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Discussions

Interactive comment on "Timescales for the development of methanogenesis and free gas layers in recently-deposited sediments of Arkona Basin (Baltic Sea)" *by* J. M. Mogollón et al.

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Mogollón and colleagues present model simulations to address an intriguing question: how does methane accumulation proceed over time on the continental shelf? To my knowledge, the problem has been discussed rarely in the literature from a dynamic perspective, let alone modeled.

I found the work interesting and insightful. I enjoyed reading the manuscript, and it makes one think. The model also contains some important concepts missing in quite a bit of the literature (e.g., the rising of SMT depth and the relative importance of AOM with increasing methane production over time).

I have no major criticisms of the work. However, I do think they could enhance the work, so that it becomes more interesting to a broader community. I also have a series of minor comments.

Lastly, I offer an apology for the lateness of my review, even though I was not asked to review the manuscript until October 31.

I trust the comments are fair and constructive.

Main Comments

(1) The "big picture" and, ultimately, the reason for the manuscript could be articulated much better. Right now, the main rationale for the work seems to be that rates of methane generation are an important and open issue in our understanding of methane and carbon cycles (p. 7625; Lines 13-15). This is not obvious, especially because the concept is not succinctly stated in the given reference (Reeberg, 2007), and because very few carbon cycle models include methane in marine sediment and relevant fluxes. Moreover, the paper discusses methane amounts, as well as methane outputs.

The manuscript (and certain sections) would become stronger if they rewrote the Introduction so as to place the totality of their work in perspective (see also Comments below).

With some liberty, here's the overall problem I think they are chasing:

- Enormous amounts of methane occur in marine sediment, on both continental shelves and continental slopes - This methane is dynamic with defined carbon fluxes to and from the ocean - A broad array of evidence suggests that the masses and fluxes of methane in seafloor sediment can vary significantly over time - For example, on the shelf, there are features indicative of gas expulsion (e.g., pockmarks; e.g., numerous papers by Hovland and Judd) or remnants of methanogenesis where none exists today (e.g., 13C-enriched authigenic carbonate; e.g., Malone et al., Mar. Geol., 2002) - However, the evolution of methane systems remains poorly constrained

(2) A series of models have been developed for the evolution of methane systems on continental slopes (e.g., Davie and Buffett, JGR, 2001, Chatterjee et al., JGR, 2011 and several others in the intervening time). While these modeling efforts have some similarities to the current one (and its predecessors), they also have some notable differences. There is no need to delve into these models in detail, given the focus of the current effort on the shelf. However, right now, there is no mention of these models or of methane cycling on the slope in general. The potential problem here is that the current effort may perpetuate several misconceptions about seafloor methane in general; more specifically, some of the results do not apply to seafloor methane cycling in deeper water, and this should be stated.

For example: - Sites on the slope also have horizons defined by methane solubility; however, gas hydrate can form, which changes the phase relationships considerably. - Sites on the slope are not subject to sub-aerial exposure and "flushing" over glacial-interglacial cycles; consequently, and with the introduction of a solid methane component, enormous amounts of methane can build-up over millions of years. - Sites on the slope almost invariably have low temperatures on the seafloor; as such, the temperature rise with depth becomes important to methanogenesis. - Sites on the slope generally receive much greater organic carbon during glacials; this is opposite to the shelf.

A very intriguing concept derives from the present work and efforts on the slope: the average depth of total methane production might vary considerably over time; that is, during interglacials, considerable methane production might occur on the shelf at the expense of methane production on the slope.

(3) As stated above, the modeling provides some interesting perspectives on methane cycling in sediment on continental shelves. However, this is not discussed in a general sense.

Above and beyond any comparisons to slope environments, their modeling may apply to other shelf environments. Although many shelves do not contain a lacustrian deposit, Holocene sections are often underlain by a hiatus emplaced during sea level lowstand and sub-aerial exposure, which may mark a time-zero for methanogenesis. I suspect their modeling provides a broader framework than presented.

(4) There are some clear tests of their modeling. For example, there should be very specific profiles for DIC (alkalinity) and the 13C of this DIC (e.g., Chatterjee et al., JGR, 2011). It would be good to state this.

(5) Temperature is discussed as a key parameter. There is also commentary on how temperature changes with seasons. However, other than a "reference temperature", values are never stated. It would be good to explicitly state temperatures and their ranges in the text (place in parentheses). To a lesser degree, the same applies for pressure and salinity.

Specific Commentary – Page 7625 – Line 5: The "tense" is mixed with the phrase "becomes deposited".

Lines 15-18: The writing seems to suggest that methane is particularly abundant in sediment under hypoxic water masses. This generally may be correct for sediment on the shelf; obviously, however, enormous amounts of methane can occur in sediment on continental slopes, which generally do not underlie hypoxic water masses. (See also Comments 1 and 2).

– Page 7626 – Line 1: Of course, methane can also be consumed aerobically, when it escapes to very shallow sediment and the water column.

Line 5: I am not sure why SMTZ is being used instead of SMT as in many papers (transition and zone seem redundant to me).

Line 6: This is correct with the caveat of venting (which can include dissolved gas and free gas bubbles).

Lines 7-10: This sentence (and concept) is not clearly presented. This is because the idea of saturation zones that relate to methane concentration and methane flux is never presented. This might be addressed with a new Figure 1 that shows the generalities of what they are trying to model (i.e., a figure showing generic methane and sulfate concentrations versus depth).

Lines 15-18: I do not follow the glacial-interglacial reference, as the model and paper strictly pertains to the Holocene. Moreover, others have certainly discussed the potential long-term impact of AOM on geochemical cycles (e.g., Dickens, EPSL, 2003; Dickens, Clim. Past, 2011).

– Page 7627 –

Lines 7-8: Is this really why stratification occurs? I thought it also reflects the large freshwater input to the Baltic Sea.

Line 14: Missing a word(s).

Line 19: As noted below, it is not clear whether the low organic carbon in the lower sedimentary units refers to TOC or reactive organic carbon.

– Page 7628 – Line 2 (and throughout): Remove "the" for proper nouns (nb. this is usually the case in the present manuscript but not always).

Line 5: Rewrite. Maybe I am wrong, but I think that it's the seafloor of the basin that is 50 m deep.

Line 8: The use of "while" is uncertain here because the gas horizon and fluffy layer do not seem conflicting geographically.

Lines 10-11 (and throughout): I would rewrite so as to make the sentence active instead of passive. "Significant . . . punctuated . . ." (This obviously stylistic but, in my opinion, makes reading much smoother and better).

Line 10 and onwards: This is a very long paragraph with multiple concepts. I would split to make reading easier.

– Page 7629 –

Line 8: This is not clear because usually sediments are described downcore (i.e., with increasing depth). Here, however, it seems to be upcore and with decreasing depth.

Lines 11-12: Fix the formatting here in regards to the referencing.

– Page 7630 – Line 1: Do the "missing tops" pertain to all cores or gravity cores? I assume the latter, but this is not clear.

Lines 6-8: I would add two sentences here briefly stating how the measurements were made. There is no need for detail if documented elsewhere; however, one should not have to read other works to know the basics.

Line 18: It should be stated that the second reaction (methanogenesis) is an abbreviated reaction. In other words, this reaction does not exist per se; rather it is a summary of intermediate reactions.

– Page 7632 – Line 17: Is alpha-o always zero? If not, why?

– Page 7633 – Line 4: The word "impressed" should be changed.

Line 11: First, clarify this with "downward" in regards to advection of free gas. More importantly, I would add a caveat. This assumption effectively means that free gas is kept below some threshold concentration. Presumably, over time, sufficient free gas could accumulate, such that this assumption is not longer valid and the model would have to be amended.

Lines 15-25: I think there is an intrinsic assumption here: namely that degradation of organic carbon through R1 and R2 proceeds similarly. In other words, the same suite of compounds is used for sulfate reduction of POC and methanogenesis. They may want to comment on this issue.

– Pages 7634/7635 – Given somewhat similar modeling of methane accumulation on continental slopes, it may be worth noting that, at the water depths and pressure in the Baltic Sea, gas hydrate cannot form, so this phase, which complicates matters significantly, can be ignored in the modeling.

– Pages 7636 – Lines 4-6: Does the 5% TOC refer to sediment below the HORM? Currently, these lines read this way, but this contradicts statements elsewhere. If so, this assumption leads to an interesting question: why is this organic carbon unreactive? Has it been subaerially exposed? (I cannot tell from the "history", above). It would be helpful to have typical TOC ranges presented in Figure 2.

–7637 –

Line 6: awkward referencing

–7639 –

not clear

– Page 7641 – Line 12: Change to "across the basin"

Line 15: This is awkward. Change to ". . . AOM, driven by upwards diffusion of methane generated . . ."

Line 21: Change "evaluate" to "predict".

The writing on this page is a bit unclear with regards to methane saturation. I assume that the 2mM measured on ship is the solubility of methane at 0.1 MPa and shipboard temperature of XX °C, whereas those modeled are at XX MPa and sediment temperature of XX °C. A bit of information and explanation would be helpful, especially to the casual reader.

– Page 7642 – Line 2: It would be helpful to express this in terms of pore space volume, rather than bulk sediment.

Line 8: This is confusing because the manuscript seems to state that these sediments have high organic carbon content (p. 7636, Lines 4-6).

– Page 7643/7644 – This section is difficult to follow given the current figures. Figure 7 does not explicitly show a deep SMT; the curves on Figure 9 are not easy to tell apart.

– Page 7644 – Lines 5-6: Another very good example of a double SMT occurs on the Peru shelf (D'Hondt et al., Science, 2004). Here, however, it is because a sulfate-rich brine lies in deeper sediment.

Line 13: Is this not for the upper SMT?

Lines 22-24: Is the discussion of temperature correct? It seems to me that this would depend on the change in bottom water temperature, time and sediment properties. Basically, how do heat variations propagate into shallow sediment (See also Comment 5).

– Page 7645 – Line 5: The notion of methane escape is not clear as presently written. Does this refer to ebullition and venting, which is not part of the model? Or does this refer to greater AOM through a steeper pore water profile?

Line 22: I do not follow "and the sulfate diffusion." Does this mean the downward flux of sulfate through diffusion?

– Page 7646 – Line 11: Does the 10-15% hold despite potential free gas accumulation? It seems to me that this might increase once free gas begins to accumulate.

– Page 7647 – Line 11: Change "considerably flat as compared" to "relatively invariant compared".

– Page 7648 – Line 17: Which high fractions? Methanogenesis? Suflate reduction of POC? Both?

– Page 7660 – Figure 3: I am uncertain what shoreline displacement means. More crucially, the vector is not clear (does this mean positive or negative sea-level?). A second curve on this panel – seafloor pressure – would be helpful.

– Page 7661 – Figure 4: It would be helpful to have a horizontal line (or better yet shaded boxes) marking the HORM and “pre-HORM”.

– Pages 7662/7663 – Figure 5: It may be the figure copy and the distinction between solid and dotted lines, but something seems incorrect between the caption and profiles for panels (a) and (d), Specifically, it appears that methane (solid line) is wrong in panel (a). Also, it seems that POC should be labeled as reactive, given that there is POC in deeper sediment (although see notes above). Lastly, it would be useful to have a horizontal line (or better yet shaded boxes) marking the HORM and “pre-HORM” intervals.

– Page 7665 – Figure 7: As above for Figure 5. Also, I am uncertain what is being modeled or shown in regards to the lower SMTZ, as there seems to be no sulfate. Is the “CH4 front 2” below the base of the panels?

Interactive comment on Biogeosciences Discuss., 8, 7623, 2011.