep sites, such as Blake Ridge (ODP Sites 994, 995, 997 ~2700 m) and Peru Trench (ODP Site 685/1230 ~5100 m). The supply of organic carbon will be far too low . . . but let's continue . . .

Figure 3 is somewhat interesting but I am uncertain of the relevance without cheating and reading the text. I'll take a guess from the literature: it will somehow relate to how they model external upward fluid advection, as this is important, but with caveats. If so, and considering previous work, the cool figure here would be a map showing the thickness of the GHSZ at average Pliocene-Quaternary conditions (i.e., addressing the potential volume issue) and external fluid flux (some combination of shading and contours). The boundaries and overlap will be complicated, emphasizing the problem with simple divides between active and passive margins.

As an aside, there is a overall notion in the literature that active margins must hold more gas hydrate than passive margins because fluid advection supplies more methane to the GHSZ; of course, such a view generally neglects the fact that enhanced fluid advection removes more methane through AOM and venting, and that it contrasts with available data (e.g., Milkov et al., Geology, 2003). Alas, I have digressed, although it will be interesting to see whether this paper addresses the issue . . .

Figure 4. Panels 1 and 2 are just silly. I remain perplexed why the authors would think Holocene POC rates relate to water depth, or even consider that Holocene POC rates are relevant to the problem. Obviously, there will be some unnecessary "excess baggage" in the text, even before reading. (But, I now more fully appreciate why airlines/journals charge excess baggage fees).

Panels 3 or 4 are interesting, because these seem more reasonable to the problem ar-

ticulated in the literature (i.e., long-term sedimentation of organic carbon on continental slopes). Of course, I now have to cheat again as we are given "see text" to have any clue as to how these maps were constructed. Set finder to "Fig. 4" and arrive at the call-out on p. 591. It's still not clear. However, with some wading . . . I move up . . . and see that these maps are based on sediment thickness maps after tossing the upper 1 Myr (p. 589). What? Why would they do this? The Holocene is largely irrelevant because considerable organic carbon deposited on the slope under "normal" conditions is emplaced on the shelf during the Holocene (and other highstands). However, the pre-Pliocene is also irrelevant to modern gas hydrate distribution, because most sediment on the slope has now passed through the GHSZ. In other words, they have excluded the critical input!

Irrespective of the above, the scale of the maps (here and in all figures) allows for limited comparison of model inputs to field data. They should have points on all global maps (say 4 widely dispersed locations at a minimum?) showing locations where gas hydrate has been recovered. The values portrayed on the maps should then be tabulated and compared to field data. This is absolutely critical (above and below).

Figure 5, which shows the potential volume of gas hydrate, is interesting and cool. However, what is the potential volume? Surely, they must have reported and discussed this parameter given previous notes on the matter? Okay. . . another cheat to the text . . . it has to be here . . . somewhere . . . somewhere . . . No, it's absent. So, how can one compare this calculated and presented volume to previous work? Dare I mention again that modeled GHSZs on the map have no comparison to field observations (above comment).

Figure 6 evokes mixed comments, the range I will refrain from expressing.

First, why are there different color scales for the same units in the two panels?

In any case, without reading any text, except for the cheats noted above, or considering the actual model for carbon/methane cycling in marine sediment on continental slopes,

the basic simulation (Fig. 6a) lacks conceptual sense. Approach #2, from earlier figures, incorporates low inputs of organic carbon to the slope within a framework where these inputs have no rationale in oceanography. I would be stunned if gas hydrate distribution looked anything like this. Seriously, given all previous literature on the topic, why would such a simulation be conducted in the first place?

Obviously, the placement of sites onto this map linking to actual data would be useful. This is mostly because it will show such a portrayal to be incorrect. Blake Ridge should be a nice yellow-green (depending on the scale used) not gray! So, what then are the blue ovals? Clearly, these are NOT the only places where significant gas hydrate occurs. Are these locations predicted by the model, the one that makes no sense? Or, are these some random places chosen because they agree with this model? (I know a triviality – but why do these ovals span land?)

Figure 6b seems to imply that two parameters, POC accumulation and the thickness of the GHSZ, lead to gas hydrate inventory. This is okay . . . but only at a really crude level . . . where POC accumulation is directly coupled to both sedimentation rate and methane diffusion . . . and advection is omitted . . . and the geotherm is ignored . . . and etc. The basic expressions for how to link these parameters are fully explained by Bhatnagar et al. (2007). Curiosity arises . . . I wonder if they even reference this work . . . no. Hmmm . . . sollten wir schreiben artikel in deutscher sprache?

Figure 7 is potentially interesting and relevant, especially given a string of papers discussing such curves and how and why such relationships exist (dare I look if these are referenced?).

It's intriguing to ponder why such a figure is presented without reading the text. Is it because they are going constrain the fraction of POC entering deep sediment via a coupled carbon-sulfur numerical model that correctly includes AOM (e.g., Bhatnagar et al., G3, 2011; Chaterjee et al., 2011)? This would be cool, because it would address one of the five problems with recent modeling efforts outlined at the start.

Instead, however, something appears fundamentally wrong (panel A). The methane flux changes significantly, but the depth of the SMT does not move. This almost necessarily means that AOM is decoupled from their modeling, so that too little organic carbon enters deeper sediment for methanogenesis. Alternatively, they have modeled advection incorrectly. Something is not right.

Figure 8 shows generic model results pertinent to the problem. These have been predicted by and discussed in previous literature. So all's good from a qualitative perspective, as long as they reference previous work and explain.

So, let's look at the quantitative details and see the comparison to field data. Well . . . unsurprisingly . . . it's not there.

Recall that outer Blake Ridge has about 40-50 g CH4/ cm2 of seafloor. It also has a GHSZ of ~450 m. So, it should plot between the red and green lines, those with fluid flux of 0.5 to 1 mm/yr on panel A. But there is no data to support such high fluid flux at this location (Egeberg and Dickens, Chem. Geol., 1999 and numerous references since). Everything . . . throughout all figures so far . . . suggests that the modeling is generating too little methane during burial. But this was guessed before looking at any figures, because it is a recurring problem in model exercises that do not incorporate advanced concepts.

The authors absolutely need to follow the comparison aspect through the manuscript if they want their exercise to be interesting and useful.

My challenge: pick a minimum of 4 widely separated sites, with somewhat different parameters, and show how these relate throughout all analyses.

My prediction: there is no way they will get this to work unless they change their modeling perspective to address the five known problems. Figure 9 deserves no comment other than that this shows that two ill-conceived models with similar frameworks give similar results.

Figure 10 shows their best guess for global gas hydrate distribution, which as emphasized above, has no grounding in theory or observations. Frankly, I do not even understand how they could get this result because the thickness of the interval around margins does not vary with organic carbon supply or bathymetry (previous figures). To no surprise, it perpetuates the unsupported idea that active margins have more methane . . . I wonder if they even discuss this issue and problem?

I give up. I cannot read the text because I already know I will just get ornery and lose any and all modicum of decorum.