

## ***Interactive comment on “Low methane concentrations in sediment along the continental slope north of Siberia: Inference from pore water geochemistry” by Clint M. Miller et al.***

**Anonymous Referee #2**

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This study, for the first time, presents geochemical data from the Eastern Siberian Margin, an area of the Arctic that is predicted to hold significant amounts of gas hydrates in the sediment. Intriguingly, the authors find no evidence for the presence of methane in the ESM sediments (asides from one site on Lomonosov Ridge) based on a range of pore-water profiles, including total dissolved sulfur and bicarbonate concentrations, and the carbon isotope composition of DIC. These profiles should show evidence of the occurrence of geochemical processes associated with the production and consumption of methane, e.g., AOM, if gas hydrates were occurring in sediment.

General comments

Overall, this study represents an important contribution to the still very limited geo-

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chemical data available from this part of the global ocean. I agree with the authors that from all we (sedimentary biogeochemists) have learned it is justified to assume that geochemical profiles, especially sulfate, alkalinity, bicarbonate (and  $\delta^{13}\text{C}$ -DIC), should show clear evidence of microbially mediated processes associated with methane production (or more accurately evidence for very high organic turnover rates) and methane consumption, especially sulfate reduction coupled to AOM. It is very intriguing that these signals are absent from the profiles present here. It is somewhat unfortunate that the authors did not conduct any direct methane analyses (and somewhat surprising given their initial aim of the research expedition) but given the other detailed geochemical data, this is not a major issue. I feel like the transects are very well spaced out thus allowing for the conclusion that the ESM is predominately gas hydrate-free. The somewhat lengthy methods section reflects the cautious and tedious job the authors have done during sample collection and analysis thus giving confidence that the provided data is of very high quality. While the methods applied in this study are not new and the lack of methane results in what can be viewed as rather “boring” profiles, it is the underlying implication of not having gas hydrates in this area despite previous predictions that makes this study so important.

However, several aspects detailed below require major revisions to strengthen the geochemical framework of this study.

Additionally, the manuscript can be shortened significantly. There are several sections that are repetitions (see next section) and to me the very detailed discussion on the fidelity of the data obtained by the Rhizone sampling technique, albeit warranted, distracts from the main message of the manuscript. Along the same lines, the authors have included several plots, e.g., Figures 13, 14 and 16 that do not help conveying the main message of the study and are irrelevant. Figures 13 and 14 are not even mentioned in the Discussion section. Figure 13c is not mentioned in the manuscript at all?!

Specific comments:

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Figures 1 and 3: I suggest placing both maps next to each other in one figure (ie., Fig.1a and 1b). This would make it much easier for the reader to find out where the sampling sites are located relative to predicted gas hydrate occurrence.

Figure 4: This is a nice picture but does not convey any important information. Given the total number of figures in this manuscript, I suggest deleting it.

Figure 6-9: These figures are hard to read. I suggest plotting each core in a specific figure in a different color rather than all data in one figure in the same color. There is very limited discussion/comparison of the ACEX data; why plot it then?

Lines 187-242 vs. lines 616-657: The sections are basically saying the same thing with a few additional points in the latter, discussion section. I suggest removing lines 616-657 and taking the few “new points” that are mentioned here and adding them to the background section. I found it tiring to read the same “intro to reading pore-water profiles” twice.

“Rhizone experiments”: These are very helpful experiments that install additional confidence in this comparably novel sampling technique. With that being said the description of these experiments, including the results and discussion of the results take up a lot of space and distract from the main story of the manuscript. I suggest moving all of this into a supplementary material section. This would include the experiment description (line 310), section 4.3, the discussion sections 5.1 and 5.2 and Figures 5 and 11 (and maybe 12 if the authors think that the porosity-rhizone aspect could also be trimmed), Tables 1 and 2. Basically, all we need to know is what is in the short summary in lines 606-614. The reader can be referred to the supplementary material for the detailed experiments.

Dissolved hydrogen sulfide “analysis”: It seems like the authors did not actually do any sulfide analyses but just “visually” observed whether white precipitates were forming when zinc acetate was added. To me this is not an appropriate “analysis” to detect hydrogen sulfide. This is especially important since the authors did not do any sulfate

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analyses but only analyzed total dissolved sulfur and –based on their visual “analysis” of the sampling vials- assumed that no hydrogen sulfide was present and the total sulfur only reflects sulfate. I strongly suggest doing at least a few hydrogen sulfide analyses with the Cline method, for example of the samples from deeper layers especially on the cores from Lomonosov Ridge, to confirm the absence of hydrogen sulfide.

Lines 176-178- Microbial processes at cold seafloor temperatures: I disagree with the authors here. There are plenty of studies that have shown that organic carbon turnover rates or “bacterial degradation” in high latitude environments are/can be as high as in mid-latitude or tropical environments. For example:

Glud et al., 1998: Benthic mineralization and exchange in Arctic sediments (Svalbard, Norway) Arnosti et al., 2005: Anoxic carbon degradation in Arctic sediments: Microbial transformations of complex substrates

Carbon isotope sections: Generally, the sections discussing the carbon isotope system, e.g., processes associated with carbon isotope fractionation, the discussion of the carbon isotope data etc. is very weak and needs more clarification. Also, it is incorrect to present equations (1) and (8) with  $^{12}\text{C}$  and state that it indicates “depletion in  $^{13}\text{C}$ ”. As such, the equations written just present the reaction of one organic molecule containing  $^{12}\text{C}$  to bicarbonate which of course also has to contain  $^{12}\text{C}$ . Please take the notations out.

Line 227-229: This needs to be expanded and maybe clarified. Both the Holler and the Yoshinaga references are discussing carbon isotope fractionation during AOM. As stated here, the authors only consider the original  $^{13}\text{C}$ -depleted value of the  $\text{CH}_4$  in explaining the light DIC formed. Additionally consider: Alperin, M.J., Reeburgh, W.S., Whiticar, M.J., 1988. Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation. *Glob. Biogeochem. Cycles* 2, 278–288. Martens, C.S., Albert, D.B., Alperin, M.J., 1999. Stable isotope tracing of anaerobic methane oxidation in the gassy sediments of Eckernforde Bay, German Baltic Sea. *Am. J. Sci.* 299, 586–

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610. And for the first part, besides from Paull et al., a reference such as Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 161, 291–314.

Line 681-687: Similar to the previous carbon isotope section, there is some more detail needed here. For example, carbon isotope fractionation during organoclastic sulfate reduction needs to be discussed. The Chatterjee reference (which should be 2011 not 2001) is insufficient here.

Line 706: “almost necessarily implies CH<sub>4</sub> oxidation.. “. This statement needs an explanation and the appropriate literature. . .

Results section: When you list what the concentrations were, they are in past tense, when you describe what the reader sees in the graph, this is in present tense.

Lines 508-519, Figure 14: This is a nice exercise but I am wondering why this is included? I could not find any reference to this approach/figure in the discussion section. If it is not relevant to your discussion-delete! Or add a section in the Discussion part that evaluates the plot.

Lines 728-733 and elsewhere: I disagree with this general interpretation. Many of the collected cores also show decreases in sulfur concentration which point to the occurrence of organoclastic sulfate reduction, and you interpret the delta<sup>13</sup>C-DIC profiles as being imprinted by this process! While the dissolved Mn profiles can be interpreted as reflecting dissimilatory manganese oxide reduction, there has been a lot of recent work discussing the –somewhat intriguing- manganese biogeochemistry of Arctic ocean sediments, including evidence for dissolved manganese profiles reflecting diagenetic remobilization of Mn and diffusion from deeper sediment intervals. I suggest preparing this section with more caution. For reference: März et al. 2011: Manganese-rich brown layers in Arctic Ocean sediments: Composition, formation mechanisms, and diagenetic overprint (and references therein).

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Line 735-737: This section is somewhat incorrect as well. What Mn and Fe is consumed ? I assume you are now referring to Mn- and Fe-oxides. I suggest: 1) making it clear that dissolved Mn and Fe are produced during dissimilatory Mn- and Fe-oxide reduction; 2) highlighting that the reason for the decline in concentrations are consumption processes (assuming steady state you would otherwise expect constant pore-water values below the current reaction zone), which likely include the reaction of Fe with hydrogen sulfide, and interactions of Fe with Mn-oxides. (Again the sedimentary Mn story may be more complicated; see comment above); 3) stepping back from the idea that there is “complete consumption of Fe and Mn”. If you are referring to the oxides, then especially in the case of Fe it is the very reactive (towards H<sub>2</sub>S) iron (oxyhydr)oxide phases that are being reduced (see Canfield et al., 1992: The reactivity of sedimentary iron minerals towards sulfide) but there is without a doubt no “complete Fe consumption”!

Section 5.7 and Figure 16: In this form, I find the plot misleading and somewhat irrelevant (or not providing any new helpful information). First, as you have discussed, sites with methanogenesis and AOM are characterized by much higher DIC concentrations and much lighter delta<sup>13</sup>C-DIC values than sites lacking these processes. If you multiply these two, of course you get more negative values at the AOM sites. Second, I am not sure what you are actually plotting as  $\delta^{13}\text{C}$  here ? You state that other authors have used the concentrations at the seafloor and the SMT. What do you do for your data where there is no SMT? Third, in line 760 you state “two basic models help explain the relationships in Figure 16.” However, you are in the following section only discussing the C:S ratios, including their relative changes with depth (as you are interpreting them from the mudline downward using the changes in DIC\*delta<sup>13</sup>C-DIC as an alternative measure for depth). Why then do such a crossplot? On a side note – why is the ratio for the OSR model increasing past 2:1? Because the DIC reflects additional bicarbonate production by dissimilatory Mn and Fe oxide reduction rather than only from sulfate reduction ? Fourth, in line 747 you are stating that “a flux of HCO<sub>3</sub><sup>-</sup> from below the SMT can augment the DIC produced. . . Thus, changes in alkalinity relative to sulfate

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often exceed 1:1...". Now the conclusion from your model/plot is that -line 768-769-  
"..CH4 charged locations with migrating DIC must have C:S molar ratios in excess of  
1:1...". So what have we learned? It would be honest to also mention the studies by  
Snyder et al., 2007 and Wehrmann et al. 2011 (Coupled organic and inorganic carbon  
cycling in the deep seafloor sediment of the northeastern Bering Sea Slope (IODP  
Exp. 323)) in lines 740-750 who used fluxes instead of concentrations.

Lines 808-816: I suggest expanding this section, and maybe including relevant liter-  
ature to support the different hypotheses, even if it means speculating. The finding  
that CH4 is low in the sediment in this part of the Arctic is the essential message of  
this study; the major question that arises is why? Do the ACEX studies provide any  
clues that would support any of your hypotheses? Lines 817-820 need more details  
and references as well!

Discussion section: the Ba and Sr data are not discussed.

Technical corrections:

Line 17: ...methane (CH4)...

Line 27: replace "nutrient" with "phosphate and ammonium"... Also, the "nutrient data"  
does not provide evidence for the dominance of metal oxide reduction but evidence for  
very low organic carbon turnover rates. Please re-phrase.

Line 35: ...substantial amounts of CH4. (or something similar)

Line 44: ...in the form of gas hydrates,

Line 79/80: Please re-phrase. Methane is not "reacting with sulfate". Obviously this  
is still debated but a term like "sulfate reduction coupled to the anaerobic oxidation  
of methane" or "sulfate reduction-coupled AOM" is more appropriate or rephrase to  
"microbes utilize methane..." or so.

Line 84: "Where CH4 flux to..."

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Line 96-100: I suggest deleting these sentences. First, giving the total number of  
samples etc. is a little too much detail for the intro. Second, putting a "conclusion"  
sentence here, seems confusing (this is not the abstract).

Lines 150-157: Change all [] to ()

Line 152: Limited information on what?

Line 193: I don't think the Schulz, 2000 reference is appropriate here. I suggest  
Boudreau (1997) and Iversen and Jørgensen (1993) instead.

Line 241: Delete summary sentence.

Line 273: Remove ; at end.

Line 314: Table 4?

Line 338: Should be Table 3.

Line 340: ..dissolved sulfur and metal concentrations...

Line 342: HNO3

Lines 353-381: Please shorten these sections. These are very common methods and  
you can reference the appropriate literature. We don't need to know exactly how much  
of which chemical you weight in etc.

Line 389: Can you find a better title for this section than "Generalities"?

Line 390: Table 1?

Line 405-412: Move to methods section.

Line 422-428, section 4.3: As outlined above, I suggest moving this to an supplemen-  
tary material section.

Line 459: I am not sure a "decrease" can "change"

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Line 477: Replace “faster” (time component) with “ displayed a steeper decrease” or so.

Line 479: Replace “sulfate” with “sulfur”

Line 480: I don't see where the 0.98 comes from.

Line 482 etc.: I suggest taking the “nutrient” term out. As you discuss, you are considering phosphate and ammonium as mineralization products. Instead of the discussion in Lines 483-485, why not just say “..the mineralization products. . .”

Line 621: Replace symbol.

Line 633: I am not sure this is correct. A concave-down sulfate concentration profile usually implies on-going organoclastic sulfate reduction above the SMT. Otherwise you get a linear profile driven by diffusion of sulfate from the sediment-water interface to the SMT.

Lines 635-637, 637-639, 639-641: These sentences need references.

Line 650 etc.: Do you actually calculate the methane fluxes somewhere? If so, how were methane fluxes calculated? What was taken into consideration? What if organoclastic sulfate reduction is occurring in close vicinity above the SMT, ie, your upward methane flux would then not be equal to the downward sulfate flux (at a 1:1 ratio). Where is the methane flux data?

Line 671: “...imply a SO<sub>4</sub><sup>2-</sup> flux..”

Line 674: 6.8 mol/m<sup>2</sup>

Line 687-688: Ok, it has a different ratio. . .and ? I am not sure you mention this here?

Line 706: 43.54%.

Line 708-709: I don't think that this is an “issue” but as you point out earlier it is very common to only observe hydrogen sulfide very close to the SMT. Nonetheless, if “none

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was detected” what do you conclude from that (ie, here please insert a short discussion on the reaction of hydrogen sulfide with dissolved iron and iron oxides, pyrite formation etc)?

Line 724: manganese oxide reduction, iron oxide reduction; also denitrification and nitrate reduction ???

Line 742: “The idea. . .” There is a word missing here.

Line 779: Can you find a better title than “Explanations”?

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