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Interactive Comment

Interactive comment on "A transfer function for the prediction of gas hydrate inventories in marine sediments" by M. Marquardt et al.

G. Dickens (Referee)

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I am new to the world of open review and discussion. In any case, I thought it good to state that this was written without reading or considering other commentary. No issues with being anonymous.

Sincerely,

Gerald (Jerry) Dickens

The abundance of gas hydrates in the pore space of marine sediment, locally and globally, is an important but difficult scientific target to understand and to constrain. The present submission attempts to offer a simple means to calculate the (minimum) abundance of gas hydrate at specific locations (those that have low upward gas flux,

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although this is not entirely clear in the abstract). The basic parameters, according to the manuscript, are the accumulation of particulate organic carbon (POC) and the thickness of the gas hydrate stability zone (GHSZ). The overall goal – a simple means to quantify the amount of gas hydrate from a few basic parameters – is admirable and desirable.

The notion that a few basic parameters might govern the amount of gas hydrate in marine sediments, including "low flux settings", is not new. Indeed, this concept has been introduced in various works (e.g., Davie and Buffett, 2001) and summarized by Bhatnager et al. (Am. J. Sci., 2007). I am the first to admit that the Bhatnager et al. paper is not easy to read. Nonetheless, the concepts for "low flux settings" are instructive and crucial for evaluating the present submission. According to Bhatnager et al., the amount of gas hydrate in a "low flux setting" should depend on several parameters; the key ones being:

1. The thickness of the gas hydrate stability zone (GHSZ); 2. The Damkohler number (Da), representing the ratio of methane production to methane diffusion; and 3. The first Peclet number (Pe1), representing the ratio of fluid advection to methane diffusion.

Note that the second parameter incorporates the accumulation of POC.

As discussed by Bhatnager et al. (and other works such as Davie and Buffett, 2001), albeit somewhat obliquely, the theoretical relationship between the accumulation of POC and the abundance of gas hydrate is complex, even for systems with similar GHSZs, similar (or no) fluid advection, and at steady-state conditions. Consider, for example, two sites, one where the accumulation of POC is very low, and one where it is extremely high because of very fast sedimentation. In the first system, methane production is low, so little or no gas hydrate may accumulate within the GHSZ. In the second case, much of the methane production may occur below the GHSZ, so little gas hydrate may accumulate within the GHSZ. (Indeed, the manuscript eventually comes round to this view). Alternatively, consider two sites with the same accumulation of

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POC, but one where the sedimentation rate is high but the POC content is low, and one where the sedimentation rate is low but the POC content is high. These should give different gas hydrate abundances because of the depth of methanogenesis and methane diffusion.

With this preamble, there are four major problems and a series of lesser but important issues regarding the present manuscript.

Major problems

- (1) The Introduction needs major changes because it is longwinded, confusing and misleading. Moreover, the purpose of the manuscript is unclear with the present Introduction. It also fails to give a sense of the current "state of the art".
- 1a. The paragraph for the rationale of gas hydrates studies (Âű1) can be cut in half. All that needs to be stated is: Gas hydrates are abundant in marine sediment along continental margins They are of interest for several reasons (there is no reason for asides and details here)
- 1b. The paragraph concerning the two types of gas hydrate systems (Âű2) can be cut in half and merged with parts of later paragraphs. What should be stated is:
- In general, two types of gas hydrate systems Define the two systems (although see notes below in specific comments) Although much attention on sites of focused flow, most gas hydrate probably occurs in low flux settings The amount and distribution of gas hydrate has been estimated in several low flux settings using a range of information collected at drill sites An outstanding issue is how to explain and to predict the amount and distribution at a given location

(Now the basic problem has been set)

1c. The present "subsection" on gas hydrate distribution is a mess. The main reasons are that it presents and discusses global gas hydrate inventory (which really has nothing to do with the manuscript), and because it conflates and mixes errors in global

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estimates with those at specific locations. The five orders of magnitude in global gas hydrate distribution do not reflect geochemical or geophysical estimates at a given location, but rather the distribution of abundance across a global potential volume (Dickens, Organic Geochemistry, 2001). Most of this can be deleted because it is irrelevant. What should be stated in Âű3 (and without any subsection) is:

- A series of numerical models for predicting the amount and distribution of gas hydrate in low flux settings has been developed (and here incorporate to the recent). - These models are complex - They typically depend on numerous parameters and are site specific - It would be worthwhile to have simpler models for predicting the amount of gas hydrate at specific locations given some basic parameters

(Now the purpose of the manuscript is clear)

- 1d. The specific point of the manuscript needs to give credit for other work. The fundamental problem here is that the authors are proposing a simple approach, with some key caveats (see below), to the understanding of a more general case that has already been presented (but they do not state this). What should be stated is: Previous work has identified a few overarching parameters that govern the amount and distribution of gas hydrate at a location in a low flux setting (i.e., where advection is minimal) One is the thickness of the GHSZ (this is obvious) The second is the rate of methanogenesis to the rate of methane diffusion The rate of methanogenesis depends on the amount of (utilizable) organic carbon as well as several other parameters The rate of methane diffusion depends on sedimentation rate and several other parameters Consequently, there might be first-order relationships between the accumulation of POC, the thickness of the GHSZ, and the abundance of gas hydrate within the GHSZ Here we examine this
- (2) Much seems to hinge on the derivation of RPOC (Equation 1). However, it is totally uncertain how RPOC was determined without some basic assumptions. What value is used for CCH4 when accurate methane concentrations are not measured? (There

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are no detailed concentration profiles for CH4 through gas hydrate systems that I am aware of). How is ageInit ascertained?

- (3) Models for various sites are "run into steady state" (sic) but there is no information regarding the time to reach steady state conditions or whether this is at all reasonable in terms of modeling pore water profiles. As mentioned in several papers, millions of years are required to account for the abundance of gas hydrate in low flux gas hydrate systems. However, there are few (if any) low flux gas hydrate systems where this likely has been the case. The general problem, when one considers sedimentation rate and diffusion, is that the present pore water profiles may not represent the long-term conditions of the system. For example, I have always thought of the Blake Ridge as a "dying" system (where past inputs of POC were much higher than today and methane loss > methane production) and the Peru Margin (i.e., Sites 685/1230) as a "growing" system (where present inputs of POC are much higher than in the past and methane production > methane loss). (Look at the sedimentation rate over time for these locations!). In my opinion, this is precisely why the pore water profiles from a steady state perspective would suggest greater gas hydrate on the Peru margin than on Blake Ridge but all measures for the abundance of gas hydrate suggest the opposite.
- (4) There are two basic issues with the model-data comparisons: (i) the data and interpretations for some sites are not correct (e.g., sediment pore space between $\sim\!200$ and 450 m on outer Blake Ridge has about 4% gas hydrate on average as determined by multiple independent methods), and (ii) the comparisons of model results and data are not very convincing in some cases. The tendency in the present manuscript is to adjust some basic parameters (e.g., add fluid advection) to make comparisons better. Instead, I strongly suspect that the overall approach is too simple. As alluded to in my preamble and as noted in the above comment, there are some obvious caveats to the approach. The two most glaring problems are: the assumption that POC accumulation is divorced from sedimentation rate and POC content (the basic problem being that sedimentation rate impacts the location of methanogenesis and diffusion); -

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the assumption of steady state conditions and that present pore water profiles reflect the long-term history of a system.

So, what to do?

I like the idea of trying to understand gas hydrate abundance at different locations from basic parameters. However, they need to approach the issue from a much broader perspective rather than trying to force the data to conform to an overly simplistic view. I would rewrite the manuscript with a general approach something like:

- a relationship between GHSZ thickness, POC accumulation and gas hydrate abundance should exist; - we examine this from a basic model perspective - there are, indeed, some relationships - there are, however, some basic problems - Then spend much of the discussion explaining where and why things do and do not work in various cases

Other issues:

(5) The link between the depth of the SMT and gas hydrate abundance (page 1069) is not presented or discussed correctly. First, Bhatnager et al. (2008) were very clear to stress that a direct relationship between the abundance of gas hydrate and the depth of the SMT should only occur in advective systems – not the "low flux" systems discussed in the present submission. Second, Dickens and Snyder (2009) did not discuss a link between the depth of the SMT and gas hydrate abundance. The point of this work was to emphasize that the depth of the SMT is related to the upward flux of methane from gas hydrate systems. Although not really discussed in either of these works, I strongly believe that the depth of the SMT is related to the top of gas hydrate occurrence in low flux settings (a point also articulated by Charlie Paull and others). This is basic geochemistry. If the modeling does not conform to this expectation, please elaborate

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Editorial issues (over the first few pages):

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– Page 1059 –

Lines 15-21: This is "backwards" as the flux system is not defined by the amount.

Line 19: Nankai what?

Lines 21: This is not good referencing as both references pertain to the same location out of numerous possible ones.

- Page 1060 -

Lines 2-3: This is confusing. As written, it seems that geochemical and geophysical methods have been used to quantify global gas hydrate abundance, and that these methods are off by orders of magnitude. Clearly, this is not the case. The variation in global gas hydrate abundance exists because of assumptions regarding the volume of the global GHSZ, and the occupancy of this space (Dickens, Org. Geochem., 2001).

Line 10: This is not really a "scenario".

Lines 11-25: This is not the problem. Yes, various techniques for quantifying gas hydrate give different amounts in the same borehole. However, rarely are such estimates off by more than a factor of two (when calibrated correctly).

Line 25: This is poor referencing because the pressure cores presented in the Heeschen et al. paper are from the seafloor at seep sites in the Gulf of Mexico! They provide little if any constraint on gas hydrate distribution, especially considering the manuscript emphasis on low-flux settings.

- Page 1062 -

Line 26 (and elsewhere): Do not use latin abbreviations in the middle of sentences.

- Page 1063 -

Lines 2-3: This does not make sense as written. Some sites drilled 200 m; some 800 m.

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- Page 1064 -

Line 18: Awkward use of percentage

Line 21: Do not use since instead of because.

Line 25: Should be 5100 m.

- Page 1069 -

Line 19: Schneider? Spelling - Snyder.

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