

## ***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 #1**

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Methane (CH<sub>4</sub>) fluxes on the East Siberian Margin (ESM), as the authors call the area, has indeed attracted much attention from the scientific community lately and caused a storm of debate. I agree that many aspects of this topic need more study because the topic itself is rather novel and has only been under investigation for a little over a decade. I also share the authors' opinion that our understanding of some processes and mechanisms controlling CH<sub>4</sub> cycling in this area requires a great deal of improvement. I believe that the authors of this manuscript could have contributed to this topic with new data; they clearly pointed out in the text that this topic was a primary goal for the SWERUS-3 expedition onboard IB Oden which was accomplished in 2014. However, this ms rather demonstrates that the current state of knowledge

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of pore water biogeochemistry in particular areas of the ocean is very incomplete; a great deal of effort will be required in order to improve our understanding of the relationship between sulfur and carbon cycling in the Arctic. The authors of the ms come to the following conclusions: 1) Based on interpretation of the pore water profiles, they found no evidence for upwardly diffusing CH<sub>4</sub>. 2) Based on these data, they strongly suggested that gas hydrates do not occur on the slopes of the ESM. 3) They claimed that previous investigators who suggested that hydrate deposits exist in the Arctic shelf/slope based on results of their investigations were simply wrong.

First of all, I do not understand why, when reporting low CH<sub>4</sub> concentrations and the relationship between CH<sub>4</sub> and sulfate dynamics in the pore water, the authors did not measure the concentrations of either parameter. Is it not logical to measure CH<sub>4</sub> and sulfate in pore water if one is going to report “low methane concentrations in the sediments”? These are rather routine measurements. The authors referred to other researchers in their ms to present supportive arguments, but none of these referenced studies avoided taking measurements. In addition, the authors of this ms speculate about the particulate organic carbon (POC) and OC content of sediment, but did not measure either parameter. OC content of sediments should be reported as a number of different carbon stocks, not just POC. Second, I do not understand why the presence or absence of CH<sub>4</sub>, either in the sediments or in the water column in this area, should be necessarily connected to the existence or non-existence of hydrates. Are hydrates the only possible source of CH<sub>4</sub> in the Arctic shelf/slope? I believe not; hydrates could be only a tiny fraction of the source, because the hydrate stability zone (HSZ) created by P/T conditions could compose only a small fraction of the sedimentary drape (a few hundred meters), while the sedimentary drape could be a few kilometers thick. Third, the purpose of this massive manuscript is not clear to me. This paper is flooded with equations and details devoted to methods, but mathematics, first of all should be applicable; then, the accuracy of mathematics does not aid in interpreting the inconclusive data. Below are my comments on some aspects of this ms. A more detailed look would be as long as the ms itself, because nearly every page of this ms would benefit

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from clarification. The methodology chosen by the authors of this ms and their level of understanding of the processes they were trying to investigate are my greatest concern. Biogeochemists working in the marine ecosystems have already gained some understanding of the fact that biogeochemical processes associated with diagenetic transformation of organic matter under anaerobic conditions in marine sediments are very complex microbe-mediated processes. These processes involve microorganisms from various physiological groups: aerobic and anaerobic saprophytic and cellulose-degrading bacteria, sulfate reducers, methanogens, denitrifiers, and methylotrophs. Transformation of organic matter is a multi-stage process: primary anaerobes decompose polymeric compounds to monomers, which, in turn, serve as a substrate for fermentation agents and gas-producing bacteria. A general conclusion is that the major fraction of OC preserved in the sediments is oxidized to CO<sub>2</sub> by the sulfate-reducing bacteria (SRB) and that 2 moles of OC are oxidized for every mole of sulfate reduced:  $4\text{H}(\text{CH}_2)_n \text{COO}^- + (3n + 1)\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow (4n + 4)\text{HCO}_3^- + (3n + 1)\text{HS}^- + \text{OH}^- + n\text{H}^+$ . When acetate is oxidized completely, the atomic ratio of OC oxidized to sulfate-S reduced is 2 : 1. However, as 'n' increases, the C: S ratio changes; the ratio between the reactants could be different because it depends on the varying nature of the organic matter (Lerman 1982). This is because most of the photosynthate is not immediately available for oxidation; only the low molecular weight (LMW) fraction of dissolved OC (DOC) is rapidly oxidized by SRB, while the high molecular weight (HMW) fraction of POC, which usually increases with depth, is refractory. There are severe restrictions on microbial activity other than substrate availability, including that SR as a biotic process may be more strongly coupled to mineralogy (Ivanov et al., 1989). The knowledge that has been accumulated by scientists so far is very limited and only applicable to those particular ecosystems which were investigated beyond the Arctic. The most reliable method to trace the course of sulfate reduction in sediments uses radioactive sulfate (<sup>35</sup>S). By the use of this method it was shown that most reduced <sup>35</sup>S-sulfate was in pyrite and organic sulfur (Lein et al., 1982). The relationship between sulfur and carbon cycling in the Arctic marine systems is even more complicated, because

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the relationships between the sites of primary production and the sites to which organic matter is translocated and deposited, including organic matter delivered to the shelf/slope from surrounding land, are difficult to establish both qualitatively and quantitatively. A recently published review of CH<sub>4</sub> emissions from the seafloor in the Arctic Ocean underscored that the role of SRB in the anaerobic oxidation of methane (AOM) is unclear and the ecology of AOM communities, particularly for high-latitude environments, is not well understood. For that reason, predicting CH<sub>4</sub> fluxes, especially those related to hydrate dissociation, remains highly speculative (James et al., 2016). This is because CH<sub>4</sub> is transported within the sediments in two different ways: as a dissolved phase (by diffusion or advection) or as free gas (ebullition). Free gas is inaccessible to microbes, which depend on a diffusive transmembrane gas transport. This means that release of free gas through the sediments might not leave any traces in the pore water (see Fig.5 in James et al., 2016). Moreover, recently published observational data show that in the Arctic environment, for example in the Alaskan Beaufort Sea continental margin sediments, substantial (30-500 μM) concentrations of sulfate can remain below the sulfate-methane transition zone (SMTZ) although mass balance cannot explain the source of sulfate below the SMTZ. In addition, sulfate reduction and anaerobic oxidation of CH<sub>4</sub> can occur throughout the methanogenic zone. Experimental data indicated decoupling of sulfate reduction and AOM and competition between sulfate reducers and methanogens for substrates, suggesting that the classical redox cascade of electron acceptor utilization based on Gibbs energy yields does not always hold even in diffusion-dominated systems (Treude et al., 2014). Although they vigorously referred to Nauhaus et al. (2002) as a proxy-establishing experiment, the authors did not give this work any critical assessment. If they had done so, they would have definitely questioned the claim that methanotrophic communities associated with SRB oxidize CH<sub>4</sub> anaerobically in a 1:1 ratio to sulfate reduction. How that could be possible if the reported 4-5-fold increase in H<sub>2</sub>S production (accumulated over 80 days!) was accompanied by an increase in CH<sub>4</sub> concentration of 3 orders of magnitude (from 0.01 to 15.8 mM)? Besides, rates of SR were so small (0.5-3.0 μM/d-1) compared to

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the concentrations of sulfate (103-1.55  $\mu\text{DJ}$ ) that the question arises: How could this little change be reliably measured (without using the 35S method, which they did not) and related to AOM? Not to mention that this effect has no applicability to the Arctic Ocean. Another concern is this: How representative of the area are these data? Only four short transects consisting of 16 stations are presented; each transect is based on data from 2-6 stations. Data from only 2-4 stations represent all core depths. Core lengths vary from 1.95 to 8.43 m (mean length 5.25 m). Eight of the 16 stations are only represented by the very uppermost layers (from 0.16 to 0.39 m) of sediment collected by the multi-corer. These shortest parts are the most valuable as they represent the least disturbed environment, but they are too short to constitute any sort of conclusive data regarding CH<sub>4</sub> cycling in the sediments. I can only guess at how the authors succeeded in dividing these tiny cores into numerous parts, each 0.2-0.3 m in length, and accumulated enough data to compare these cores with one of two idealistic schemes to characterize the specific dynamics of processes occurring over a sediment depth of 100 m (Fig.1). Data obtained by other types of sampling (piston/gravity coring) should be treated and interpreted very cautiously as the cores are not only severely disturbed during the coring process, but also chemically altered as they are extracted from the sea floor and lifted onto the ship. Finally, the authors plotted water concentration profiles along each transect collectively (!) using colors and symbol types which make it virtually impossible to distinguish between these symbols, making interpretation of the data sets very difficult. From this, it follows that the authors assumed complete uniformity of processes occurring not only in the observed settings located tens of kilometers apart from each other, but also over the entire slope area! This is despite the fact that CH<sub>4</sub> fluxes on the East Siberian Arctic Shelf (ESAS), which could be associated with CH<sub>4</sub> releases from decaying hydrates, have been reported to vary by orders of magnitude within much smaller scales (Shakhova et al., 2015). I see a clear discrepancy between the basic assumptions made by the authors and the methodology used to test these assumptions. The authors assumed CH<sub>4</sub> was being released from destabilizing hydrates, most likely via bubbles and the convective flow of geofluids. Despite that,

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all equations used for estimates refer to the diffusive transport of CH<sub>4</sub> and other substances in the sediments. This is understandable; they used what was available. The problem is that the mathematics associated with diffusive transport cannot be used to describe the release of free gas from decaying hydrates. When assuming CH<sub>4</sub> release from gas hydrates, one should realize that hydrates convert to free gas; the released gas travels upward much faster than diffusion occurs, through very efficient gas migration paths (chimneys etc.). In most cases, ascending CH<sub>4</sub> can avoid oxidation in a few ways. 1) Because free gas resulting from hydrate decay is over pressured, it builds up a gas front; this disturbs sediment layering, creating the characteristic marks of gas release (pockmarks etc.). 2) Only CH<sub>4</sub> dissolved in pore water is reachable by microbial communities; CH<sub>4</sub> released as free gas (ebullition) is not consumable by microbes. 3) AOM rates are only remarkable as compared to rates of modern methanogenesis, because all synergetic processes should be energetically efficient for all members of the microbial community, including SRB, methanogens and methanotrophs, etc. Finally, the authors of the ms used three assumptions to explain their findings. Their first assumption is that bottom seawater on the slope north of Siberia is warming, leading to hydrate destabilization. There are no reports of increased bottom water temperatures along the slope of the Arctic during either the last glacial cycle (Cronin et al., 2012) or the Holocene (Biaostoch et al., 2011; Dmitrenko et al., 2011; James et al., 2016). All papers published so far project the response of the hydrate inventory to possible future climate change in the Arctic. The paper of Stranne et al., (2016) the authors refer to assumes a linear rise in ocean bottom water temperatures of 3°C over the coming 100 years. This speculative warming of the Arctic is intentionally set higher than in other studies (<2°C by Biaostoch et al., 2011; <1°C by Kretschmer et al., 2015) while modeling assumptions contradict the existing hydrological data (Biaostoch et al., 2011; Dmitrenko et al., 2011; James et al., 2016). Their second assumption is the quintessential statement that "Implicit of this finding is that sediments sequences along the ESM lack gas hydrates" following the authors' speculations about why predictions of hydrates on the ESM are so markedly wrong. The authors then suggest that: 1) the sig-

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nificant sea-ice concentration on the ESM diminishes net primary production (NPP); 2) the extremely broad continental shelf prevents accumulation of terrestrial organic-rich sediments; and 3) sediment accumulation is highly variable, so organic matter can be consumed during intervals of low deposition. None of these explanations is true. It was recently shown that the total OC (TOC) content in the ESAS/ESM sediments measured along the transect spanning more than 800 km from the Lena River mouth to the shelf (2000–3000 m water depth) varied between  $\sim 2\%$  at shallow water depths and  $0.8\%$  in deeper water (Bröder et al., 2016). In addition, TOC values and general patterns, which reflect fractions of terrigenous OC reaching the slope (based on biomarkers), were within the same range as those measured for the North American Arctic margin (Stein and Fahl, 2000, 2004; Goni et al., 2013). For comparison, an average value for the continental slope of the Gulf of Mexico, where large storage of CH<sub>4</sub> hydrates has been proven to exist, is  $0.8\% \pm 0.2$  (Gulf of Mexico Hydrate Research Consortium). Moreover, according to Arrigo and van Dijken (2011), the total annual NPP over the Arctic Ocean exhibited a statistically significant increase by 20% between 1998 and 2009, due mainly to increases in both the extent of open water (+27%) and the duration of the open water season (+45 days). Most importantly, increases in NPP over the 12 year study period were largest in the eastern Arctic Ocean, most notably in the Siberian (+135%) sector. It is interesting that the authors themselves confirmed that: 1) environmental conditions on the ESM are highly conducive for gas hydrates; 2) hydrate occurrence in the other areas of the Arctic, where hydrates were predicted, was confirmed by hydrate recovery; and 3) all the models developed by generations of geologists to predict hydrates in the Arctic used the same assumptions. If the authors agree that these statements are true, they failed to be critical of their own work, which is based on a handful of inconclusive data obtained on a single expedition, groundless methodology, and a few erroneous assumptions. Instead of casting doubt on the results of others, I would suggest that the authors question their own results and make a greater effort to accumulate clear, interpretable data. I believe I have made it quite clear that there is a huge discrepancy between the results presented by the authors

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and the far-reaching conclusions they are trying to support with these data. I see no way to support publication of this manuscript in its current state.

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