

1) FIRST REVIEWER:

The manuscript (ms) by Sapart et al. presents valuable information on the origin of methane in the East Siberian Arctic Shelf (ESAS), long been discussed based on assumptions and speculations. I like that this data set represents results of triple-isotope analysis. To my knowledge, this is first presentation of such a kind collected in the marine Arctic. This fact itself makes this ms novel. Besides, the data are from the potentially globally important region, because a predominant fraction of submarine permafrost is there; the ESAS was suggested to incorporate much of organic carbon and, probably, hydrocarbon stocks and hydrates in the sediments beneath permafrost. It was also shown to be warming due to natural warming as well as global warming. I believe this new data would be of great interest to scientists working in different disciplines and areas of the Arctic: to geologists, biogeochemists, oceanographers, atmospheric scientists, climatologists and climate scientists.

Authors report methane concentrations and triple isotope data analyzed on gas extracted from sediment (four long cores down to ~ 53m depth) and water sampled over the ESAS from 2007 to 2013. Samples were taken from different areas of the ESAS, which represent different state of subsea permafrost (frozen to thaw) extending from the coastal zone to the outer shelf. The manuscript is clearly written. The approach is valid and the applied techniques are appropriate – I have no questions regarding triple isotope measurements accomplished by the authors in the best European laboratories. I can't completely agree with the authors that the predominant presence of methane is not of thermogenic/natural gas origin, but resultant from microbial methane formation using as primary substrate glacial water and old carbon preserved in the subsea permafrost or below, but I can share the logic of the authors of this ms, which is mostly resultant from limitations possessed by currently available methods of triple-isotope data interpretation.

1)AUTHORS: We thank reviewer 1 for his/her comments. We agree that our triple isotope dataset does not allow us to totally exclude the presence of thermogenic methane in the ESAS sediment. But we state that at the sediment sampling locations, the methane present in the sediment porewater is clearly of biogenic origin and no thermogenic signatures have been observed there.

It is interesting that most of methane in the ESAS sediments is of Pleistocene age or older – in my understanding, this should mean that submarine permafrost is somehow permeable for gases. I am not satisfied with explanations presented by the authors regarding the contribution of super-modern radiocarbon in methane – anthropogenic sources would have been explaining this fact plausibly if it has been methane from the water column, not from the sediment cores. I understand that it must be very complicated to come up with more realistic explanations, but the authors should be working further on it.

2)AUTHORS: As we stated in the main text (lines 267-274) and in more detail in the SI (section 3), ^{14}C levels >200 pmC do not occur in nature and have never been introduced by atmospheric nuclear bomb tests, the most common source of super-modern ^{14}C levels from 100-200 pmC in the environment from the 1950s until today. It should be noted that the unit pmC refers to the $^{14}\text{C}/^{12}\text{C}$ isotopic ratio of a sample related to the ratio of a standard value of the "modern" level. Due to the usage of $^{14}\text{C}/^{12}\text{C}$ isotopic ratios, any geochemical transformation of carbon will keep its pmC value. It should be further noted that for the sediment samples, the

largest enrichment in 14C is observed at 30m depth in the seabed thus sea water cannot be the cause of this enrichment. We believe that the most likely hypothesis to explain this highly enriched 14C values is that nuclear wastes have been deposited somewhere in the permafrost (likely inland) and that leakages from this area are contaminating the groundwater aquifer and thus lateral underground transport may transfer organic matter or gases highly enriched in 14C to the subsea permafrost.

However, we agree that it is very complicated to corroborate our explanations by independent analyses. We have had, together with all co-authors and other specialists in nuclear physics, substantial discussions on alternative approaches. It came out that only data based on other radionuclides could help us to identify more precisely the origin of this enrichment, but such measurements were not possible to perform with the samples we had in hands at the time we found out about this issue. Therefore, a special field campaign to cover a larger area (terrestrial and marine) and aiming to extract much larger volume of sediments would have been required to obtain such data, but we did not have either the funding nor the authorization for such a deployment.

Specifically:

- Why did not authors consider results published by Franke and Cramer (2005) and Bussmann et al., (2013), who presented clearly thermogenic signature of methane sampled in the same area?

3)AUTHORS: *These publications as well as the one of Preuss et al.,2013 will be discussed in the section 3.5.*

-Why did not authors collected gas from bubbles included in the sea ice (reported by Shakhova et al., 2010) to measure triple-isotope signature of methane? Would not it give a kind of integral isotope signature of methane potentially approaching the atmosphere?

4)AUTHORS: *We have tried many times to sample gas from the bubbles (directly in the water and in extracting the gas from the ice on the field), but that is highly complicated (much more than on lakes), because of the harsh conditions on the sea ice in the winter and the lack of stability while working on the ice. We have a system to measure methane isotopes on ice samples in our laboratory (see Sapart et al., AMT, 2011) that has been adapted and used for sea ice samples, but the transport of ice samples from Russia to Europe has never worked.*

-Why did not authors consider release of super-modern methane found further off-shelf (lines 327) by groundwater transported from the land (lines 327-329)?

5)AUTHORS: *This is indeed our main hypothesis (nuclear contamination transported in the groundwater through the thawing permafrost layers to the subsea permafrost and sea water) (see comment 2 for more details). This will be rewritten in a clearer way in the discussion.*

- How would the authors explain enrichment of d13C by <50 per mil if residence time of shelf water is only few months?

6)AUTHORS: *We do not understand to what the 50pmil enrichment refers to, because we do not observe such an enrichment at any of our water sampling locations. Nevertheless, an enrichment in heavy isotopes could be explained:*

- *by removal and/or diffusion processes if it is accompanied by a decrease in concentrations, however diffusive fractionation would be generally very small.*

- *by the adding of methane from a more enriched reservoir if the concentration increase.*
- *by a mixture of both processes.*

Many other questions could be raised, but I realize that this manuscript is based on multi-year work in the harsh Arctic environment. It is clear to me, that one paper, even incorporating that extensive data set, cannot answer all scientific questions regarding the complex, and previously unstudied, Arctic marine methane cycle. I appreciate that the authors have been accumulating data for a long period trying to cover as much aspects of this novel topic as possible. I also understand limitations possessed by current state of isotope biogeochemistry, which make it difficult to interpret isotope data collected in actual environmental conditions where methane of different origin, age, from different sources could be contributing differently in different areas – it differs so much from all idealized conceptions used to interpret the data. I suggest that these questions would be addressed in further work on this topic and the current ms would be taken as a baseline, relative to which results of further investigations in this area could be evaluated. At this point, I recommend that this paper is published as is.

2) SECOND REVIEWER:

Overall:

The paper: “The origin of methane in the East Siberian Shelf unraveled by triple isotopic analysis” reports isotopic data from methane in sediments and seawater. This unique data set comprises methane $\delta^{13}\text{C}$, $\delta^{14}\text{C}$ and $\delta^2\text{D}$ values with concentrations enabling an unusual insight into isotopic shifts between sediments and sea water but also between different sediment cores in this polar region. The data clearly reveal the predominance of biogenic methane. Longterm speculations about thermogenic/natural gas methane sources could not be confirmed. Beside this basic news the most surprising outcome is the fact that methane in sediments of the ESAS shelf is much more depleted in ^{13}C and D than expected when considering the two main pathways of methane formation, i.e. acetate fermentation and CO_2 reduction. Unfortunately the interpretation of this unique data set is biased by just focusing to prove the existence of methane diffusing from larger depths by thawing permafrost to the sediment surface and further through the water column up to the atmosphere. There is no doubt about the existence of carbon sources from Pleistocene age. Old particulate organic matter derived from permafrost soils, ice complexes and coastal erosion and transported by the Lena represents an important contribution to Siberian shelf sediments. Hence the option of a more recent methane formation with old C (terrestrial C?) should be at least also discussed. Pleistocene aged water is argued to be involved in methane formation by CO_2 reduction. While I am able to follow that argument of upward diffusing of Pleistocene aged methane as one possibility, the data are ambiguous and should be discussed in a broader context.

7)AUTHORS: We would like to thank Reviewer 2 for his/her comments. At reading the review, we have realized that the quality of our discussion has suffered from the numerous edits and shortening the paper went through, therefore section 3 will be restructured and a thorough discussion on the different sources of carbon in the ESAS will be added.

Especially as both the $\delta^{13}\text{C}$ and the δD values are clearly out of the range of bacterial methane formation by both pathways, i.e. CO_2 reduction and acetate formation. The samples shown here have either δD values or $\delta^{13}\text{C}$ values untypical for the proposed pathways. The shift in δD values from hotspot cores to the background core is conspicuous. I would appreciate a discussion of this circumstance. Furthermore, the hotspot sediment cores show δD values, which are in a “normal” range for acetate formation, while just the $\delta^{13}\text{C}$ values vary in a broader range. However, this pathway is unable to prove inclusions of old glacial water in methane. In contrast, the background core rather refers to CO_2 reduction as pathway of methane formation but this core is not localized at a “hotspot” position and also not Pleistocene aged. Especially in the context of the hydrogen sources in methane, further non-competitive pathways are worthwhile to be discussed. Summarized, it remains questionable if the isotopic signature of methane (especially the δD values as evidence for the CO_2 reduction pathway) in the sediments is really 1:1 related to the former pathway of methane formation or if there are additional fractionation effects which modify the final signature.

8)AUTHORS: *The main factor causing the difference between the $\delta^{13}\text{C}$ of the background and hotspot cores must be the origin and the state of the carbon substrate. The background core has a clear CO_2 reduction $\delta^{13}\text{C}$ signature, but some methane formed by acetate fermentation could add to the CO_2 -reduced methane pool which would involve the range observed for the hotspot cores. We state that for the background core, methane cannot be formed in situ, because sea water has percolated all the way down the core. This means that:*

- 1) sulfate is present all along the core and will inhibit acetate fermentation at the depth where the core was drilled.*
- 2) seawater would be the substrate for methane in the case it is produced by carbonate reduction in situ. But that is not the case as shown by the δD data of the background core.*

For the hotspot cores, because of harsh conditions in the field, we could not obtain very good salinity profiles, so it remains unclear how deep exactly the seawater has mixed with meltwater from buried meteoric ice. There, we might have a mixture of acetate fermentation and carbonate reduction using old carbon as substrate as shown by the $\delta^{14}\text{C}_{\text{CH}_4}$ results. However, if we had a mixture of CO_2 reduced methane (using as substrate present mean ocean water) and methane formed by acetate fermentation, our sediment data point (the diamonds) should be between the dotted lines on Fig.3. This is not the case, because δD is about -130‰ more depleted in heavy isotopes. The only way for methane to have such depleted deuterium signatures is to use a substrate (water in the case of CO_2 reduction) very depleted in deuterium. To our knowledge, meltwater from buried meteoric ice is then the only possible substrate sufficiently depleted in deuterium to explain the δD data we obtained for both background and hotspot cores.

We have done investigations on the role of diffusive transport on the fractionation, and the few data we have found show that the fractionation involved was small in with the signal we measured for both stable isotope signatures (Fuex, 1979, Prinzhofer and Pernaton, 1997, Chanton et al. 2005)

Concerning the sea water data, the main result is to see the decoupling between sediments and water above. Without any information on the bathymetric regime any

interpretation remains speculative.

9)AUTHORS: The table below with detailed information on each drilling site will be added to the revised manuscript.

Borehole/s shelf area of sampling	Latitude	Longitude	Water depth, m	Water temperature surface/ bottom	Water salinity surface/ bottom	Time since inundation	Distance from the shore, km
ID-11	71,6926	130,3669	12.5	-0.52/-0.92	10.8/19.4	~8÷7 kyr BP	18.6 km from Muo- stakh Isl and 39.8 km from Bykovsky Peninsula
IID-13	71,6288	129,8534	2.5	-0.41/-0.61	12.8/13.2	~7÷6 kyr BP	2.5 km
IID-13	71,6219	129,8517	4.1	-0.40/-0.61	12.8/13.2	~7÷6 kyr BP	2.5 km
VD-13	71,7449	129,4048	3.6	-1.01/-1.03	22.6/22.6	Lagoon, ~7÷6 kyr BP (Romanovsky et al., 1999)	Lagoon adjacent to the coast
Lena Delta Str. 42* 47* 70** 71**	72,977 72,427 72.687 72.683	130,141 130,151 130.640 130.267	12.5 8.5 20 12	3.74/1.42 4.42/2.53 2.40/2.83 1.02/2.47	16.3/22.3 0.5/4.6 19.0/21.5 9.0/19.1	~7÷6 kyr BP	-
Dmitry Laptev Str. 31* 36* 79** 80** 81** 82** 83** 84** 85**	72,882 73,118 73.030 73.169 73.316 73.297 73.104 72.930 72.886	140,620 139,517 139.393 139.574 139.768 140.085 140.352 140.619 140.643	15.5 13.5 15.0 15 9 11 14 12 24	3.38/3.76 3.30/3.44 1.92/3.04 1.67/2.42 1.85/1.79 1.6/1.46 1.75/2.19 1.77/1.77 1.69/1.77	18.7/20.3 19.8/24.0 19.8/23.3 19.3/26.7 18.6/24.8 24.17/26.4 20.3/26.5 21.1/21.1 20.8/20.9	~8÷7 kyr BP	-
Buor- Khaya Gulf	Drilling sites					~8÷7 kyr BP	-
Shelf edge Sts. 9* 13* 28** 32** 36** 37**	76,897 76,894 77.000 77.029 76.398 76.648	127,8047 127,8032 125.985 127.289 125.051 125.048	62 63 91 74 62 70	3.54/-1.33 3.47/-1.40 3.87/-0.82 3.00/-1.21 1.26/-1.17 1.89/-1.19	28.0/33.4 29.1/33.3 28.8/34.4 21.9/34.2 19.0/34.1 17.3/34.2	~15÷13 kyr BP	-

Although I completely agree that this data set raises much more new questions than it is able to answer, a careful interpretation of this data set would improve the quality of the discussion.

Finally, it would be worthwhile to revise the conclusions and those should be based on the data rather than on speculations which remain to be proven at this stage. I recommend major revisions.

Details:

Abstract

Line 30-37 is an introduction only remotely related to the data discussed here

Line 49-53 this assumption is not proved by the data shown here

10)AUTHORS: The abstract has been rewritten as follows:

“The Arctic Ocean, especially the East Siberian Arctic Shelf (ESAS) has been proposed as a significant source of methane that might play an increasingly important role in the future. However, the underlying processes of formation, removal and transport associated with such emissions are to date strongly debated.

CH₄ concentration and triple isotope composition were analyzed on gas extracted from sediment and water sampled at numerous locations on the shallow ESAS from 2007 to 2013. We find high concentrations (up to 500μM) of CH₄ in the pore water of the partially thawed subsea permafrost of this region. For all sediment cores, both hydrogen and carbon isotope data reveal the predominant occurrence of CH₄ that is not of thermogenic/natural gas origin as it has long been thought, but resultant from microbial CH₄ formation. At some locations meltwater from buried meteoric ice and/or old organic matter preserved in the subsea permafrost were used as substrates. Radiocarbon data demonstrate that the CH₄ present in the ESAS sediment is of Pleistocene age or older, but a small contribution of highly ¹⁴C-enriched CH₄, from unknown origin, prohibits precise age determination for one sediment core and in the water column. Our sediment data suggest that at locations where bubble plumes have been observed, CH₄ can escape anaerobic oxidation in the surface sediment.“

Introduction

In general a short introduction in using delta13C and deltaD values is needed.

Processes which might modify the signature additionally to pathways of formation are completely missing and should be included.

11)AUTHORS: We have added the paragraph below: “Each type of CH₄ formation/removal pathway produces CH₄ with a characteristic isotopic signature (δ¹³C and δD) depending on the isotopic composition of the substrate and the isotopic fractionation associated with the respective chemical reaction involved. Microbes take up more easily lighter isotopologues hence CH₄ produced by methanogenesis has a lighter isotopic signature than its substrates but when it is consumed, its remaining reservoir will become isotopically more enriched in heavy isotopes (e.g. Whiticar 1999, Conrad, 2005). Similarly, diffusive transport can cause isotopic discrimination because lighter isotopologues diffuse faster than heavier ones. However, this fractionation is considered to be relatively small (<5‰: Fuex, 1979, <20‰: Prinzhofer and Pernaton, 1997 and 3‰: Chanton et al. 2005) in comparison with the isotopic fractionation associated with methanogenesis (7-95‰ for δ¹³C and 260-430‰ for δD) and with CH₄ oxidation (2-39‰ for δ¹³C and 66-350‰ for δD) (Whiticar, 1999, Holler et al., 2009)”

Line 65- concerning the remobilization of carbon from the Pleistocene: terrestrial carbon transported by the Lena River into the shelf sediments should also be mentioned, see: Winterfeld et. al., 2015 Biogeoscience).

12)AUTHORS:*This sentence has been modified as follows: “The four suggested key mechanisms controlling the release of Pleistocene carbon to the ESAS are gas hydrate degradation, the deepening of the permafrost level, coastal erosion and riverine (e.g. Shakhova et al., 2005, 2009, 2010a,b, O’Connor et al., 2010, Winterfeld et al., 2015, James et al., 2016).”*

Line 78 Further pathways for methanogenesis should be at least mentioned (methylotrophic with non-competitive substrates- see also Whiticar et al, 1999).

13)AUTHORS:*This has been added.*

Line 91-96 The “Whiticar scheme” considering the relationship between the isotopic composition and pathway of methane formation has been developed for sediments. Using this scheme for sea water data should include at least a discussion about further fractionation effects in order to avoid over-interpretation of data. For example: Methane diffusion through sediments might induce fractionation effects just described by Prinzhofer and Pernaton 1997.

14)AUTHORS:*This has been added as discussed in comment 11).*

Further, there is no proof that the isotopic signature of methane dissolved in sea water (outside a plume) can be used in a simple way for source identification of methane formation in sediments or from gas fields.

15)AUTHORS: *We did not do such a claim in our ms and we do not believe that sea water can be used in a simple way for source identification, because as written in the ms (l.372-380), in shallow areas, the gas bubbles from the sediment do not have time to equilibrate totally with the gas dissolved in the seawater hence, our water measurement represent a mixture of what is coming from the sediment and from potential other sources (riverine and aerobic formation in the surface water). As explained in the ms (l. 336-350), aerobic surface production is unlikely, however, we will add a paragraph about the potential input of riverine methane in discussing our data together with the data of Preuss et al., 2013, Bussmann et al., 2013 and Franke and Cramer, 2005.*

Line 97-122 gives a detailed description about potential methane source at the ESAS, however, that paragraph about potential gas hydrates and gas bubbles in that region does not introduce the topic of the paper and is not a helpful tool to understand the isotopic data shown here. Further, this paragraph is misleading as the data shown in the paper are not in that range to push forward the knowledge about the role of gas hydrates and gas bubbles and are not needed to introduce the paper.

Line 115 this citation is wrong in that context. Measured concentrations should be related to the atmospheric equilibrium concentration in ESAS. I recommend adding supplement information into the introduction (physical factors) as this contribution is essential for understanding and interpretation of this data set.

16)AUTHORS: *L 97-122 are removed and replaced by a corrected section (physical factors) of the SI.*

Methods

Line 173 the term “largest samples” is misleading and should be improved.

17)AUTHORS: *largest samples refers to sample with at least 20micrograms of methane. That will be added.*

Results and Discussion

For my knowledge these is the first data set of methane isotopic signatures in frozen sediments hence potential freezing effects on isotopic fractionation should at least be taken into account.

Line 213-215 how differences in lithology influence differences in the isotopic signature should be discussed in the main text.

18)AUTHORS: *To our knowledge, no data exist on the role of the lithology on the physical fractionation of gases therefore a discussion on this matter would be speculative. The meaning of this sentence (l.213-215) is that according to the type of lithology (hence of sediment) different types (or amount) of substrates could be available at the different location. This sentence will be rephrased.*

Line 219-222 most of the isotopic signatures of the deep sediment cores are not included in the range of CO₂ reduction or acetate formation. Potential reasons should be discussed.

Line 223and Figs 3 and 4: yes, methane is unusually depleted in $\delta^{13}\text{C}$ and δD . The samples shown here have either δD values or $\delta^{13}\text{C}$ values untypical for the proposed pathways. More in detail: for acetate formation the $\delta^{13}\text{C}$ values are untypical while the δD are in a “normal”range. However, this pathway is unable to prove the inclusion of old glacial water. But these cores are from the “hotspot stations” and show a Pleistocene age. In contrast, the background core rather refers to CO₂ reduction as pathway of methane formation but this core is not at a “hotspot” location.

19)AUTHORS: *This section will be reworked. See comment 8).*

Line 253- 259 when methane is formed by acetate fermentation the whole methyl group is used to produce methane, which means that at least 3 of the 4 hydrogens are formerly fixed in organic matter and not in water.

20)AUTHORS: *We state that methane is likely formed by CO₂ reduction using meltwater from buried meteoric ice or (and) by acetate fermentation, but we do not imply that meltwater from buried meteoric ice is used in acetate fermentation.*

Line 263 high concentration in frozen sediments just show that methane is available.

21)AUTHORS: *This sentence will be rephrased as follows: “High CH₄ concentrations are also observed in frozen sediment showing the presence of CH₄ in the permafrost layers.”*

Line 310 $\delta^{14}\text{C}$ values show old carbon, not clear that it is old methane.

22)AUTHORS: *The $\delta^{14}\text{C}$ values presented here are $\delta^{14}\text{C}$ -CH₄ data. It shows that methane is formed on old substrate and that is what we mean by old methane. This will added to the revised version.*

Line 331 Additional to oxidation, the isotopic signature of methane in seawater is influenced by mixing and dilution. The combination of all these processes will modify the isotopic signature. Assumptions about potential sources for thermogenic methane can neither be confirmed nor neglected. This assumption is not possible by using just this dataset.

23)AUTHORS: *We agree with this comment and we have been careful not drawing clear conclusions on the presence of thermogenic methane. In l.335, we write: Thermogenic emissions are possible,but we have not measured it at our sediment sites”*

Conclusions

Based on the discrepancies between the data and the biased interpretations the conclusions are not on a scientifically based fundament.

Line 385 this assumption is just one possibility

Line 391 this conclusion is not related to the data as this paper gives no data about gas bubbles.

Line 405-410 the data shown in this paper shows neither the emission of large amounts of methane nor the role of submarine thawing permafrost for methane release to the atmosphere.

24)AUTHORS: *the conclusion has been rewritten in focusing on the key results according to the suggestions of some of the reviewers. The conclusion is now written as follows: “Our triple isotope dataset of CH₄ from the sediment and water of the shallow ESAS reveals the presence of CH₄ of microbial origin formed on old carbon with unexpectedly low stable carbon ($\delta^{13}\text{C}$ as low as -108‰) and hydrogen (δD as low as -350‰) isotope signatures down to about 50m under the seabed in the thawed permafrost. These data demonstrate that at location where a thick marine clay layer is present, this CH₄ is partially oxidized before reaching the seawater. However at locations where ebullition was observed from the seabed, no oxidation was identified in the stable isotope surface sediment profile. In that case and considering the very shallow water column (<10m) in this area, this microbial gas will likely reach the atmosphere when sea ice is absent. Our results show that thawing subsea permafrost of the ESAS emits CH₄ with an isotopic signature that cannot be easily distinguished from Arctic wetland emissions when looking only at stable isotope data. This similarity might complicate recent efforts to quantify Arctic CH₄ source strengths on the basis of isotopic- and back-trajectory analysis of atmospheric CH₄. Further *in situ* work is necessary – specifically on the isotopic composition of CH₄ in gas bubbles that reach the atmosphere – to better quantify the contribution of the ESAS to the global methane budget.”*

Table 1 where in the text is this table discussed/mentioned?

25)AUTHORS: *As required by P. Crill in his short comment, Fig. 4 has been replaced by a concentration/isotope plot, therefore this table is not used anymore and is therefore removed.*

When discussed this table should include the fractionation factor epsilon for this data set.

3) SHORT COMMENT BY PATRICK CRILL:

The paper makes a very important point about the limitations of the isotope data to resolve sources. It should eventually be published but major revisions are required.

It is really difficult to extract the point of indistinguishable but biogenic sources. The paper looks like it has been reworked for different journals with additions and subtractions making for a confusing mix of irrelevant obfuscation and discussion. The Supplement could be removed though Figs S1 and S3 contribute to the narrative and could be added to the main text.

It should be noted by the editor that I have active projects with some of the co-authors, one of whom is a current graduate student in my laboratory.

Some general comments:

More information about the individual cores themselves would be very useful. What was the overlying water depth? How far from shore were they? How long ago is it estimated that they were flooded? It is very confusing throughout the paper with what samples are from frozen sediments and what are not.

26)AUTHORS: A table (see comment 9) has been added with all the information required for each core and that will be discussed in the section 2.1.

The paper needs to be rewritten in a consistent and organized way. There are a number of irrelevant references. The ms is littered with irrelevant and unbalanced (in the sense of number) references while a range of recent references is not considered. The use of irrelevant and multiple in-house references are not useful.

The use of single and double quotation marks is inconsistent, baffling and distracting.

Quotes should only be used for direct attribution.

27)AUTHORS: The abstract (see comment 10), part of the introduction, section 3.2 and 3.5 as well as the conclusion (see comment 24) have been rewritten and restructured according to the suggestions of the referees.

I offer specific comments below to improve the presentation. Hope it helps.

Some particular comments:

Abstract does not express the point of the ms. The first paragraph seems out of place.

I. 35: It is unclear as to what "Large scale CH₄ super saturation" refers. And it should be noted that "super saturation" is in reference to atmospheric values. I note this because it could be confused because the paper is about sediments (where bubbles are formed only after saturation with a pure CH₄ atmosphere).

I. 49: This is likely to be a problem for its use as a background metric given that the contaminated core is the core to which the others are compared.

II. 51-53: This probably should be the third sentence of the first paragraph and, at the same time, this is not a conclusion this is a motivation for the research. It's more like "might be true".

28)AUTHORS: The abstract has been rewritten (see comment 10) and the four comments above have been taken into account.

I. 67: Are all the processes mentioned not releasing subsea Pleistocene carbon?

29)AUTHORS: Yes as it is written in the ms, the four processes mentioned are allowing the remobilization of subsea Pleistocene carbon.

II.67-69: Did not know that thermokarst formation (talik deepening maybe) and active layer deepening affects subsea emissions. The active layer is a seasonal

feature. Are you saying that there is a seasonal freeze-thaw cycle in subsea sediments?

30)AUTHORS: This sentence has been corrected and rewritten (see comment 12).

l. 78: change “and” to “or”

31)AUTHORS: this has been corrected.

l. 86: Methane oxidation is not restricted to surface sediments especially AOM. This can occur to significant depths depending upon the OM content, porosity and the availability of CH₄ and SO₄.

32)AUTHORS: the word “surface” has been removed.

l. 90: More correctly perhaps, “It is surmised that...” As written, it confuses assumptions with observations.

33)AUTHORS: The fact that each type of biological or chemical reactions to produce methane (or other trace gases) is associated to characteristic isotopic fractionation factors is not an assumption, but something that is well established. Therefore, we do not believe that it is appropriate to write “It is surmised that...” in that context.

ll. 97-122. It seems that there is a lot of irrelevant speculation here. Is the purpose of this ms to test if there are reservoirs of CH₄ in the ESAS that are at risk of thawing? It seems that the observations of relatively high CH₄ concentrations are a reason for looking into the isotopes to see if different sources can be defined.

l. 98. It might help if a calculation based on temperature and pressure can be presented for the depth where hydrates can be expected to form on the shelf and slope.

l. 102: Recent papers by Stranne and Archer might be considered here..

l. 108: The reasons for the recent warming are unclear (probably Atlantic water intrusion) and are they relevant to this discussion? The issue is the rate of deepening of permafrost thaw which is an ongoing process since the area was originally flooded rather than hydrate decomposition. Temperature data from the boreholes would be useful. Is citation of a 30 year old paper sufficiently recent? Also there are more recent assessments of hydrates in the Arctic Ocean, eg Ruppell 2014 and references therein.

l. 109: I do not understand. It is first claimed that it is extensive and now you're saying it is largely degraded?

l.117: Good to note this. It should also be noted in the abstract.

l. 120: I thought this paper was about origins of sedimentary CH₄. Though they might provide a rationale for examining the isotopes, these air/sea flux references are irrelevant. No connection is made between the signatures of the CH₄ dissolved in porewater and water with atmospheric values.

ll. 120-121: "high concentration" of what? High concentration of plumes? I do not remember seeing any bubble, porewater or water column concentration data specifically in the plumes in these papers. It's good enough to say that coring was done in a region with a high frequency of observed plumes. This implies that the coring was done directly in a sediment supplying a plume.

l. 122: Could be true. Cannot tell if sediment source refers to diffusive flux across the sediment/water boundary or from CH₄-rich bubble plumes that originate

deeper in the sediments traversing the water column. This implies a diffusion-limited source from the surface sediments and is highly inconsistent with the vigorous mixing throughout the water column depth posited in the papers referenced at the beginning of this sentence.

34)AUTHORS: *Considering the comments above and the suggestions of the second reviewers, this paragraph (l.97-122) has been removed.*

l. 145: “straight after” How soon after drilling? How long is “immediately”?

35)AUTHORS: *Straight after and immediately mean here a few minutes. This has been corrected in the revised ms.*

ll.153-155: I am confused with the description. All these different detectors and columns were used on one g.c. while analyzing every sample? What was the precision? These different detectors will have very different response curves. What standards were used?

36)AUTHORS: *The GC method we have used is very commonly used, therefore we did not add details in the ms about it. Here is a more detailed paragraph which could be added in the Supplementary Information if requested: “ The GC used to measure CH₄ concentrations has two 10-Port Gas Sampling Valves, 2 meter MoleSeive 13X column, 30 m capillary column and 6 channel PeakSimple usb data system and was equipped with a flame ionization detector (FID), which was used for concentrations of CH₄ <200 ppmv, and a thermal Conductivity Detector (TCD), which was used for concentrations of CH₄ >200 ppm. The GC oven was operated isothermally (40°C) and the maximum detector temperature was held at ≈250°C. The carrier gas used was helium. Daily calibration was performed with a certified 1.96 ppmv and 99.999 ppmv CH₄ gas standard with the air (Air Liquide, USA). The standard deviation of duplicate analyses (three to five replicates) was <2%. Reproducibility was ~1% based on multiple standard injections during daily calibrations. The standard deviation of duplicate analyses (3-5 replicates) was less than 2%. GC precision had standard error of only 1%. The concentration of dissolved CH₄ in the water and sediment samples was calculated with the Bunsen solubility coefficient for CH₄ [Wiesenburg and Guinasso, 1979] for the appropriate equilibration temperature, pressure and the volume of headspace and water/sediment in the bottles. “*

Probably generalize here and provide careful DETAILS in the supplement.

l. 162: What does this add?

As it's presented it is a calculated estimate based on the total bulk density which would be sufficient. This might be important if you were trying to model variations in diffusion coefficients x tortuosity of the sediments or even try to identify regions that might be more amenable to advective flux but this is the only place it is mentioned.

37)AUTHORS: *This sentence has been removed from the ms.*

l. 173: Largest? In what sense? Concentration? Volume? Why not just give the mass of C required for each analysis and/or what cut off you used.

38)AUTHORS: *The sample containing more than 20micrograms of CH₄. This has been added as follows: “Radiocarbon analyses could be performed only on the largest samples (containing more than 20micrograms of CH₄)”*

l. 184: There seems to be a logic error here, how do you "expand" something into a smaller volume?

39)AUTHORS: Here we meant that part of the sample was transferred "by expansion" from the burette to a smaller volume. The word "expanded has been replaced by transferred" in the revised ms.

l. 187: Not separating the Results and Discussion makes the information hard to find and the explanations very much harder to follow.

40)AUTHORS: We have done several attempts to write the results and the discussion separately, but that had obliged us to make a lot of repetitions. Therefore, we have done the choice to write one section Results and discussions and we believe that it is the most appropriate manner to present our data. However, we have worked on the structure of section 3 to discuss each point in a more structured and thorough way.

l. 191: So you're comparing four cores taken off of Tiksi with water samples that are taken 100's of km away in different water column depths and different marine environments with no physical oceanographic data to demonstrate that these environments are connected. A word or two more here would help understand the rationalization.

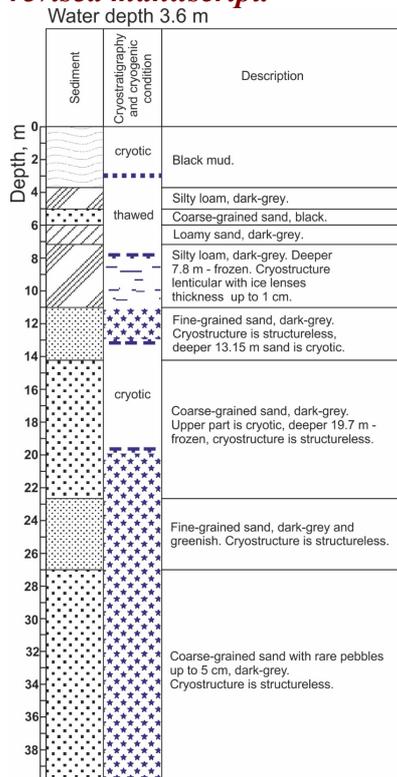
41)AUTHORS: These different entities belong to the same shelf system, which begins from the near-shore (where we drilled) and extends to the shelf edge (where we sampled water), but please note that most of our water samples were taken close to the coast where we also sampled surface sediment (see Fig.2) This entire shelf was exposed above the sea level during the last glacial period, froze to the depth of few hundred meters and was believed to been keeping its integrity until recent times. So the most quintessential, fundamental part of this marine ecosystem, which builds up the unity of this environment, is subsea permafrost, which is underlying seafloor - a unique component of this marine environment. Investigating different parts of the shelf is crucially important because current state of subsea permafrost depends on duration of inundation and this duration varies from <1000 years in the near-shore zone to >10 000 years in the outer shelf and the shelf edge. The ideal approach would be to sample water and recover long sediment cores in each of observed settings. The problem is that drilling at greater water depths requires incomparably greater funding than what scientists usually can obtain from scientific funding agencies. Moreover, the very harsh conditions during the winter (when the deeper cores were drilled) did not allow us to reach the shelf edge. Therefore, we present the existing data, which are the results of many years of fieldwork in this region as a first attempt to better understand the origin of the methane in the coastal ESAS.

l. 198: It is not clear as to why is this a background site? Especially given how contaminated the core is. So it is a "non-ebullition" site, or a "non-bubbling" site. It is certainly not background for ^{14}C .

42)AUTHORS: We named the site where no ebullition was observed a background site, before the ^{14}C enrichment was observed and we have kept this denomination. However, to help the reader to grasp the main difference, we changed this denomination to "non-ebullition site" in the revised version.

l. 200: "IID-13, IIID-13 and VD-13 cores were thawed down to 19, 17 and 12m, respectively." It is not clear how the thaw front is defined (ice-bound permafrost?). Also, the thaw depth of core IIID-13 is not displayed in Figure S1.

43)AUTHORS: A more detailed scheme for each core (as shown below as example) is added to replace Fig. S1 and this scheme are discussed in section 3.1 of the revised manuscript.



L 206: There is no section 3.1.

44)AUTHORS: this has been corrected in the revised ms.

l. 206: Why “deep” here and not “surface” in the subsequent section. Use quotes only for direct attribution.

45)AUTHORS: This has been corrected in the revised ms.

l. 216: Why 4 references here and none elsewhere for this list. And are not these specific refs more about terrestrial OM transport rather than sedimentary microbial biogeochemistry?

46)AUTHORS: We wrote that differences in isotope composition of our samples could be dependent on a variety of factors, among which one factor (the heterogeneity in substrate availability), for which we provided four citations. It appears that this first point has been more investigated in this study area than the three others and that is why more references are added there.

l. 225: “salinity measurements” Seawater in all the sediment cores below the permafrost boundary? How can they be halfway frozen? Salinity data for all cores should be shown to support this claim would be helpful.

47)AUTHORS: We have corrected this sentence as follows: “However, salinity measurements along the ID-2011 core indicate the presence of interstitial seawater all the way down the core.” And this section is rewritten as discussed in comment 8. The conditions on the field and the funding availability for the 2013 campaign (when the hotspot cores were drilled) were very different to the 2011 campaign (when the “background core” was drilled). In 2013, the weather conditions did not allow for much safe time on the ice, which prevented us to perform good quality salinity measurements and sampling for other biogeochemical species when the core was extracted. However, considering that no other study has yet been published on this area showing more than one isotopic signature of methane in one

sediment core, we believe that our dataset brings substantial information to allow for a better understanding of the origin of methane in different sectors of the ESAS.

l. 228: Why aren't the sulfate (and other chemical) data for any but the contaminated core presented? Also some indication of the frozen depth in the other cores should be presented in Fig. 2.

48)AUTHORS: Please see comment 43 and 47.

l. 231 and throughout: in situ is simply italicized – not hyphenated nor placed in quotes.

49)AUTHORS: This has been corrected in the revised ms.

l. 232: Suppressed? It is possible given the potential presence of SO₄ (though no data are given) but no evidence is presented for active inhibition which is what is implied. There is actually not so much OM. And given the references noted above (but not here), they would imply that the available OM will be heavily degraded terrestrial material and so it is not surprising that acetoclastic methanogenesis could be substrate limited – though SO₄ inhibition is more likely. The presence of SO₄ and AOM will also have implications for the stable isotope signatures.

50)AUTHORS: As discussed in comment 8, this part is rewritten and the role of acetate fermentation and the difference in substrate availability is discussed further.

l.241: Which sampling location? And how does the CH₄ migrate? It could be argued from the very light del-D values and the age of the CH₄ C that the CH₄ is produced in place if it is hydrogenotrophic soon after thaw in the presence of freshwater and then does not migrate very fast at all. Migration pathways are an important part of the deepproduction hypothesis, and a short discussion could be extracted from the SI and incorporated here in the main text.

51)AUTHORS: In the revised manuscript, this sections has been rewritten in discussing more in detailed the different hypotheses (transport and formation) that could involve a depletion in dD.

l. 247: Another overlooked reference, Koch et al. 2008 reports distributions of methanogenic communities in subsea permafrost that might support the hypothesis of in situ production in partially thawed cores. This indicates that the CH₄ might not have to be from migration through ice.

52)AUTHORS: Koch et al, 2008 have showed the presence of methanogenic communities in the subsea permafrost and they indeed claim that permafrost thaw ignites methanogenesis in sediments. This supports our interpretation, but contradicts the claims of Overduin et al., that methanogenesis does not occur in thawed sediments but rather oxidation does. We will add a paragraph of discussion about in the revised ms.

l. 250: What is the del-D of the frozen porewaters?

53)AUTHORS: We do not have such measurements, however we believe that it is appropriate to assume that the dD data of permafrost meltwater measured by e.g. Brosius et al., 2012 in North Siberia is of the same range as the dD of the meltwater of the ESAS subsea permafrost, because the latitude difference between the study locations is small and these regions have been exposed to relatively similar conditions during the last glacial period.

l. 254: The very light ¹³C values could be due to AOM recycling which could drive the ¹³C signatures much lighter. This is the most common explanation for

very light marine CH₄. E.g. Geprägs et al. 2016 has a nice explanatory figure. CO₂ reduction of substrate from recent OM only gets us down to -80 or so.

54)AUTHORS: *Thank you for the suggestion, this reference as well as a short discussion about it has been added to section 3.1. of the revised ms.*

l. 261: What high concentrations? These values look like permafrost values everywhere (actually a bit low) going back to Kvenvolden.

There is no need to invoke a very highly and more improbable migration through ice. And the low del-D as well are consistent with in situ production that hasn't moved much. By the way, it is very difficult to see where the frozen sediment values are in Fig 2 which is relevant.

55)AUTHORS: *To our knowledge, Kvenvolden et al has never reported methane concentrations in the frozen sediment, so we do not believe that our data can be compare to this work. dD-CH₄ data cannot be interpreted alone and at looking at both stable isotope signatures, especially for the core ID-2011 where we have a clear CO₂ reduction d13C signature and where sea water is present along the whole core, the dD data show that it not possible that methane was formed there using sea water as substrate. Our data cannot give information on how deep it was formed, but it was not formed at the depth where the core was drilled. This section 3.2. has been totally rewritten and this issue is discussed further in the revised ms.*

l. 266: Just curious but where was the sea level then? I have seen values of 55 m or so lower 15000 years ago. Or is this material transported in?

56)AUTHORS: *To our knowledge, such information are not precisely known, but our sediment sampling locations where in the state of terrestrial permafrost during the Pleistocene period.*

l. 269: A reference to Fig 2 would fit here nicely.

57)AUTHORS: *This has been added to the revised ms.*

l. 275: I think you are right. It's the only explanation. You pushed some surface contamination down core. I think this is a serious problem with calling this core "background" There is very little that you can compare with this.

58)AUTHORS: *We are convinced that this ¹⁴C enrichment is not coming from the water or sediment surface, because the largest enrichment is at about 30m depth in the sediment (Fig.2d) and at this site, there is a thick marine clay layer that would not facilitate downward migration. This situation also clearly excludes the possibility of a contamination of the samples during coring, which would have caused a trend of decreasing pmC values with increasing sediment depths, whereas we observed exactly the opposite trend (Fig. 2d). See additional explanations on the definition of the unit pmC and its relevance for the interpretation of the location of the contamination origin in comment 2.*

portion of their core. However, as this last sentence is written, it misrepresents what the Overduin paper is saying that the CH₄ is removed by oxidation with sulfate at the surface sediment. This is deceptive, because nearly 100% of the CH₄ loss in the Overduin et al core happens at the thaw front where SO₄ intrusion is keeping up with the thaw boundary.

59)AUTHORS: *This has been corrected in the revised manuscript.*

l. 300: The figure shows reflectors that could be ice not necessarily free gas. It's ok (and better) to express the ambiguity. Anyway, Figs. S1 and S3 should be incorporated into the main text.

60)AUTHORS: *The difference between gas and ice is indeed difficult to identify with such acoustic techniques. However, in our case, the entire sediment core (ID-2011) recovered from the borehole was thawed to the depth of 52 m as seen from*

Fig. S1(the left-most core). Therefore, the acoustic anomaly observed in the seismic image could not be ice.

l. 301: relatively impermeable? is that like relatively dead? Better to use "relatively less permeable"

61)AUTHORS: This has been corrected in the revised ms.

l. 302: I don't understand this. Are you saying this is why there are specific plume sites? Is there evidence of free gas pressures or changes in horizontal advective/diffusive mechanisms driving the gas loss? I can imagine it but would the fine grained pelite lithologies allow this?

62)AUTHORS: Here we state that gas is accumulating under the thick marine clay layer as shown by our acoustic and methane concentration data and we assume that part of it must migrate horizontally and could potentially be released from the sediment to the water at locations where the marine clay layer is thinner or absent. This is rephrased in the revised manuscript.

l. 306: Possible but not sure it is likely. Why are the surface seds laminated? or demonstrate distinct lithologies (Fig S1)? Wouldn't that (especially the fine grained) be disrupted by vigorous advective flux.

63)AUTHORS: We write that ebullition may disturb the surface layers (that would explain our sediment surface stable isotope data, but the processes involved there are not yet understood. Vigorous advection may also play a role and that will be added in the revised version.

l.312: There are no sediment age data shown - only CH4 data.

64)AUTHORS: This has been corrected in the revised ms.

l. 328: The reasons for comparing water samples and trying to link them to cores taken 100's of km away is not articulated well.

65)AUTHORS: Section 3.5 has been totally rewritten and restructured in order to discuss more thoroughly the different types of methane sources possible in the ESAS coastal water and in adding more references as discussed in comment 15.

l. 336: What is meant by "deep Earth layers"?

66)AUTHORS: Here we mean the Earth's crust. That has been corrected in the revised ms.

l. 338: again with the distracting quotes. Who or what are you citing here?

And the pycnocline, and the well-known low rates of methanogenesis within it has been observed for decades, however it is not usually found at the bottom.

67)AUTHORS: The quotation mark has been removed in the revised manuscript

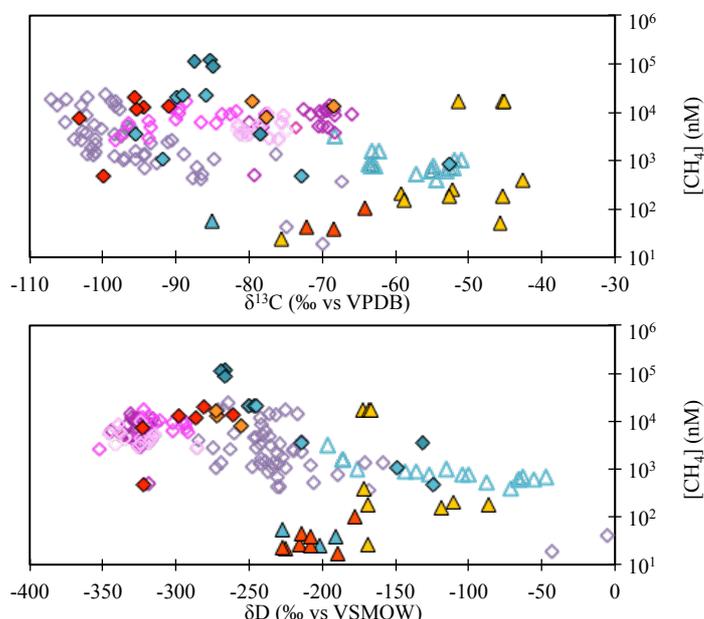
l. 344: 40 cm!! Everywhere on the ESAS? This is simply wrong. Should be removed There are so many things wrong with this statement. It might be true locally for very short periods (spring runoff?) but it cannot be true over the entire ESAS. You can find videos on line and satellite data as well if you need demonstration. Even the Amazon with some of the highest TSS loads in the world, the light penetrates to close to a meter.

It would also imply an extremely large deposition rate to the sediments – not seen. It would also imply a huge role for Fe cycling in OM degradation – not seen.

68)AUTHORS: Here, we discuss about the shallow coastal area where most of our water samples were sampled. This has been rephrased as follows: "In the near-shore ESAS (depth <30 m, about 75% of the total area), where most of our water samples were collected, the pycnocline is very shallow and a very low primary production is expected...." (see also comment 99).

L 351: A concentration vs isotope plot could be very helpful in supporting claims about oxidation.

69)AUTHORS: *A concentration vs isotope plot (see below) has been added to replace Fig. 4 and is discussed in the revised version of section 3.5 methane in the water.*



ll. 352-353: The isotopic values (as well as they can be seen in Fig2) in the cores are not really shifted that much.

In the under ice water column samples there does not appear to be a gradient between the deep samples and the near-surface samples, i.e. it's hard to see a "substantial" oxidation signal.

One could even argue that the very light values in the sediments is more of a signal of AOM due to C recycling (e.g. Geprägs et al. 2016).

70)AUTHORS: *This sentence is removed from the revised ms and the potential role of AOM is discussed further in the revised 3.5 section.*

l. 358: No sense in having both Figs 3 and 4. Both are too busy anyway and could do with some simplification.

71)AUTHORS: *Fig. 4 is replaced by a concentration vs isotope plot (see comment 69).*

l. 362: Did I miss a plot of concentration vs signature?

I do not understand this argument for a number of reasons. It seems the assumption is that the same processes are acting at similar rates on the water, frozen sediments and thawed sediment samples. We know that's not the case (AOM for instance). If one looks at the water samples alone, they seem to follow a nice oxidation trend.

72)AUTHORS: *The concentration vs isotope plot (see comment 69) shows that most of the water samples do not show a nice oxidation trend. This is discussed in the revised version of section 3.5.*

l. 387: This is an assumption and perhaps maybe likely but No information is given on gas hydrate or gas distribution in the cored areas.

ll. 388-389: This is an odd statement because migration of the gas is not "shown." Rather, an almost plausible interpretation of the data along those lines could be made.

ll. 393-394: I agree but you cite a number of papers where such “quantitative” estimates are made. So again, please check the relevance of your references and trim those that are not needed.

ll. 404-405: This is not consistent with the statement made in line 394. And a prediction of large amounts of CH₄ from thawing does not follow from any of the data presented in this paper.

73)AUTHORS: *The conclusion has been rewritten (see comment 24) in order to focus on the main message of the paper and to answer to the 4 comments above and to the suggestions of other reviewers.*

Table 1: Not really used in the paper. Why are values in the table expressed as fractionation factors rather than delta ratios as used everywhere in the text?

74)AUTHORS: *Table 1 was used to give the range of fractionation factor for Fig.4. This figure has been removed from the revised ms, hence table 1 is removed as well.*

Fig.2: Is very busy and the depth scales are confusing. I understand the challenge of trying to convey so much information on a given figure but it should be clear.

I especially miss noting the frozen depths, temperatures and chemistry (especially SO₄). And the 14C of the OM.

75)AUTHORS: *We have done many attempts to produce a clear figure to show all our data at once, and this figure came out as the best possible figure we could obtain. As noted in comment 47, we do not have the all set of biogeochemical and physical data for each core, but we have shown everything we had available and that was relevant for the interpretation of our data in Fig.2 and in Fig.5. We do not believe that combining these two figures would make any improvement on the readability of the figure.*

Figs 3 and 4: It is difficult to resolve the diamond and square shapes. Why do you even have the square shapes when I cannot find them discussed in the text.

76)AUTHORS: *The square shapes are a mistake and are removed in the revised ms.*

Probably do not need both figures. Maybe replace Fig. 4 with a concentration vs isotope plot.

77)AUTHORS: *That has been done, see comment 69.*

Fig. 5: Why is this figure shown alone and not in comparison with the other cores. Also it is difficult to relate the specific scale to the specific line.

78)AUTHORS: *see comment 47.*

Supplementary Information:

This entire first section is not useful. Probably best if the core descriptions were removed and perhaps moved to the main text.

79)AUTHORS: *This has been done in the revised ms.*

For example, none of the lithologies described in Arenson and Segou are related to those described in Fig. S1. I am confused by the black lines alongside two of the cores. Only two of the four cores had evidence of freezing? How close together were the cores? They seem close but I can't really tell from the figure. Cryostructures are not the same thing as frozen nor do they represent ice-bound permafrost. Polygonal ground structures and cryoturbation are cryostructures and they are not frozen. Relic structures can persist. That's why we know certain areas have been

frozen before. In fact, if they are persisting it is indicative that there is not a lot of

advective turbation - i.e. bubbles or a lot of water - flowing through. It also seems there is a basic confusion about the salinity of the frozen interstitial fluids.

80)AUTHORS: *Fig.S1 will be replaced by better schemes (see comment 43) to describe more thoroughly the structure of each core.*

If the permafrost was formed subaerially then it is likely that the ice will have very low salinities. This is certainly indicated by the del-D values of the deeper CH₄.

81)AUTHORS: *Indeed, that could be expected, but this would be the case only if seawater has not reached yet the thawed permafrost layers.*

The relevance of the Biggar et al, study is not clear. That study was about sands and gravels with very low moisture contents in essentially polar desert. It has NO relevance to subsea permafrost. it is about non-aqueous phase liquid migration.

82)AUTHORS: *This section has been removed from the SI.*

In the SI there is discussion about higher HCs yet no data on higher hydrocarbons in the paper. (though C₂+C₃ could go a long way to resolving and testing the assumptions made in this ms).

83)AUTHORS: *According to the suggestions of all reviewers, we have focused the revised discussion on our key isotopic signature results. Therefore, this paragraph will be removed from the revised SI.*

You could move Figs S1 and S3 to the main body of the ms. Those Figs are already discussed there and make up part of your narrative.

Fig. S2 can be removed. We know the core is contaminated and that is more or less ok. No need to make up confusing stories about why. It does not matter.

84)AUTHORS: *Fig.S1 is now much larger and includes much more details for each core (as requested by the reviewers), but we believe that these information are complementary but do not need to be in the main manuscript to understand the main message. Therefore we believe it is better to keep this figure with a detailed discussion on the lithology in the SI. However, Fig. S3 is added to the revised main manuscript and Fig. S2 is removed.*

4) COMMENT BRETT THORNTON:

For disclosure, I have active research projects with two of the coauthors, and have worked on past projects with some of the coauthors as well. However, I had nothing to do with the research behind or the drafting of the present Sapart et al. manuscript; the first time I saw it was when it appeared in Biogeosciences Discussions.

CH₄ emissions from the East Siberian Arctic Shelf have been the subject of intense interest since reports of very high atmospheric CH₄ in the area, and later, reports that such enhancements were being driven by CH₄-containing bubble plumes from the seafloor. This manuscript presents a new dataset of CH₄ concentrations and CH₄ isotopologue studies in the sediment beneath 3 nearshore areas of the Laptev Sea, along with similar studies of CH₄ in the water column in these areas. Additional water column measurements are also provided for a far offshore site in the central Laptev Sea, near the top of the continental slope.

So, I was very interested to read this manuscript, and I strongly feel it should be published because of its unique dataset of CH₄ and CH₄ isotopologues in this region. However, there are some issues with the manuscript that should be cleared up. The other reviewers raise many important points, and I generally agree with them. The main problem with the manuscript is that it loses sight of the main results, in my opinion. The main observations are unique and should be published! See especially

my comment about lines 404-407, where the reader finally is told the biggest result.

85)AUTHORS: *We thank Dr Thornton for his comments and suggestions. We agree that the key message of the paper is coming too late in the paper and that has corrected in the revised version of the paper. The abstract has been rewritten (see comment 10) and some part of the introduction have been replaced to focus more on what needs to be introduced to understand the main message of the paper. Then section 3 has been largely rewritten so that the main message will be clearly stated in this section already and the conclusion section has been rewritten (see comment 24).*

The first section of the supplement needs rewritten or removed (I would vote for removed, because it's not especially critical to the arguments in the manuscript.)

86)AUTHORS: *This section has been removed from the revised version.*

Specific questions:

Line 45 "primary substrate glacial water" – I am not sure what "glacial water" means in this context; normally glacial water comes from glaciers... I think the authors mean water that has been frozen in to the subsea permafrost since formation, but I'm not sure. See also line 255.

87)AUTHORS: *Here we mean water from buried ice (probably segregation ice) of meteoric origin since it has initially been formed by precipitation that have infiltrated the ground and then refrozen. We replace glacial water by " meltwater from buried meteoric ice" in the revised version.*

Line 51-53—I don't see anything in this manuscript that says that the sediment CH₄ studied in this manuscript rapidly migrates through the water column. Bubbles were not trapped and analyzed. The last sentence of the abstract should be removed.

88)AUTHORS: *This sentence has been removed from the revised version, see comment 10.*

Line 66-70: "The four key mechanisms controlling the release of Pleistocene carbon from thawing subsea permafrost are gas hydrate degradation, thermokarst development, the deepening of the permafrost active layer and coastal erosion (e.g. Shakhova et al., 2005, 2009, 2010a,b, O'Connor et al., 2010, James et al., 2016)."

Several things wrong with this statement, it is talking about subsea permafrost but gives examples that only apply to land! (1) I have never heard of active layer deepening in subsea permafrost. This implies an annual freeze-thaw cycle, as happens to permafrost regions on land, not at sea. (2) Similarly, I'm not sure what undersea thermokarst is—thermokarst landscapes form due to seasonal cycling. Are you saying there are annual freeze-thaw cycles in subsea permafrost? (3) Coastal erosion does not, by definition, release carbon from subsea permafrost—it releases carbon from the eroding coast line. The entire sentence should be removed or rewritten.

89)AUTHORS: *This sentence has been corrected and rewritten as follows adding the Winterfeld reference as requested by other reviewers: "The four key mechanisms controlling the release of Pleistocene carbon to the ESAS are gas hydrate degradation, the deepening of the ice-bonded permafrost table, coastal erosion and riverine (e.g. Shakhova et al., 2005, 2009, 2010a,b, O'Connor et al., 2010, Winterfeld et al., 2015, James et al., 2016)."*

Line 100-102: " Below this gas hydrate stability zone, CH₄ occurs as free gas and can be advected towards the surface through faults in the sediment." Why would this free gas not be incorporated into hydrates as it passes through the stability zone? Or are you suggesting that CH₄ released BELOW the gas hydrate stability zone migrates

upwards so fast through the sediment that it is never trapped as hydrates?

90)AUTHORS: This section has been removed, see comment 16.

Line 120: "vigorous bubbling" is undefined with no sense of scale.

91)AUTHORS: "vigorous bubbling" is defined in the paper cited in the same sentence (Shakhova, N, et al. The East Siberian Arctic Shelf: towards further assessment of permafrost-related methane fluxes and role of sea ice. Phil. Trans. R. Soc. A 373, 20140451 (2015) and more detailed are given there on how the bubbling was observed.

Line 184: "expanded into a smaller flask for storage". Impossible to expand something into a smaller volume.

92)AUTHORS: Here we meant that part of the sample was transferred "by expansion" from the burette to a smaller volume. The word "expanded has been replaced by transferred" in the revised ms.

Line 191: The reader has no clue as to the logic behind the four core identifiers: "ID-11, IID-13, IIID-13, VD-13". To the reader, these are just random numbers and letters, and they are similar enough to be confusing. It would be far less confusing if they were simply designated background, 1,2,3 (or 1,2,3,4) in this manuscript. OR, if the core names themselves are somehow significant, or correspond to information in other papers, that should be explained.

93)AUTHORS: The name of the cores depend on the year they were drilled, so ID-2011, was the first core of 2011, and then we have second core of 2013 (IID-2013), third core of 2013 (IIID-2013) and fifth core of 2013 (VD-2013). This is how the cores are referred to therefore we believe it is appropriate to keep this denomination in this paper in order to be consistent with the work of others.

Line 199-201: The cores are shown in supplement Figure S1 (I think this figure should be in the main text). But in Figure S1, the white and black bars beside the cores show frozen/unfrozen.

94)AUTHORS: Fig.S1 has been replaced by more detailed schemes (see comment 43). Therefore, Fig.S1 is now much larger and includes much more details for each core (as requested by the reviewers), but we believe that these information are complementary but do not need to be in the main manuscript to understand the main message. Therefore we believe it is better to keep this figure with a detailed discussion on the lithology in the SI.

But here, it says that " IID-13, IIID-13 and VD-13" are partly frozen, yet IIID-13 is shown as completely thawed in figure S1.

95)AUTHORS: This has been corrected in the revised version.

Line 215: Another good reason to move figure S1 to the main text!

96)AUTHORS: see comment 94.

Line 255: Here, old water frozen in the permafrost is called "meteoritic"—so again, why is it called "glacial water" on line 45?

97)AUTHORS: Here we mean meltwater from buried meteoric ice, thus water derived from precipitation during glacial times.

Line 282: "strong evidences that CH₄ from old reservoirs (Pleistocene age or older) is being released there." -- or that the CH₄ is being formed from old carbon being released from reservoirs.

98)AUTHORS: In this case, we mean methane that is formed (or was formed) using old carbon reservoirs. Triple isotope data cannot allow to identify when exactly the methane was formed, but on which type of substrate. That will be clarified in the revised version.

Line 296-297: This seems like a slight misunderstanding of the Overduin et al paper;

in that core, almost all the loss of CH₄ occurred at the thaw front, not near the sediment surface / seawater interface. Compare Figure 4 in the Overduin et al paper with your Figure 2. I see no sharp cutoff in CH₄ values at the thaw front in your paper as Overduin et al report. (However, the use of a log plot in Figure 2 makes it somewhat hard to see.) Also, label the thaw front in Figure 2 for each core.

99)AUTHORS: This has been clarified and discussed more thoroughly in the revised manuscript.

Line 340-345: " In the ESAS, the pycnocline is very shallow and a very low primary production is expected because of darkness and ice cover in the winter and because of the little available sunlight in the summer due to the high solar zenith angles and the very turbid waters (light penetrates only down to 40cm)".

The statements about light penetration depth are NOT TRUE. As written, this is about the entire ESAS. I suppose that close to shore, turbid water can occur (and can be seen from space), but farther from shore, water is not so turbid (again, can be seen from space). 40 cm light penetration depth is extremely shallow. Yes, water surfaces are more reflective at shallow light incidence angles, but there is a lot of sunlight in the summer in the Arctic! Photos have been published showing blue waters around islands in the study area in the summer. I don't know if there is in situ production of CH₄ in the water column or not, but I am 100% certain that light penetrates far deeper than 40 cm in waters of the ESAS.

100)AUTHORS: See comment 68). Since the depth of penetration can vary from one place to another, we remove the 40cm from the revised version. See Fig. S5 of Semiletov et al., Acidification of East Siberian Arctic Shelf water through addition of freshwater and terrestrial carbon. Nature Geosciences, 18 April 2016, doi:10.1038/NGeo2695. They show the distribution of SPM in the surface water of the ESAS that gives information on the turbidity of the surface water at some locations where our water sampling was carried out. This reference will be added to the discussion in the revised version.

Also, the authors have previously claimed (in this journal!) that the ESAS waters have high productivity! [dx.doi.org/10.5194/bg-8-1745-2011](https://doi.org/10.5194/bg-8-1745-2011).

101)AUTHORS: Some of the authors of this paper have cited other studies, who investigated rates of productivity in different areas of the ESAS. For example, Sorokin (1996) reported rates in the Lena River estuary that were moderately high in the Lena Delta but drop orders of magnitude shelf ward. In the Chukchi Sea, there is also a well-known spot of high productivity, where whales found their feeding habitat. But they did not claim high levels of primary productivity (PP) in the ESAS.

Line 385-387: " This gas is formed continuously from old substrates at depth and/or has been stored as gas hydrate and/or gas pockets in or below the subsea permafrost."

This sounds like you are 100% ruling out biogenic CH₄ production in the nearseafloor sediment, where such production might happen utilizing recently deposited carbon sources mobilized from terrestrial and coastal erosion sources? Interesting that you rule that out. Really?

102)AUTHORS: The conclusion has been rewritten, please see comment 24.

Line 393-394: "No quantitative estimate of this CH₄ source is to date possible,"

Some of the papers you cite give quantitative estimates. So do some papers you don't cite. Maybe you mean something else here?

103)AUTHORS: The conclusion has been rewritten, please see comment 24.

Line 404-407: " Our results show that thawing subsea permafrost emits large amounts

of CH₄ that is depleted in heavy isotopes and that such emissions cannot be easily distinguished from Arctic wetland emissions when looking only at stable isotope data.” I believe this is the most important result of the study, and this potential caveat about isotopic studies in this region should also be mentioned in the abstract, and earlier in the text.

104)AUTHORS: *This has been put forward earlier in the text and in the revised conclusion, see comment 24.*

Other items:

I do not understand why we are presented Figure 5, which shows sulfate, Corg, chloride, and Si for only the background core. Why not for all 4 of the cores discussed here?

105)AUTHORS: *Please see comment 47.*

Or, better still, because the dataset presented here is unique and will be of interest to many, I strongly encourage the authors to make the all data shown in Figure 2 available with the manuscript, perhaps as a supplement.

106)AUTHORS: *We will make all the data shown in Figure 2 available when the paper will be published.*

I find the title a bit curious. Saying ”unraveled” suggests that the mystery has been solved; I would say it has not been (but that is okay!!). To me, there appears to be vast areas of the ESAS which have not been sampled yet for sediment CH₄. Hence, the title seems--premature. Unless the authors mean to imply that our understanding is being unraveled?

107)AUTHORS: *We do not believe that our dataset allows to solve fully the issues, but it brings the knowledge and the understanding further. Therefore, we propose the following revised title: “The origin of methane in the East Siberian Arctic Shelf investigated with triple isotope analysis”.*

Supplementary Material

Line 5-9: Doesn’t make much sense as written. Perhaps the authors mean something like: ”Although thawing is the most obvious factor affecting the permeability of permafrost to gases, there are other factors to consider, which we discuss below”.

Line 16: ”the content of unfrozen water”—should be ”the fraction of unfrozen water”.

Line 22-23: ”as it has been demonstrated”—should be ”as has been demonstrated”.

Line 27-31: Doesn’t make sense as written. Groundwater and porewater are not the same but are apparently used interchangeably here. Suggest something like: ”The salinity of this cryogenic porewater usually ranges between 10 and 300psu. Freezing-point depression is also due to the dissolved-solids content of this cryogenic porewater (Gilichinsky et al., 2007). The high salinity and solids content is due to inclusion of brines from the freezing of marine sediments.”

Line 32-34: Doesn’t make sense as written. Suggest something like: ”These water layers are usually connected to each other, building up a multi-level transport system which allows gases and geofluids to migrate through subsea permafrost and potentially be released to the water column, possibly via taliks.”

Lines 35-38: redundant.

Line 35: Biggar et al study is not relevant here. It’s about (as the title gives away) spilled fuels migrating downwards.

Line 40, Section 1.2. This seems to be about terrestrial permafrost; but this section is headed ”Factors affecting gas transport in subsea permafrost”.

Line 44: ”alterations of compression” doesn’t make much sense. Maybe something like ” they affect frozen soils and sediments by alternately compressing and stretching them during freezethaw cycles.”

Line 53: Section 1.3. This entire section is messy and difficult to read. It is also about processes happening far below the study zone of this manuscript. In my opinion, it can be removed without any loss to the manuscript.

108)AUTHORS: Section 1 of the Supplementary Material has been removed.

Line 140-141: The problem with explaining the 14C-hot samples is that they are hottest at depth, right? Why would anthropogenic contamination not be greater at the top of the sediment, instead of under 30 m of sediment? That is a mystery. Seems like some comment should be made about this (at least to acknowledge the mystery.)

109)AUTHORS: Please see comment 58 and comment 2.

Line 155 "was abnormal" should be "were abnormal".

110)AUTHORS:that has been corrected in the revised version

Figure S1: Should be part of main text. Label which core is the background core.

111)AUTHORS: Please see comment 84.

The origin of methane in the East Siberian Arctic Shelf unraveled with triple isotope analysis

^{1,2}Célia J. Sapart*, ^{3,4}Natalia Shakhova, ^{3,4,5}Igor Semiletov, ^{1,6}Joachim Jansen,
⁷Sönke Szidat, ⁵Denis Kosmach, ⁵Oleg Dudarev, ¹Carina van der Veen,
⁸Matthias Egger, ⁹Valentine Sergienko, ⁵Anatoly Salyuk, ¹⁰Vladimir Tumskey,
²Jean-Louis Tison and ¹Thomas Röckmann.

¹Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht University,
Princetonplein 5, 3584CC Utrecht, The Netherlands.

²Laboratoire de glaciologie, Université Libre de Bruxelles (ULB), Avenue Roosevelt 50, 1050
Brussels, Belgium.

³University Alaska Fairbanks, International Arctic Research Center, 930 Koyukuk Drive,
Fairbanks, USA, 99775.

⁴Tomsk Polytechnic University, 30 Prospect Lenina, Tomsk, Russia.

⁵Russian Academy of Sciences, Far Eastern Branch, V.I. Il'ichov Pacific Oceanological
Institute, 43 Baltiyskaya street, Vladivostok 690041.

⁶Department of Geological Sciences and Bolin Centre for Climate Research, Stockholm
University, Svante Arrhenius väg 8, SE 114 18, Stockholm, Sweden.

⁷Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change
Research, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.

⁸Center for Geomicrobiology, Department of Bioscience, Aarhus University, Ny Munkegade
114, 8000 Aarhus, Denmark

⁹Russian Academy of Sciences, Far Eastern Branch, Institute of Chemistry, 159 Prospect
100-letiya Vladivostoka, Vladivostok 690022.

¹⁰Moscow State University, 1 Leninskie Gori, 119991, Moscow, Russia.

Abstract

The Arctic Ocean, especially the East Siberian Arctic Shelf (ESAS) has been proposed as a significant source of methane that might play an increasingly important role in the future. However, the underlying processes of formation, removal and transport associated with such emissions are to date strongly debated.

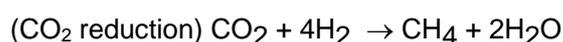
CH₄ concentration and triple isotope composition were analyzed on gas extracted from sediment and water sampled at numerous locations on the shallow ESAS from 2007 to 2013. We find high concentrations (up to 500 μM) of CH₄ in the pore water of the partially thawed subsea permafrost of this region. For all sediment cores, both hydrogen and carbon isotope data reveal the predominant occurrence of CH₄ that is not of thermogenic/natural gas origin as it has long been thought, but resultant from microbial CH₄ formation. At some locations meltwater from buried meteoric ice and/or old organic matter preserved in the subsea permafrost were used as substrates. Radiocarbon data demonstrate that the CH₄ present in the ESAS sediment is of Pleistocene age or older, but a small contribution of highly ¹⁴C-enriched

46 CH₄, from unknown origin, prohibits precise age determination for one
47 sediment core and in the water column. Our sediment data suggest that at
48 locations where bubble plumes have been observed, CH₄ can escape
49 anaerobic oxidation in the surface sediment.

51 1.Introduction

52
53 The Arctic subsea permafrost harbors a very large active carbon pool
54 of similar size as the terrestrial Siberian permafrost reservoir (Shakhova et al.,
55 2010a). Between 12 and 5kyr Before Present (BP), the Holocene
56 transgression (Bauch et al, 2001) submerged extensive parts of the
57 Pleistocene age terrestrial permafrost in Northern Siberia, forming the very
58 shallow ESAS (Romanovskii et al., 2005). As a result, the formerly terrestrial
59 permafrost has been continuously exposed to increasing seawater
60 temperature, salt and anoxic conditions (Dimitrenko et al., 2011, Nicolsky et
61 al., 2012) allowing the remobilization of carbon from the Pleistocene
62 reservoirs. The four suggested key mechanisms controlling the release of
63 Pleistocene carbon to the ESAS are the deepening of the permafrost level,
64 gas hydrate degradation, coastal erosion and riverine discharge (e.g.
65 Shakhova et al., 2005, 2009, 2010a,b, 2015; O'Connor et al., 2010, Wintereld
66 et al., 2015, James et al., 2016). Holocene age carbon originating mainly from
67 coastal erosion and riverine discharge (Charkin et al., 2011; Semiletov et al.,
68 2012; Karlsson et al., 2011, 2016) has accumulated on the ESAS shelf and
69 overlays the Pleistocene age sediment (Vonk et al., 2012, 2014 ; Feng et al.,
70 2013).

71 Under anaerobic conditions and depending on its type and quality
72 (Schuur et al., 2013), the remobilized carbon can be used to produce CH₄, a
73 strong greenhouse gas (IPCC, 2013). Microbial CH₄ is produced by
74 methanogenesis using as main substrates carbon dioxide (CO₂) or acetate
75 according to the following reactions (Whiticar, 1999):



79 In the deep Earth layers, CH₄ can also be formed through thermal
80 degradation of organic matter (e.g. Schoell, 1988) and migrate towards the
81 surface. This CH₄ is considered thermogenic. A large part of the CH₄ formed
82 in the seafloor is removed by anaerobic oxidation with seawater sulfate in
83 sediments (e.g. Reeburgh, 2007, Knittel and Boetius, 2009) or in the water
84 column where CH₄ can be consumed by aerobic methanotrophic bacteria
85 under specific nutrient and redox conditions (e.g. Kessler et al., 2011, Mau et
86 al., 2013, Steinle et al., 2015). Each type of CH₄ formation/removal pathway
87 produces CH₄ with a characteristic isotopic signature (δ¹³C and δD)
88 depending on the isotopic composition of the substrate and the kinetic isotope
89 effect associated with the respective chemical reaction involved.
90 Microorganisms need less energy to metabolize molecules with smaller bond
91 energy, which leads to discrimination against heavy isotopes. Therefore, CH₄
92 produced by methanogenesis has a lighter isotopic signature than its

93 substrates but when it is consumed, its remaining reservoir will become more
94 enriched in heavy isotopes (e.g. Whiticar 1999, Conrad, 2005). Diffusive
95 transport can also cause isotopic discrimination, because lighter
96 isotopologues diffuse faster than heavier ones. However, this fractionation is
97 considered to be relatively small (<5‰: Fuex, 1980, <20‰: Prinzhofer and
98 Pernaton, 1997 and 3‰: Chanton et al. 2005) compared to the isotopic
99 fractionation associated with methanogenesis (7-95‰ for $\delta^{13}\text{C}$ and 260-430‰
100 for δD) and with CH_4 oxidation (2-39‰ for $\delta^{13}\text{C}$ and 66-350‰ for δD)
101 (Whiticar, 1999, Holler et al., 2009).

102 Shakhova et al., 2010b, have shown that CH_4 concentrations in the
103 ESAS water were anomalously high (up to 500 nM) compared to CH_4 values
104 generally observed in ocean waters (~5 nM, Damm et al., 2008). Vigorous
105 bubbling events (1.5 to 5.7 bubbles per second) were observed at some sites
106 (Shakhova et al., 2013) as well as seepages of thermogenic CH_4 (Cramer
107 and Franke, 2005) indicating that part of the water column supersaturation
108 likely results from a seabed source. The destabilization of gas hydrates is the
109 most discussed CH_4 source from this region (e.g. Kvenvolden, 1988,
110 Romanovskii et al., 2005, Shakhova et al., 2010a), however, important gaps
111 exist in the assessment of the quantity and the nature of the CH_4 stored or
112 formed in the Arctic seabed (e.g. Ruppel et al., 2014).

113 To disentangle the origin(s) of this CH_4 anomaly, we measured CH_4
114 concentration, stable isotope composition and (on selected samples)
115 radiocarbon content on sediment and water samples from several winter
116 campaigns and summer cruises from 2007 to 2013 on the ESAS shelf and
117 shelf edge. While stable isotope analyses help identify the chemical
118 pathways involved in CH_4 removal and formation processes, radiocarbon
119 measurements give information on the age of the CH_4 substrate. The
120 combination of the isotope information thus helps determining the possible
121 origin(s) of this gas.

122
123

124 **2.Method**

125

126 **2.1.Drilling and sediment sampling**

127

128 Summer surface sediment drilling and water sampling campaigns were
129 carried out on research vessels while the winter field campaigns were
130 accomplished using an equipment caravan, which traveled over the sea ice to
131 the drilling locations. In the latter case, casings were drilled through the fast
132 ice into the seabed, allowing dry drilling using a rotary drill with 4 m casing
133 with a newly built URB-4T drilling rig (made in 2011 by the Vorovskii Factory
134 for Drilling Equipment, Ekaterinburg, Russia). Thawed and frozen sediments
135 for each core were subsampled straight after (i.e. maximum a few minutes
136 after) the drilling using ice screws for frozen samples and a heavy plastic
137 syringe-like sampler for thawed samples at 20 cm vertical resolution.

138 **2.2. Gas extraction and measurement in sediments**

139 Sediment subsamples were subsequently immersed in glass vials filled
140 with a saturated sodium chloride solution to drive gases out of solution and
141 capped with a septum for equilibration in an ultrasonic water bath at a

142 temperature of 20°C. The gas chromatograph (GC) used to measure CH₄
143 concentrations was equipped with two 10-Port gas sampling valves, a 2 m
144 MolSieve 13X column, a 30 m capillary column and a 6 channel PeakSimple
145 data system. A flame ionization detector (FID) was used for concentrations of
146 CH₄ <200 ppm and a thermal conductivity detector (TCD) for concentrations
147 of CH₄ >200 ppm. The GC oven was operated isothermally at 40°C and the
148 maximum detector temperature was held at ≈ 250°C. The carrier gas used
149 was helium. Daily calibration was performed with certified 1.96 ppm and
150 99.999 ppm CH₄ gas standards from Air Liquide, USA. The standard
151 deviation of duplicate analyses (three to five replicates) was <2%.
152 Reproducibility was ~1% based on multiple standard injections during daily
153 calibrations. The concentration of dissolved CH₄ in the water and sediment
154 samples was calculated with the Bunsen solubility coefficient for CH₄
155 (Wiesenburg and Guinasso, 1979) for the appropriate equilibration
156 temperature, pressure and the volume of headspace and water/sediment in
157 each vial.

158 The stable isotope measurements were performed using a Continuous
159 Flow Isotope Ratio Mass Spectrometry (CF-IRMS) system as described in
160 Brass and Röckmann, 2010 and Sapart et al., 2011. Radiocarbon analyses
161 could be performed only on the largest samples (containing more than 20 µg
162 of CH₄). In that case, CH₄ was preconcentrated and combusted to CO₂. The
163 ¹⁴C content of the CO₂ was measured by accelerator mass spectrometry
164 (Szidat et al., 2014) using a specific gas inlet (Ruff et al., 2010).

165

166 2.3. Gas extraction and measurement from seawater samples

167

168 Water samples were collected directly from the Niskin bottles. Gas
169 from seawater samples was extracted using a modified headspace vacuum-
170 ultrasonic degassing method (Schmitt et al., 1991, Lammers et al., 1994).
171 The gas released was accumulated in an evacuated burette to measure its
172 quantity and was then transferred into a smaller flask for storage, and
173 analysed as described in Section 2.2.

174

175 3. Results and discussion

176

177 We present results of CH₄ concentrations, stable isotope composition
178 and (on selected samples) radiocarbon content on four shallow sediment
179 cores (<3m), four deep sediment cores (ID-11, IID-13, IIID-13, VD-13) (down
180 to a maximum depth of 53m in the Buor-Khaya Bay (BKB)) and about fifty
181 water samples from four coastal areas of the ESAS: the Lena Delta (LD),
182 BKB, the Dmitry Laptev Strait (DLS) and the Shelf Edge (SE) (Fig.1) (see
183 Table S1 for more detailed on the sample locations). Because of the harsh
184 field and weather conditions during this campaign, no sediment drilling was
185 possible at the SE, hence only water data are presented for this site. All
186 water and sediment sampling, except for the ID-11 core, was performed at
187 hotspot sites, i.e., at locations where active gas bubbling from the seafloor
188 and high concentrations of dissolved CH₄ were previously observed as
189 discussed in Shakhova et al., 2010a. The location of core ID-11 is therefore

190 referred to as 'non-ebullition site'. This core as well as the IID-core were
191 thawed all the way down (>50 m) while the IID-13, and VD-13 cores were
192 thawed down to 19 and 12m, respectively. Note that for the two latter cores,
193 sampling was continued through the deeper frozen sediment to 30 and 35m
194 respectively. For more details on the lithology, the cryostructure and the
195 sediment properties, see SI, section 1 and Fig.S1-S4.

196
197
198

3.1 CH₄ formation pathways in the sediment

199
200
201
202
203
204
205
206
207
208
209
210

Depth profiles of CH₄ concentration, stable isotope composition ($\delta^{13}\text{C}$ and δD) and the radiocarbon content (in percent modern carbon, pmC) are presented in Fig.2. In both hotspot and non-ebullition cores, CH₄ concentrations are far above values observed in the water column and CH₄ is strongly depleted in heavy stable isotopes in all sediment cores. CH₄ in the hotspot cores IID-13, IID-13 and VD-13 is more depleted in D and slightly more enriched in ¹³C than in the non-ebullition core. These differences can be caused by the distance of the drill sites from the coast, the amount of time each site has been inundated and the differences in lithology (SI, section 1). These factors will play a role on the substrate availability (Karlsson et al., 2011, 2016, Tesi et al., 2014, 2016). We will focus the discussion on the origin of the substrate(s) for each core below.

211
212
213
214
215
216
217
218
219
220
221
222

The expected stable isotope signatures of the three potential CH₄ formation pathways in marine sediment (e.g. Whiticar, 1999): CO₂ reduction, acetate fermentation and thermal degradation of organic matter are depicted together with our water and sediment stable isotope data in a dual isotope plot (Fig.3). Overall, the deep sediment core data (diamonds) fall in between the isotope source signatures of the two main microbial CH₄ formation pathways: carbonate reduction and acetate fermentation. These untypical stable isotope signatures could imply that CH₄ is formed by a mixture of both microbial pathways or/and by using different substrates from the ones considered in Whiticar, 1999. It is unlikely to be explained by physical alteration (e.g. diffusion, gravitational settling) because these processes would result in equal fractionation for the CH₃D and ¹³CH₄ isotopologues.

223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239

For the non-ebullition core ID-11, most of the $\delta^{13}\text{C}$ values are typical (though on the light end side) of the reduction of carbonates, but about 2/3 of the samples show δD values that are considered too low (down to about -60‰) for such a pathway. The most enriched δD data correspond to the top of this core and are discussed in section 3.2. For this core, salinity measurements (from 20 PSU at the surface to 13 PSU at depth) indicate the presence of interstitial seawater all the way down the core. When the seawater sulfate enters the marine sediment, it provides sulfate reducing bacteria with the electron acceptor they need to outcompete methanogens for acetate (Lessner, 2009). This indicates that for this core *in situ* (i.e. at the depth where the samples were taken) acetoclastic CH₄ formation may be suppressed, despite an abundance of organic material. CO₂ and water remains therefore the most likely non-competitive substrate for methanogens if CH₄ formation would occur in the thawed permafrost. In that case, the very light δD values can be due to 1) a mixture of carbonate reduced (formed *in situ* or not) and acetoclastic (migrating vertically or horizontally) CH₄ or 2) the use of isotopically depleted hydrogen substrate for CH₄ formation by

240 carbonate reduction. On the dual isotope plot (Fig.2), the area of the
241 carbonate reduction pathway considers modern seawater as water substrate
242 for carbonate reduction. However the meltwater present in subsea permafrost
243 originates from buried meteoric ice with a much more depleted $\delta D(H_2O)$
244 signatures. Chanton et al. (2006) and Brosius et al. (2012) reported values
245 for $\delta D(H_2O)$ of $-135 \pm 25\%$ and $-220 \pm 30\%$, respectively in old Arctic permafrost.
246 This is about 200‰ to 105‰ more depleted in deuterium than modern Arctic
247 seawater (Friedman et al., 1964). We suggest that methanogens present in
248 the thawing permafrost (Koch et al., 2009) use and/or have used such
249 depleted permafrost meltwater or unfrozen porewater as a hydrogen source
250 to form CH_4 with low δD values as it is observed in the non-ebullition core.

251 For the hotspot cores IID-13 IIID-13 and VD-13, the δD values are
252 characteristic of acetate fermentation, but the $\delta^{13}C$ signatures are about 30‰
253 too depleted in ^{13}C in comparison to what has been measured previously
254 from this pathway (e.g. Whiticar, 1999, Walter et al., 2008). This depletion in
255 ^{13}C must originate from 1) the addition of carbonate reduced CH_4 to an
256 acetoclastic pool or/and 2) the recycling of CH_4 after AOM-mediated carbon
257 isotope equilibrium under sulfate limitation conditions (Yoshinaga et al., 2014,
258 Geprägs et al., 2016). For the latter, the ^{13}C depletion must be accompanied
259 by a decrease in CH_4 concentration, but this was not observed: the CH_4
260 concentrations in our cores were relatively constant and not correlated with
261 the $\delta^{13}C$ values (Fig.4). For these cores and because of the harsh conditions
262 on the field, no reliable sulfate and salinity profiles could be retrieved, so
263 unfortunately no sulfate data are available to support the interpretation.

264 The ^{14}C content of CH_4 from the hotspot cores covers a range from
265 0.79 to 3.4pmC corresponding to a radiocarbon age of 26 to 39kyBP (Fig.2).
266 This indicates a carbon substrate of Pleistocene age. For the ID-11 non-
267 ebullition core, ^{14}C values are unexpectedly high and vary from 87pmC
268 (radiocarbon age=1kyBP) to 2367pmC (Fig.2), which represents a substantial
269 enrichment above the natural background. The same applies to water
270 samples from the SE. Note that levels close to 100pmC indicate modern
271 values. Even samples that had been affected by the nuclear bomb testing in
272 the 1950s and 1960s would show levels below 200pmC thus ^{14}C values
273 >200pmC cannot be caused by known natural processes. As discussed in the
274 SI section 2, local anthropogenic nuclear contribution, e.g. from nuclear waste
275 buried in the coastal permafrost, is the most likely explanation for these
276 elevated radiocarbon levels. The drilling location is shallow (12.5 m) and very
277 difficult to reach hence waste burial is very unlikely to have occurred directly
278 in this area. Moreover the highest contamination is observed at 30 m depth in
279 the sediment showing that it is not originating from the surface. Our first
280 assumption is that this anthropogenic contamination has been laterally
281 transported in the pore-water of the thawing subsea permafrost in the form of
282 CH_4 or of one of its precursors (e.g. dissolved inorganic carbon) from the
283 coastal terrestrial permafrost to our drilling site (see SI section 2 for more
284 detailed). More data, e.g. of other radionuclides would be essential to confirm
285 this assumption.

286 The shallow sediment samples from hotspot sites have $^{14}CH_4$ values
287 from 3 to 88pmC (radiocarbon age = 1-26kyBP) showing the presence of old
288 CH_4 in surface sediment of relatively modern age and thus confirming the
289 migration of old gas from deeper layers towards the surface. Note that the

290 overall low content of organic carbon (<2.3%) with a high fraction of lignin
291 (Bröder et al., 2016; Vonk et al., 2014) in the surface sediment (Fig.5) and the
292 likely presence of sulfate, would severely inhibit CH₄ formation in the marine
293 layer hence *in situ* methanogenesis there is highly unlikely.

294 We conclude that the CH₄ present in the surface thawed subsea-
295 permafrost is formed mainly microbially. For the non-ebullition core, our
296 observations imply that CH₄ is at least for a part not formed *in situ* in thawed
297 subsea permafrost but that it migrates vertically or laterally to the surface of
298 the partially thawed ESAS subsea permafrost. For the hotspot cores, which
299 are closer to the shore and more recently inundated (Table S.1), most of the
300 methane present is of acetoclastic origin and formed with Pleistocene carbon
301 remobilized in the thawing subsea permafrost.

302

303

304 3.2. CH₄ removal pathways in the sediment

305

306 The ID-11 non-ebullition site was the only coring location where no
307 active bubbling was observed from the surface sediment. Here, the top 5.8m
308 consist of a thick silty-clay layer (Fig.S1) of marine origin as indicated by the
309 higher salinity and silica concentrations (Fig.5), typical of a marine
310 environment enriched in diatoms. The increase in sulfate concentration
311 together with the strong CH₄ concentration decrease and the isotopic
312 enrichment in both ¹³C and D towards the sediment surface indicate that most
313 of the CH₄ diffusing through this thick Holocene marine layer is removed by
314 anaerobic oxidation with sulfate in the surface sediment before reaching the
315 water column.

316 This marine layer may also act as a physical barrier preventing gas to
317 migrate towards the surface directly. The increase in CH₄ concentration from
318 9 to 5.8m depth without strong isotopic shifts (Fig. 5) and the acoustic data
319 (Fig. 6) show that gas accumulates under this less permeable layer. Part of
320 this gas might migrate laterally and be released to the water at locations
321 where the marine clay layer is thinner or absent. The isotopic signatures of
322 the CH₄ in the pore water of the hotspot cores do not show isotopic
323 fractionation toward the surface (Fig.2). At these sites, ebullition processes
324 may disturb the sulfate-reducing layer and advection may occur. This would
325 reduce the amount of CH₄ subject to anaerobic oxidation (only dissolved CH₄
326 is accessible for methanotrophic organisms) and allow direct gas release to
327 the water column.

328 Overduin et al., 2015 have reported CH₄ concentration and δ¹³C
329 values measured on one sediment core drilled in the Buor-Khaya Bay. The
330 carbon isotopic signature of that core was typical of acetate fermentation in
331 the frozen part of the core, but they observed a strong enrichment in ¹³C
332 associated with a decrease in CH₄ concentration directly above the ice-
333 bonded permafrost. They concluded that CH₄ was strongly oxidized in the
334 thawed subsea permafrost before reaching the water column. Our dataset
335 does not support this interpretation, because no enrichment in either D or ¹³C
336 associated with a decrease in CH₄ concentration has been observed at the
337 ice-bonded permafrost table for the partly frozen cores IID-13 and VD-13 (Fig.
338 2 and Fig. S.2 and S.4).

339

Comment [C1]: One sentence removed

340 **3.3. CH₄ in the water**

341

342

343

344

345

346

347

348

349

350

351

352

353

354

Compared to the sediment samples, CH₄ in the water samples is more enriched in heavy isotopes. The highest CH₄ concentrations in the water column are observed close to the seabed and at the surface in the presence of sea ice (Fig.2a blue triangles). The ¹⁴C values of water samples are between 83 and 9560pmC (radiocarbon age= 2kyBP to strongly enriched above natural present day values) (Fig.2d) (SI section 2). For the water samples we only encountered the highly enriched ¹⁴CH₄ values at the shelf edge. As demonstrated by the ¹⁴CH₄ data in the non-ebullition core ID-11, this anomaly likely originates from anthropogenic contamination in the sediment. Hence, we suggest that this signature may be diluted over the shelf but become indiscernible at locations where strong release of old CH₄ from the sediment occurs. This could explain the broad range of pmC values observed in the water column.

355

356

357

358

359

360

361

362

363

364

365

366

367

368

369

370

371

372

373

374

375

376

Several scenarios may explain the difference in stable isotope signatures between the water- and sediment samples. The first assumes a mixture of microbial CH₄ with a source that is more enriched in heavy isotopes. This source could be either a water source or thermal degradation of organic matter in the deep Earth's crust. In the marine environment, CH₄ could in principle be produced at the pycnocline, where natural differences of water density create a "fluid bottom", on which organic particles and pellets could accumulate as substrate for *in situ* methanogenesis (Damm et al., 2008, Karl et al., 2008, Sasakawa et al., 2008). In the ESAS, the pycnocline is very shallow and at the location of sampling, low primary production is expected because of darkness and ice cover in the winter and because of the little available sunlight in the summer due to the high solar zenith angles and the very turbid waters (Semiletov et al., 2016). Bussmann et al. (2013) have investigated the distribution of CH₄ in the estuary of the Lena, one of the largest Russian rivers draining into the ESAS. They reported high CH₄ concentrations (up to 1500 nM) in the river and in the creeks draining from permafrost soil and a strong decrease in the Buor-Khaya Bay (down to 26-33nM). They concluded that the CH₄ contained in the rich waters of the river was, for most of it, not reaching the marine waters, but that it was released by diffusion into the atmosphere before reaching the bay. A large water source is therefore unlikely to explain the CH₄ saturation we observe in the ESAS coastal waters.

377

378

379

380

381

382

383

384

385

386

Thermogenic emissions from the sediment are possible, especially from the fault zone near the shelf edge where we find strong heavy isotope enrichment in the water. While we have not measured any CH₄ with a thermogenic stable isotopic signature in our deep sediment cores from the continental shelf, it could be present in the sediments of the shelf edge (which we were unable to sample due to rough field conditions). Moreover, no measurements could be performed directly on gas bubbles (because of the low probability to trap bubbles in the Niskin bottles during sampling), which at the shelf edge might partly originate from thermal degradation of organic matter.

387

388

389

The difference between the water and sediment samples may also result from substantial oxidation of the CH₄ emitted from the deep sediment. Such a process should involve enrichments in D and ¹³C associated with a

390 decrease in CH₄ concentration. This pattern is only observed for the winter
391 water samples of the Lena Delta (Fig.4, blue open triangles) where CH₄
392 trapped under the sea ice could be removed by aerobic oxidation. All other
393 water data were collected in the summer and do not show any clear isotopic
394 enrichment correlated with concentration decrease. This could be explained
395 by the continuous addition of CH₄ from the sediment and its direct diffusion
396 from the water into the atmosphere in the summer, especially during storms
397 (Shakhova et al., 2013). These processes as well as water column mixing
398 could mask any oxidative isotope signature.

399 In the winter, CH₄ likely accumulates under the sea ice where the
400 bubble and dissolved phases could equilibrate and aerobic oxidation could
401 occur, while in the summer the gas bubbles will directly reach the atmosphere.
402 In the sediment, gas bubbles have time to equilibrate with pore water,
403 especially when the gas is trapped under relatively impermeable sediment,
404 e.g. the Holocene marine silty-clay layer. Therefore, we assume that in the
405 sediment, the pore water can be in equilibrium with the gas bubbles, while we
406 suggest that in the summer the seawater bubbles may travel too rapidly to
407 reach an isotopic equilibrium with the dissolved gas and to be oxidized. This
408 means that the CH₄ isotopic signature of the gas bubbles may not strongly
409 affect the CH₄ dissolved in seawater, which could also explain the difference
410 observed between the water and sediment stable isotopes values.

411 412 **4. Conclusion**

413
414 Our triple isotope dataset of CH₄ from the sediment and water of the shallow
415 ESAS reveals the presence of CH₄ of microbial origin formed on old carbon
416 with unexpectedly low stable carbon ($\delta^{13}\text{C}$ as low as -108‰) and hydrogen
417 (δD as low as -350‰) isotope signatures down to about 50m under the
418 seabed in the thawed permafrost. These data demonstrate that at location
419 where a thick marine clay layer is present, this CH₄ is partially oxidized before
420 reaching the seawater. However at locations where ebullition was observed
421 from the seabed, no oxidation was identified in the stable isotope surface
422 sediment profile. In that case and considering the very shallow water column
423 (<10m) in this area, this microbial gas will likely reach the atmosphere when
424 sea ice is absent. Our results show that thawing subsea permafrost of the
425 ESAS emits CH₄ with an isotopic signature that cannot be easily
426 distinguished from Arctic wetland emissions when looking only at stable
427 isotope data. This similarity might complicate recent efforts to quantify Arctic
428 CH₄ source strengths on the basis of isotopic- and back-trajectory analysis of
429 atmospheric CH₄. Further *in situ* work is necessary – specifically on the
430 isotopic composition of CH₄ in gas bubbles that reach the atmosphere – to
431 better quantify the contribution of the ESAS to the global methane budget.

432 433 434 435 436 **ACKNOWLEDGEMENTS**

437
438 We are grateful to the help of Gary Salazar (University of Bern) with the ¹⁴C
439 measurements. This research was supported by the Russian Government

440 (No. 14.Z50.31.0012/03.19.2014), the US National Science Foundation (OPP
441 ARC-1023281; 0909546); the NOAA Climate Program office
442 (NA08OAR4600758). N.S., D.K., and O.D. acknowledge support from the
443 Russian Science Foundation (No. 15-17-20032).

444 We would like to thank Jorien Vonk, Alain Prinzhofer, Helge Niemann, Nadine
445 Mattielli and Dominique Weiss for the fruitful discussions and precious help in
446 the interpretation of these data and Rebecca Fisher, Elise van Winden and
447 Joralf Quist for their help with the stable isotope measurements and system
448 calibration.

449

450

451 **AUTHOR CONTRIBUTION**

452

453 **C.J.S., N.S., T.R., J.J., S.S., I.S., J.L.T. and M.E. worked on the scientific**
454 **interpretation and wrote the manuscript. N.S. and I.S. planned the**
455 **research and organized the multiyear fieldwork campaigns. C.vd.V.,**
456 **C.J.S., S.S. and J.J. performed the isotopic analyses. I.S., D.K., O.D.,**
457 **V.S., A.S. and V.T. performed the water sampling, sediment drilling, the**
458 **headspace preparation and CH₄ concentration measurements on the**
459 **field.**

460

461

462 **REFERENCES**

463

464

465 Bauch, H. A., Mueller-Lupp, T., Taldenkova, E., Spielhagen, R. F., Kassens,
466 H., Grootes, P. M., Thiede, J., Heinemeier, J., & Petryashov, V. V.:
467 Chronology of the Holocene transgression at the North Siberian margin.
468 *Global Planet. Change*, 31, 125-139, 2001.

469

470 Brass, M., & Röckmann, T.: Continuous-flow isotope ratio mass spectrometry
471 method for carbon and hydrogen isotope measurements on atmospheric CH₄,
472 *Atm. Meas. Tech.*, 3, 1707–1721, 2010.

473

474 Bröder, L., Tesi, T., Andersson A., Eglinton T.I., Semiletov I. P., Dudarev O.
475 V., Roos P., Gustafsson Ö. (2016), Historical records of organic matter supply
476 and degradation status in the East Siberian Sea, *Organic Geochemistry*, Vol.
477 91, P. 16-30, 2016.

478

479 Brosius, L. S., Walter Anthony, K. M., Grosse, G., Chanton, J. P.,
480 Farquharson, L. M., Overduin, P. P. & Meyer, H.: Using the deuterium isotope
481 composition of permafrost meltwater to constrain thermokarst lake
482 contributions to atmospheric CH₄ during the last deglaciation. *J. Geophys.*
483 *Res.*, 117, G01022, 2012.

484

485 Bussmann, I.: Distribution of methane in the Lena Delta and Buor-Khaya Bay,
486 Russia, *Biogeosciences*, 10, 4641-4652, 2013.

487

488 Chanton, J. P.: The effect of gas transport on the isotope signature of
489 methane in wetlands, *Organic Geochemistry*, 36, 753–768. 2005.

Comment [C2]: The reference list
has been updated

490
491 Chanton, J. P., Fields, D., & Hines, M. E.: Controls on the hydrogen isotopic
492 composition of biogenic methane from high-latitude terrestrial wetlands. *J.*
493 *Geophys. Res.*, 111, G04004, 2006.
494
495 Charkin A.N., Dudarev O.V., Semiletov I.P., Kruhmalev A.V., Vonk J.E.,
496 Sánchez-García L., Karlsson E., and Ö. Gustafsson: Seasonal and
497 interannual variability of sedimentation and organic matter distribution in the
498 Buor Khaya Gulf – the primary recipient of input from Lena River and coastal
499 erosion in the SE Laptev Sea, *Biogeosciences*, 8, 2581–941, 2011.
500
501 Cramer, B., and Franke, D.: Indications for an active petroleum system in the
502 Laptev Sea, NE Siberia. *J. Petr. Geology*, 28(4), 369-384, 2005.
503
504 Damm, E., Kiene, R.P., Schwarz, J., Falck, E & Dieckmann, G.: Methane
505 cycling in Arctic shelf water and its relationship with phytoplankton biomass
506 and DMSP, *Marine Chemistry*, 19, 45-59, 2008.
507
508 Feng, X., Vonk, J. E., van Dongen, B. E., Gustafsson, Ö., Semiletov, I. P.,
509 Dudarev, O. V., Wang, Z., Montluçon, D. B., Wacker, L., & Eglinton, T. I.:
510 Differential mobilization of terrestrial carbon pools in Eurasian Arctic river
511 basins. *PNAS*, 110, 14168-14173, 2013.
512
513 Fuex, A.N.: Experimental evidence against an appreciable isotopic
514 fractionation of methane during migration. In: Douglas, A.G., Maxwell, J.R.
515 (Eds.), *Advances in Organic Geochemistry*, Pergamon, Oxford, 1980.

516
517
518 Friedman, I., Redfield, A. C., Schoen, B., & Harris, J.: The Variation of the
519 Deuterium Content of Natural Waters in the Hydrologic Cycle. *Rev. of*
520 *Geophys.*, 2(1), 177-224, 1964.
521
522 Geprägs, P., M. E. Torres, S. Mau, S. Kasten, M. Römer, and G. Bohrmann:
523 Carbon cycling fed by methane seepage at the shallow Cumberland Bay,
524 South Georgia, sub-Antarctic, *Geochem. Geophys. Geosyst.*, 17, 1401–1418,
525 2016.
526
527 Holler, T., Wegener, G., Knittel, K., Boetius, A., Brunner, B., Kuypers, M. M.
528 M., & Widdel, F.: Substantial ¹³C/¹²C and D/H fractionation during anaerobic
529 oxidation of methane by marine consortia enriched in vitro. *Environ. Microbiol.*
530 *Rep.*, 1, 370-376, 2009.
531
532 IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution*
533 *of Working Group I to the Fifth Assessment Report of the Intergovernmental*
534 *Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor,
535 S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)].
536 Cambridge University Press, Cambridge, United Kingdom and New York, NY,
537 USA, 1535 pp, 2013.
538

539 James, R. H., Bousquet, P., Bussmann, I., Haeckel, M., Kipfer, R., Leifer, I.,
540 Niemann, H., Ostrovsky, I., Piskozub, J., Rehder, G., Treude, T., Vielstädte, L.
541 and Greinert, J.: Effects of climate change on methane emissions from
542 seafloor sediments in the Arctic Ocean: A review. *Limnol. Oceanogr*, special
543 issue, 2016.
544
545 Karl, D.M., Beversdorf, L., Bjorkman, K.M., Church, M.J., Martinez, A. &
546 Delong, E.F.: Aerobic production of methane in the sea, *Nature Geoscience*,
547 1, 473-478, 2008.
548
549 Karlsson, E. S., Charkin, A., Dudarev, O. Semiletov, I. P., Vonk, J. E.,
550 Sánchez-García, L., Andersson, A., and Gustafsson, Ö.: Carbon isotopes and
551 lipid biomarker investigation of sources, transport and degradation of
552 terrestrial organic matter in the Buor-Khaya Bay, SE Laptev Sea,
553 *Biogeosciences*, 8, 1865-1879, 2011.
554
555 Karlsson, E. et al.: Different sources and degradation state of dissolved,
556 particulate, and sedimentary organic matter along the Eurasian Arctic coastal
557 margin. *Global Biogeochemical Cycles*, 30(6), 898–919, 2016.
558
559 Kessler, J. D. et al. A persistent oxygen anomaly reveals the fate of spilled
560 methane in the deep Gulf of Mexico. *Science*, 331, 312–315, 2011.
561
562 Knittel, K.; Boetius, A. Anaerobic oxidation of methane: Progress with an
563 unknown process. *Annu. Rev. Microbiol.*, 63, 311–334, 2009.
564
565 Koch, K., C. Knoblauch, and D. Wagner: Methanogenic community
566 composition and anaerobic carbon turnover in submarine permafrost
567 sediments of the Siberian Laptev Sea, *Environ. Microbiol.*, 11(3), 657–668,
568 2009.
569
570 Kvenvolden, K. A.: Methane hydrates and global climate. *Glob. Biogeochem.*
571 *Cy.*, 2(3), 221–229, 1988.
572
573 Lammers, S., Suess, E.: An improved head-space analysis method for
574 methane in seawater, *Marine Chemistry* 47, 115-125, 1994.
575
576 Lessner, D. J.: Methanogenesis Biochemistry. In: *Encyclopedia of Life*
577 *Sciences (ELS)*. Chichester, UK: Wiley and Sons Ltd, 2009.
578
579 Mau, S., Blees, J., Helmke, E., Niemann, H. & Damm, E. Vertical distribution
580 of methane oxidation and methanotrophic response to elevated methane
581 concentrations in stratified waters of the Arctic fjord Storfjorden (Svalbard,
582 Norway). *Biogeosciences*, 10 6267–6278, 2013.
583
584 Nicolsky, D., Romanovsky, V. E., Romanovskii, N. N., Kholodov, A. L.,
585 Shakhova, N. E., & Semiletov, I. P.: Modeling sub-sea permafrost in the East
586 Siberian Arctic Shelf: The Laptev Sea region. *J. Geophys. Res.*, 117, F03028,
587 2012.
588

589 O'Connor, F. M., Boucher, O., edney, N., ones, C. D., Folberth, . A., Coppel,
590 R., Friedlingstein, P., Collins, W. J., Chappellaz, J., Ridley, J., & Johnson, C.
591 E.: Possible role of wetlands, permafrost and methane hydrates under future
592 climate change: a review. *Rev. Geophys.*, 48, RG4005, 2010.
593

594 Overduin, P. P., S. Liebner, C. Knoblauch, F. Günther, S. Wetterich, L.
595 Schirrmester, H.-W. Hubberten, & M. N. Grigoriev: Methane oxidation
596 following submarine permafrost degradation: Measurements from a central
597 Laptev Sea shelf borehole, *J. Geophys. Res. Biogeosci.*, 120,965–978,
598 doi:10.1002/2014JG002862, 2015.

599 Prinzhofer, A., and E., Pernaton: Isotopically light methane in natural gas:
600 bacterial imprint or diffusive fractionation?, *Chemical Geology*, 142, 193-200,
601 1997.

602 Romanovskii, N. N., Hubberten, H.-W., Gavrillov, A. V., Eliseeva, A. A., &
603 Tipenko, G. S.: Offshore permafrost and gas hydrate stability zone on the
604 shelf of East Siberian Seas. *Geo-Mar. Lett.*, 25, 167-182, 2005.
605

606 Reeburgh, W. S. Oceanic methane biogeochemistry. *Chem. Rev.*, 107,
607 486–513, 2007.
608

609 Ruff, M., Szidat, S., Gäggeler, H. W., Suter, M., Synal, H.-A., & Wacker, L.:
610 Gaseous radiocarbon measurements of small samples, *Nucl. Instr. and Meth.*
611 *B*, 268, 790-794, 2010.
612

613 Ruppel, C.: Permafrost-associated gas hydrate: Is it really approximately 1%
614 of the global system?, *J. Chem. Eng. Data*, 60, 429–436, 2014.
615
616

617 Sapart, C. J., van der Veen, C., Vigano, I., Brass, M., van de Wal, R. S. W.,
618 Bock, M., Fischer, H., Sowers, T., ... Röckmann, T. (2011). Simultaneous
619 stable isotope analysis of methane and nitrous oxide on ice core samples.
620 *Atm. Meas. Tech.*, 4, 2607- 2618.
621

622 Sasakawa, M., Tsunogai, U., Kameyama, S., Nakagawa, F., Nojiri, Y. and
623 Tsuda, A.: Carbon isotopic characterization for the origin of excess methane
624 in subsurface seawater, *Journal of Geophysical Research*, 113, CO3012,
625 2008.
626

627 Semiletov I.P., Shakhova N. E., Sergienko V.I., Pipko I.I., and O. Dudarev:
628 On Carbon Transport and Fate in the East Siberian Arctic Land-Shelf-
629 Atmosphere System, *Environment Research Letters*, 7, 2012.
630

631 Semiletov et al., Acidification of East Siberian Arctic Shelf water through
632 addition of freshwater and terrestrial carbon. *Nature Geosciences*, 9, 361-365,
633 2016.
634

635 Schmitt, M., Faber, E., Botz, R., and Stoffers, P.: Extraction of methane from
636 seawater using ultrasonic vacuum degassing, *Anal. Chemistry* 63, vol. 5, 529-
637 532, 1991.

638

639 Schoell, M.: Multiple origins of methane on Earth. *Chemical Geology*, 71, 1-
640 10, 1988.

641

642 Schuur, E.A.G., Abbott, B. W., Bowden, W. B., Brovkin, V., Camill, P.,
643 Canadell,.... and Zimov, S. A.: Expert assessment of vulnerability of
644 permafrost carbon to climate change. *Climatic Change*, 119(2), 359-374,
645 2013.

646

647 Shakhova, N., I. Semiletov, and G. Panteleev: The distribution of methane on
648 the Siberian Arctic shelves: Implications for the marine methane cycle,
649 *Geophysical Research Letters*, 32, L09601, 2005.

650

651 Shakhova N.E., Nicolsky D., and I. P. Semiletov: On the current state of sub-
652 sea permafrost in the East-Siberian Shelf testing of modeling results by
653 observational data. *Transactions of Russian Academy of Sciences, Vol. 429*
654 (5), 2009 (translated in English by Springer), 2009.

655

656 Shakhova, N., Semiletov, I., Leifer, I., Rekant, P., Salyuk, A., & Kosmach, D.
657 Geochemical and geophysical evidence of methane release from the inner
658 East Siberian Shelf. *J. Geophys. Res.*, 115, C08007, 2010a.

659

660 Shakhova, N, I. Semiletov, A. Salyuk, V. Yusupov, D. Kosmach & O.
661 Gustafsson: Extensive methane venting to the atmosphere from sediments of
662 the East Siberian Arctic Shelf, *Science*, 327, 1246-1250, 2010b.

663

664 Shakhova, N., Semiletov, I., Leifer, I., , Sergienko, V., Salyuk, A., Kosmach,
665 D., Chernikh D., Stubbs Ch., Nicolsky D., Tumskoy V., and O.
666 Gustafsson Ebullition and storm-induced methane release from the East
667 Siberian Arctic Shelf, *Nature Geosciences*, vol.7, No.1, 64-70, 2013.

668

669 Shakhova N., Semiletov, I., Sergienko, V., Lobkovsky, L., Yusupov, V.,
670 Salyuk, A., Salomatin, A., Chernykh, D., Kosmach, D., Panteleev, G.,
671 Nicolsky, D., Samarkin, V., Joye, S., Charkin, A., Dudarev, O., Meluzov, A.,
672 Gustafsson, O.: The East Siberian Arctic Shelf: towards further assessment
673 of permafrost-related methane fluxes and role of sea ice. *Phil. Trans. R. Soc.*
674 *A*, vol. 373: 20140451, 2015.

675

676 Steinle, L, Graves, C., Treude, T., Ferré, B., Biastoch, A., Bussmann, I.,
677 Berndt, C., Krastel, S., James, R.H., Behrens, E., Böning, C.W., Greinert, J.,
678 Sapart, C.J., Scheinert, M., Sommer, S., Lehmann, M.F. and Niemann, H.:
679 Water column methanotrophy controller by a rapod oceanographic switch.
680 *Nature Geoscience*, 8, 378-382, 2015.

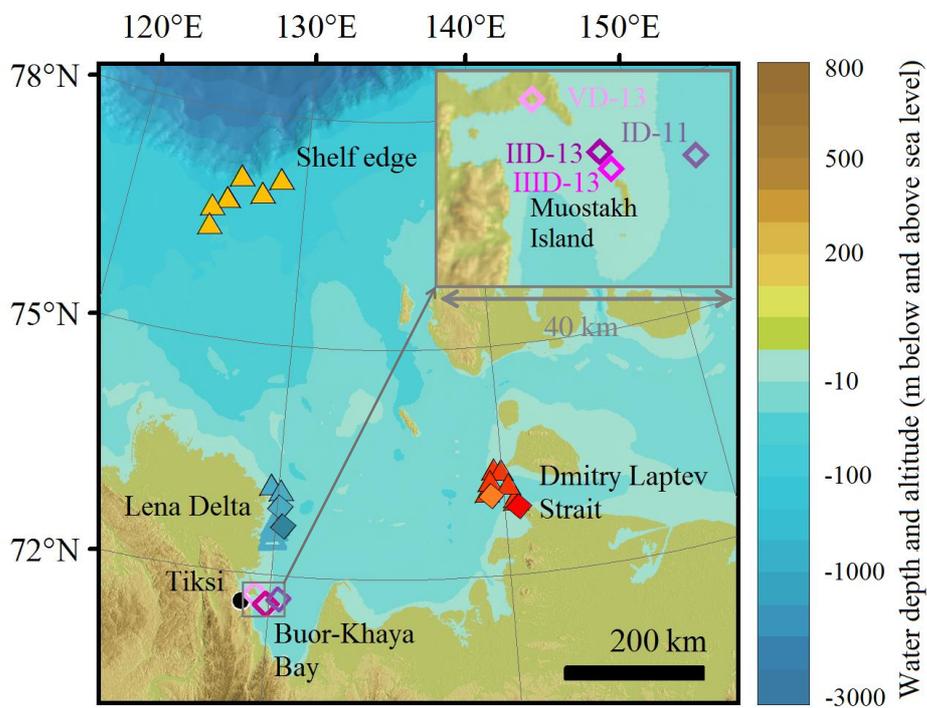
681

682 Szidat, S., Salazar, G. A., Vogel, E, Battaglia, M., Wacker, L., Synal, H.-A.
683 and Türler, A.: 14C analysis and sample preparation at the new Bern

684 Laboratory for the Analysis of Radiocarbon with AMS (LARA), *Radiocarbon*,
685 56, 561-566, 2014.
686
687 Tesi, T., Semiletov, I., Hugelius, G., Dudarev, O., Kuhry, P., and Gustafsson,
688 Ö.: Composition and fate of terrigenous organic matter along the Arctic land-
689 ocean continuum in East Siberia: Insights from biomarkers and carbon
690 isotopes, *Geochimica et Cosmochimica Acta*, 133, 235–256, 2014.
691
692 Tesi, T., I. Semiletov, O. Dudarev, A. Andersson, and Ö. Gustafsson: Matrix
693 association effects on hydrodynamic sorting and degradation of terrestrial
694 organic matter during cross-shelf transport in the Laptev and East Siberian
695 shelf seas, *J. Geophys. Res. Biogeosci.*, 121, 2016.
696
697 Vonk, J. E., Sánchez-García, L., van Dongen, B. E., Alling, V., Kosmach, D.,
698 Charkin, A., Semiletov, I. P., Dudarev, O. V., Shakhova, N., Roos, P.,
699 Eglinton, T. I., Andersson, A., & Gustafsson, Ö.: Activation of old carbon by
700 erosion of coastal and subsea permafrost in Arctic Siberia. *Nature*, 489, 137–
701 140, 2012.
702
703 Vonk J.E., Semiletov, I.P., Dudarev O.V., Eglinton T.I., Andersson A.,
704 Shakhova N., Charkin A., Heim B., Gustafsson: Preferential burial of
705 permafrost derived organic carbon in Siberian-Arctic shelf waters, *J. Geophys.*
706 *Res.*, Vol. 119, N 12, P. 8410-8421, 2014.
707
708 Walter, K. M., J. P. Chanton, F. S. Chapin III, E. A. G. Schuur, and S. A.
709 Zimov: Methane production and bubble emissions from arctic lakes: Isotopic
710 implications for source pathways and ages, *J. Geophys. Res.*, 113, 305-315,
711 2008.
712
713 Wiesenburg, D. A., & Guinasso Jr., N. L.: Equilibrium solubilities of methane,
714 carbon monoxide and hydrogen in salt and sea water. *J. Chem. Eng. Data*,
715 24(4), 356-360, 1979.
716
717 Winterfeld, M., Laepple, T., and Mollenhauer, G.: Characterization of
718 particulate organic matter in the Lena River delta and adjacent nearshore
719 zone, NE Siberia – Part I: Radiocarbon inventories, *Biogeosciences*, 12,
720 3769-3788, 2015.
721
722 Whiticar, M. J.: Carbon and hydrogen isotope systematics of bacterial
723 formation and oxidation of methane. *Chem. Geo.*, 161, 291-314, 1999.
724
725 Yoshinaga, M. Y., T. Holler, T. Goldhammer, G. Wegener, J. W. Pohlman, B.
726 Brunner, M. M. M. Kuypers, K. Hinrichs, and M. Elvert: Carbon isotope
727 equilibration during sulphate-limited anaerobic oxidation of methane, *Nat.*
728 *Geosci.*, 7(3), 190–194, 2014.
729
730
731
732
733

734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756

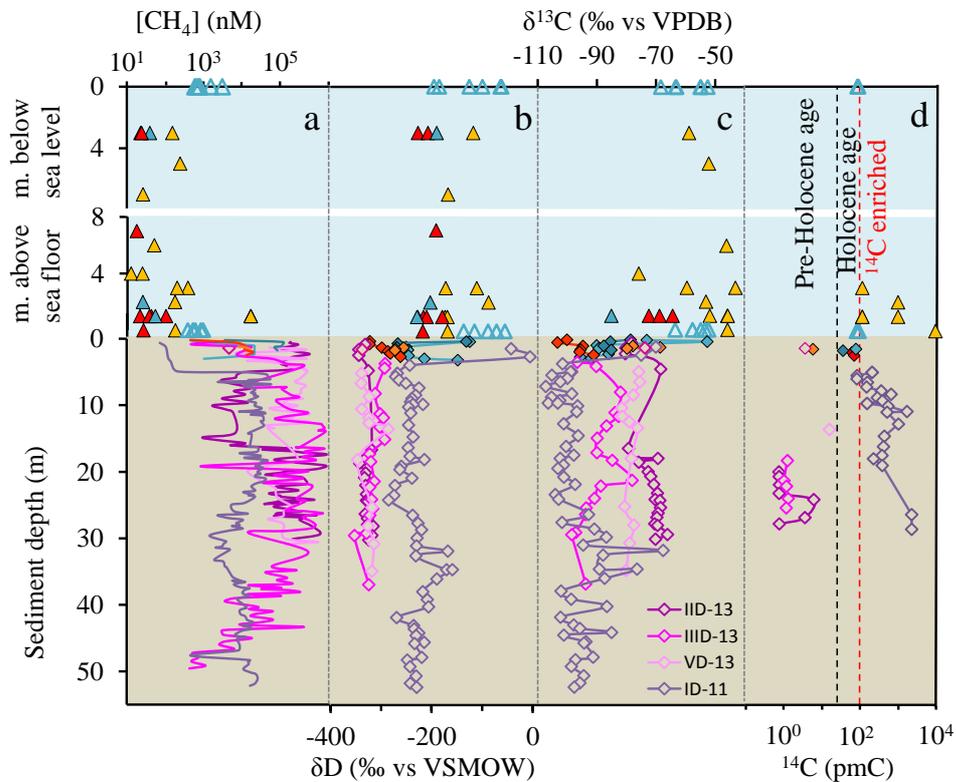
Figures



757
758
759
760
761

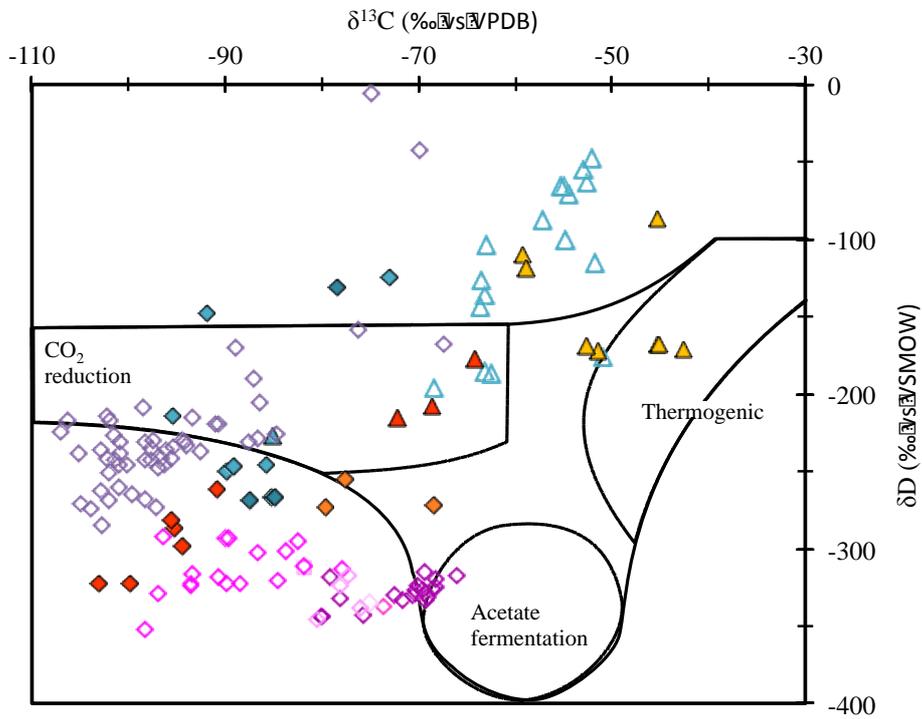
Figure 1: Sampling location. Water sampling (triangles), sediment drilling (diamonds). Summer sampling (close symbols) and winter sampling (open symbols). The color legends of the deep sediment cores are shown on the top right.

Comment [C3]: Figure 1 has been updated as required by the reviewers



763
764
765
766
767
768
769
770
771
772
773

Figure 2: CH₄ data from sediment and overlying water sampled on the East Siberian Arctic Shelf. Water sampling (triangles), sediment cores (diamonds). Summer sampling (close symbols) and winter sampling (open symbols). Buor-Khaya Bay (purple, ID-11: non-ebullition site and IID-13, IIID-13 and VD13 hotspot sites), Dmitry Laptev Strait (red and orange), Lena Delta (light blue) and Shelf Edge (yellow) (see Fig.1 for detailed location). (a) CH₄ concentrations, (b) δD (‰ vs VSMOW), (c) δ¹³C (‰ vs VPDB), (d) ¹⁴C (pmC). The red dotted line corresponds to modern values (i.e., 100pmC) and the black dashed line corresponds to the onset of the Holocene (11,000 years BP). Note that y-axis for the water samples is divided in two sections. The upper part corresponds to the depth from the sea surface and the lower part corresponds to the depth from the seabed. See Fig. S1-S4 for the ice-bonded permafrost table depths and Table S1 for bathymetric information.



774

775 **Figure 3: Dual-isotope CH₄ plot. Legend is similar to Fig.2. Areas delimited by black lines correspond**
 776 **to the three main CH₄ formation processes and their isotopic signatures (Whiticar, 1999).**

Comment [C4]: Fig. 3 has been updated, the squares were removed.

777

778

779

780

781

782

783

784

785

786

787

788

789

790

791

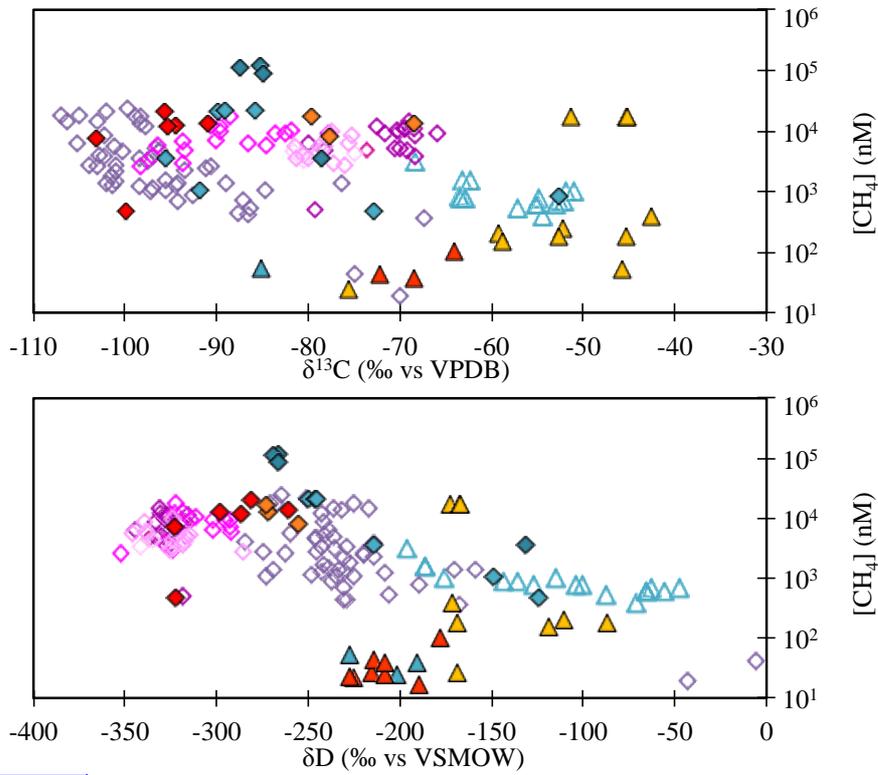
792

793

794

795

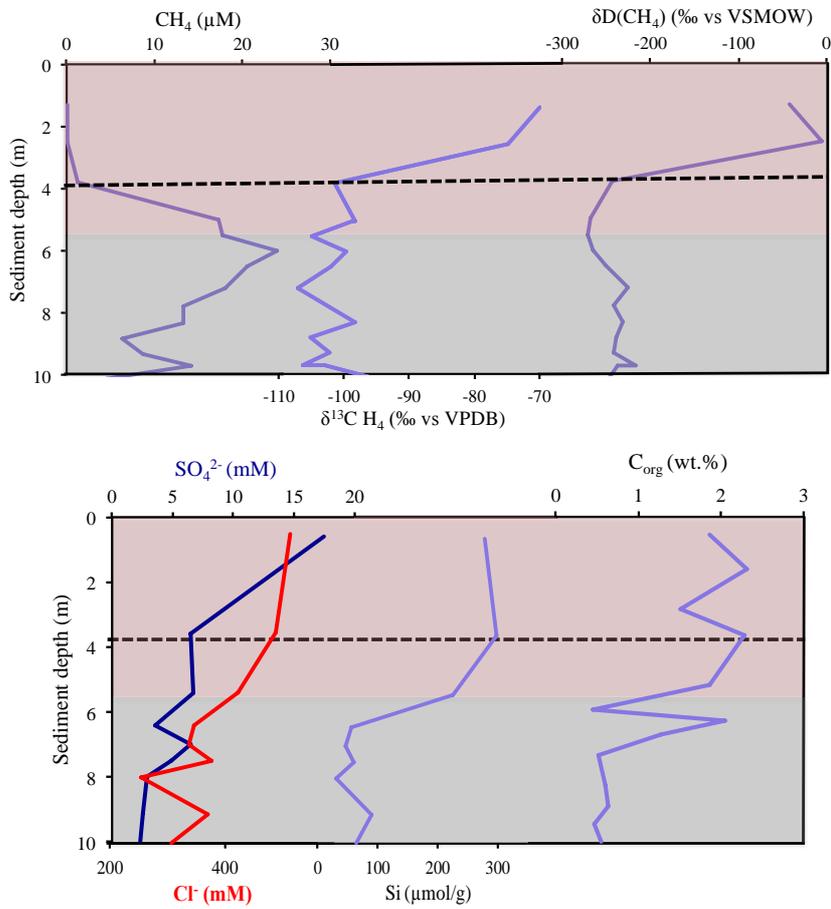
796



797
798
799
800
801
802

Figure 4: CH₄ concentration versus stable isotope plots. Water sampling (triangles), sediment cores (diamonds). Summer sampling (close symbols) and winter sampling (open symbols). Buor-Khaya Bay (purple, ID-11: non-ebullition site and IID-13, IIID-13 and VD13 hotspot sites), Dmitry Laptev Strait (red and orange), Lena Delta (light blue) and Shelf Edge (yellow) (see Fig.1 for detailed locations and Table S1 for bathymetric information).

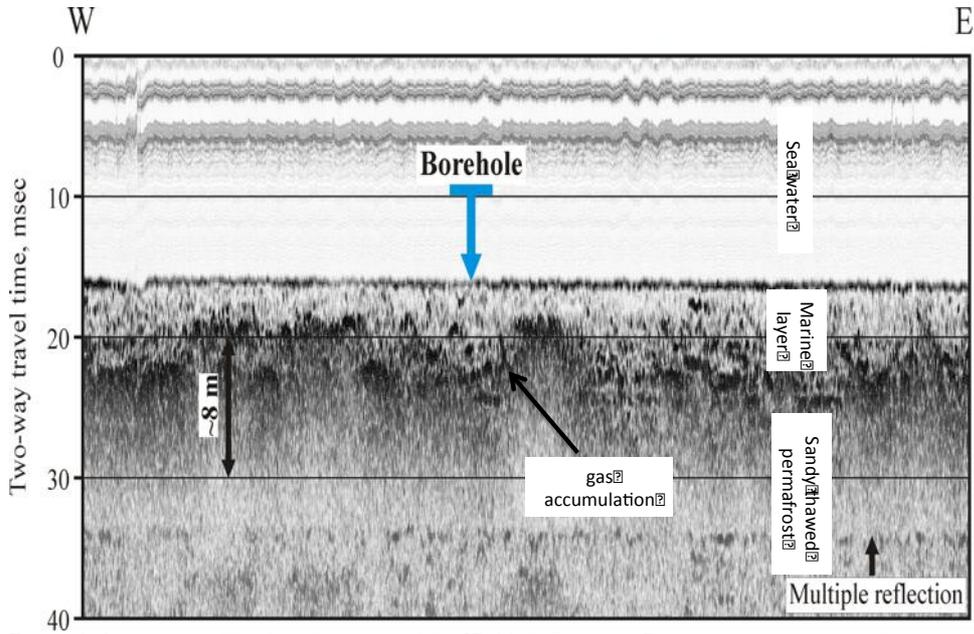
Comment [C5]: The former fig. 4 has been replaced by a Concentration vs stable isotope plot as requested by the reviewers.



803
804
805
806
807
808

Figure 5: Close-up of the CH₄ concentration, stable isotope and other biogeochemical data of the surface of the non-ebullition sediment core ID-11, from the Buor-Khaya Bay. Red shaded area corresponds to the marine sediment deposited during the Holocene transgression and the grey shaded area corresponds to the thawed permafrost layer. The black dotted line corresponds to the depth where CH₄ oxidation starts to occur.

809



810
811
812
813
814

Figure 6: Acoustic profile of the borehole of the ID-11 drilling site. Darker areas represent changes in density between the different horizontal layers (Sergienko et al., 2012). We assume that these changes in density indicate gas accumulation, because the sediment at this location is totally thawed, so it is very unlikely to be ice.

815

SUPPLEMENTARY INFORMATION

1. DEEP CORE LITHOLOGY

Table S1 shows the coordinates, bathymetry, distance from the coast and inundation time data of the deep cores. The major differences in the lithology of the deep cores drilled in 2011 and 2013 are the thickness and the origin of the Holocene age sediment. In the non-ebullition core, Holocene age marine sediments compose the upper 5.5m. They represent disperse pelite-aleurite deposits predominantly of alluvial origin, which are accumulations of river-derived matter formed in coastal marine conditions with high rates of sediment accumulation (Fig.S1). Holocene sediments are underlain with terrestrial accumulations (5.8m to 52.3m) of late Pleistocene age, which are represented by consolidated aleuro-sands inter-layered by fine-grained aleurite accumulations with inclusions of pebbles and wood remains.

The other deep cores (the hotspot cores) were drilled in 2013 near the Muostakh Island. In the IID-13 and IIID-13 cores, the Holocene age sediments represent only the upper 0.5m and consist of remains of the coastal ice-complex (IC or Yedomia) of Muostakh Island. This area represents a former part of the coastal alluvial plain, the upper part of which is composed of IC that thaws very fast during the last century. Sediment morphology reflects the nature of the sediments: fine-grained sand-aleurite-pelite is interlayered with gravel-pebble material with inclusions of wood remains and plant debris.

Sediment core VD-13 stands out of all the other cores drilled in 2013. Its morphological structure is different as its frozen fraction is presented by sands interlayered by gravel-pebble accumulations.

2. INTERPRETATION OF THE ^{14}C - CH_4 RESULTS

The observation of unexpectedly high ^{14}C values for the ID-11 non-ebullition core and water samples from the shelf edge needs further discussion. As explained in the main text, ^{14}C values $>200\text{pmC}$ do not exist in nature in any carbonaceous material including CH_4 , not even at the height of surface nuclear bomb tests of the mid-20th century. We assume that a local anthropogenic nuclear contribution is the most likely explanation for our elevated radiocarbon levels, which is justified in this section.

In the ID-11 non-ebullition sediment, the higher ^{14}C values correspond to the lower CH_4 concentrations (Fig. S5). That implies a possible mixture between a older CH_4 source and a background highly enriched in ^{14}C . A Keeling plot shows that the highly enriched ^{14}C contribution is relatively small in terms of CH_4 quantity and that the main CH_4 substrate is relatively old (Fig. S5). For the hotspot sites, where CH_4 concentrations are larger, no mixture with a “younger” source is identified. All data points are showing very low ^{14}C ($<1.5\text{pmC}$) so the main CH_4 substrate at these sites is clearly of Pleistocene age. Note that all points of the IID-13 core were below the analytical detection limit of 0.8pmC hence no conclusions could be drawn from the Keeling plot of this core.

The very high ^{14}C values $>200\text{pmC}$ may either originate from *in situ* cosmogenic or nuclear production of radioactive CH_4 or its substrate.

Comment [C1]: Former section 1: “FACTORS AFFECTING GAS TRANSPORT IN SUBSEA PERMAFROST” as been removed

Comment [C2]: The last paragraph has been removed

51 Enhanced ^{14}C has been found in meteorites (Firemann, 1978) and can be
52 produced at the surface of ice sheets (Baudin et al., 1973), but in both cases,
53 the quantity of ^{14}C formed is very small compare to what we observed in the
54 Buor-Khaya Bay and shelf edge sediment and water samples. Nuclear
55 production of ^{14}C involves formation by neutron activation as consequence of
56 a nuclear chain reaction, which may either take place naturally or artificially.
57 The only place on Earth, where nuclear fission has occurred naturally, was
58 reported to be occurring about 1.7 billion years ago in Oklo, Gabon (Nuclear
59 Wastes in the Arctic report, 1995). However, such natural reactors cannot be
60 active anymore today, as the relative abundance of fissile ^{235}U has now
61 decayed below that required threshold for a sustainable nuclear reaction
62 chain.

63 The Arctic Ocean has been used as a disposal area for radioactive
64 wastes (Nuclear Wastes in the Arctic report, 1995, Johnson-Pyrtle and Scott,
65 1991). We therefore believe that anthropogenic nuclear contamination is the
66 most likely explanation for these ^{14}C -enriched CH_4 background contribution.
67 Similar cases but with slightly lower values have been observed in gas
68 samples from marine basins along the Californian coast (Kessler et al., 2008).
69 We suggest that nuclear anthropogenic contamination could have been
70 laterally transported from thawing terrestrial permafrost in the pore-water of
71 the thawing subsea permafrost in the form of CH_4 or of one of its precursors
72 (e.g. dissolved inorganic carbon) to our drilling site and further on the shelf.
73 Note that more data, e.g. of other radionuclides would be essential to confirm
74 this interpretation.

75 We exclude a possible contamination during sampling, extraction and
76 analysis, because no radioactive tracers were used during the sampling
77 expeditions. The samples affected by enriched ^{14}C values were not sampled
78 in a similar manner. The sediment samples were drilled from the ice in 2011
79 while the shelf edge water samples were sampled in 2012 from a ship
80 together with other water and surface sediment samples showing no
81 enrichment in ^{14}C values. For the rest of the sampling and analysis process,
82 all samples were handled in a similar way and measured in a random order,
83 but only samples from these two specific locations show highly enriched ^{14}C
84 values. None of the reference and blank measurements were abnormal either.

85
86
87
88

SUPPLEMENTARY REFERENCES

Comment [C3]: The reference list has been revised

89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113

Baudin, G., Blain, C., Hagemann, R., Kremer, M., Lucas, M., Merlivat, L., Molina, R., Nieff, G., Prost Marechal, P., Regnaud, F. & Roth, E.: Quelques données nouvelles sur les réactions nucléaires en chaîne qui se sont produites dans le gisement d'Oklo, C.R. Acad. Sci. Paris, 275D, 2291, 1973.

Fireman, E. L.: Carbon-14 in lunar soil and in meteorites, Proc. Lunar Planet. Sci. Conf. 9th, 1647-1654, 1978.

Johnson-Pyrtle, A. and Scott, M.R.: Distribution of ¹³⁷Cs in the Lena River Estuary-Laptev Sea System, Marine Pollution Bulletin Vol. 42, No. 10, pp. 912-926, 2001.

Kessler, J. D., Reeburgh, W.S., Valentine, D.L., Kinnaman, F.S., Peltzer, E.T., Brewer, P.G., Southon, J. & Tyler, S.C.: A survey of methane isotope abundance (¹⁴C, ¹³C, ²H) from five nearshore marine basins that reveals unusual radiocarbon levels in subsurface waters, J. Geophys. Res., 113, C12021, 2008.

Nuclear Wastes in the Arctic: An Analysis of Arctic and Other Regional Impacts from Soviet Nuclear Contamination, OTA-ENV-623 (Washington, DC: U.S. Government Printing Office, September), 1995.

114
115

SUPPLEMENTARY FIGURES AND TABLE

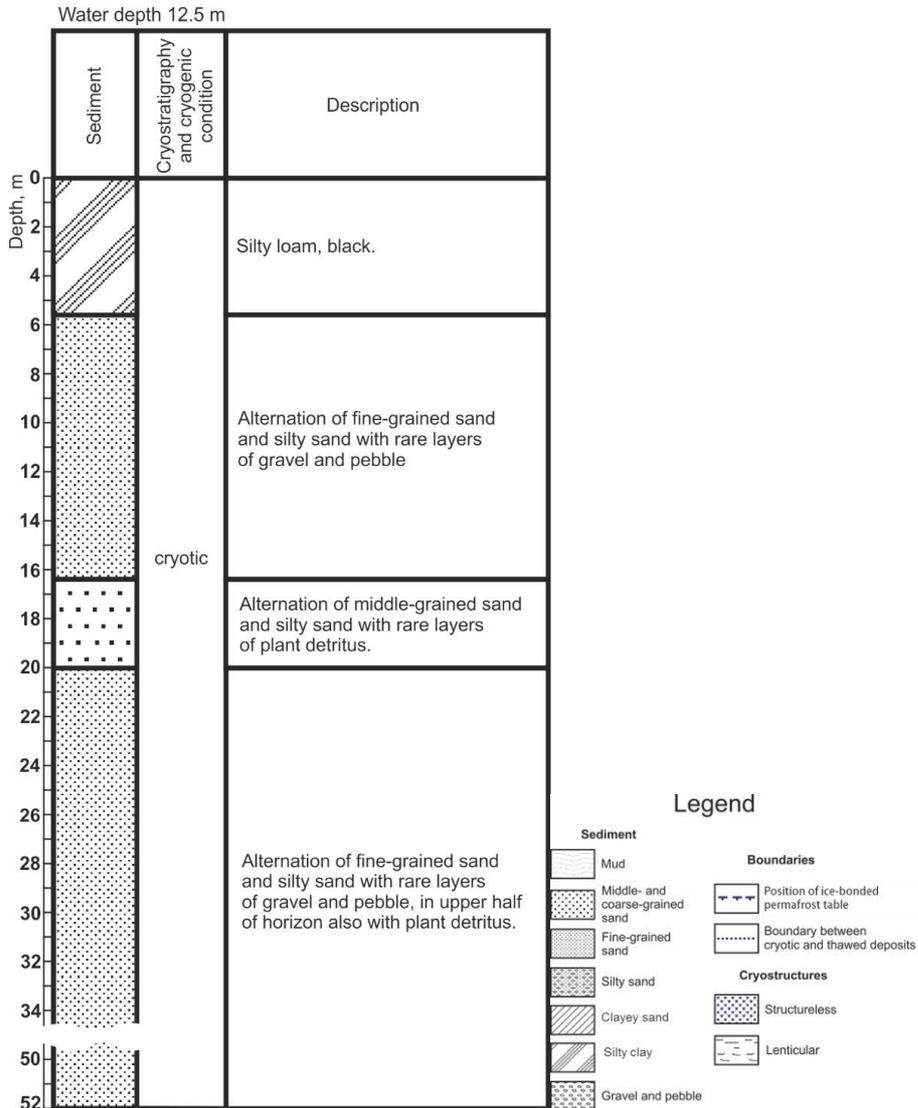
Comment [C4]: Table S1 and Fig. S1-S4 have been revised.

Borehole/shelf area of sampling	Latitude	Longitude	Water depth, m	Water temperature surface/bottom	Water salinity surface/bottom	Time since inundation	Distance from the shore, km
ID-11	71,6926	130,3669	12.5	-0.52/-0.92	10.8/19.4	~8÷7 kyr BP	18.6 km from Muostakh Isl and 39.8 km from Bykovsky Peninsula
IID-13	71,6288	129,8534	2.5	-0.41/-0.61	12.8/13.2	~7÷6 kyr BP	2.5 km
IID-13	71,6219	129,8517	4.1	-0.40/-0.61	12.8/13.2	~7÷6 kyr BP	2.5 km
VD-13	71,7449	129,4048	3.6	-1.01/-1.03	22.6/22.6	Lagoon, ~7÷6 kyr BP (Romanovsky et al., 1999)	Lagoon adjacent to the coast
Lena Delta Str. 42* 47* 70** 71**	72,977 72,427 72,687 72,683	130,141 130,151 130,640 130,267	12.5 8.5 20 12	3.74/1.42 4.42/2.53 2.40/2.83 1.02/2.47	16.3/22.3 0.5/4.6 19.0/21.5 9.0/19.1	~7÷6 kyr BP	-
Dmitry Laptev Str. 31* 36* 79** 80** 81** 82** 83** 84** 85**	72,882 73,118 73,030 73,169 73,316 73,297 73,104 72,930 72,886	140,620 139,517 139,393 139,574 139,768 140,085 140,352 140,619 140,643	15.5 13.5 15.0 15 9 11 14 12 24	3.38/3.76 3.30/3.44 1.92/3.04 1.67/2.42 1.85/1.79 1.6/1.46 1.75/2.19 1.77/1.77 1.69/1.77	18.7/20.3 19.8/24.0 19.8/23.3 19.3/26.7 18.6/24.8 24.17/26.4 20.3/26.5 21.1/21.1 20.8/20.9	~8÷7 kyr BP	-
Buor-Khaya Gulf	Drilling sites					~8÷7 kyr BP	-
Shelf edge Sts. 9* 13* 28** 32** 36** 37**	76,897 76,894 77,000 77,029 76,398 76,648	127,8047 127,8032 125,985 127,289 125,051 125,048	62 63 91 74 62 70	3.54/-1.33 3.47/-1.40 3.87/-0.82 3.00/-1.21 1.26/-1.17 1.89/-1.19	28.0/33.4 29.1/33.3 28.8/34.4 21.9/34.2 19.0/34.1 17.3/34.2	~15÷13 kyr BP	-

116
117

Table S1: Coordinates, bathymetry, temperature, salinity, distance from the coast and inundation time for all sample locations.

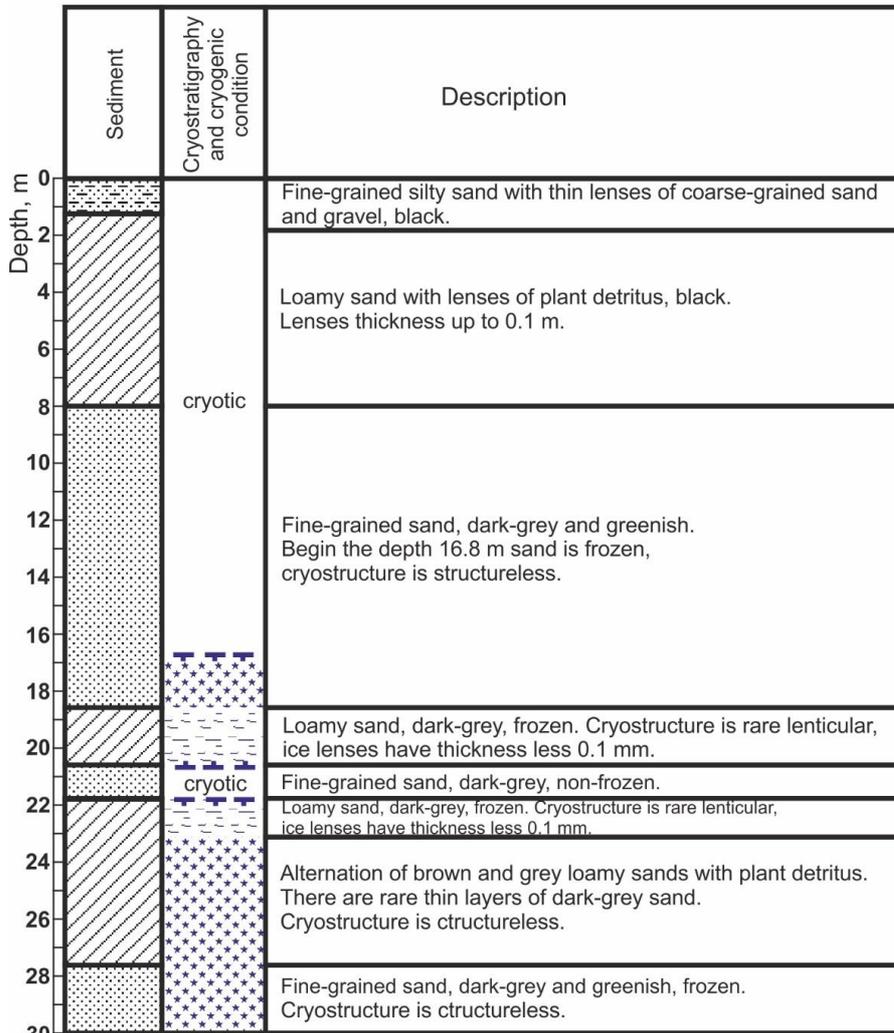
118
119
120
121
122



123
124
125
126
127

Figure S1: Lithology and cryostratigraphy of the sediment core recovered from the borehole ID-11 in the near-shore zone of the ESAS. Ice-bonded permafrost table was not reached during the drilling. The sediments from 0 to 52 m below the seafloor were cryotic, that is unfrozen under temperatures <0°C.

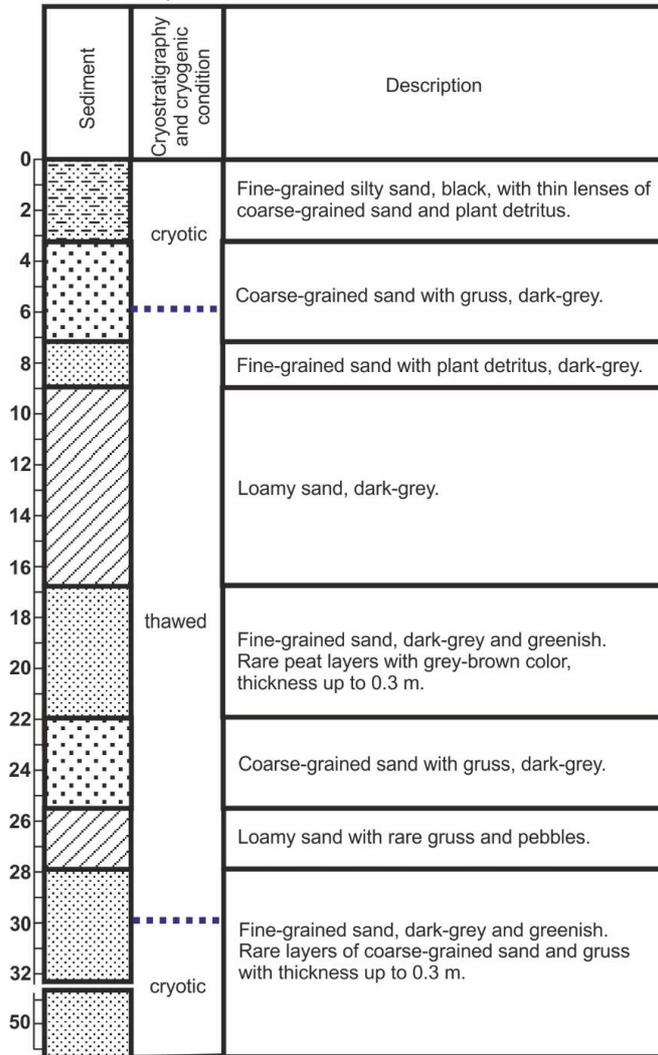
Water depth 2.5 m



128
 129 **Figure S2. Lithology and cryostratigraphy of the sediment core recovered from the borehole IID-13**
 130 **in the near-shore zone of the ESAS. Ice-bonded permafrost table was reached at 16.4 m below the**
 131 **seafloor during the drilling. The sediments from 0 m to 16.4 m below the seafloor were cryotic, that**
 132 **is unfrozen under temperatures <0°C. A thin layer (1.2 m) of cryotic sediments was also observed**
 133 **at depth of 20.5 m below the seafloor. Legends, see Fig. S1.**

134

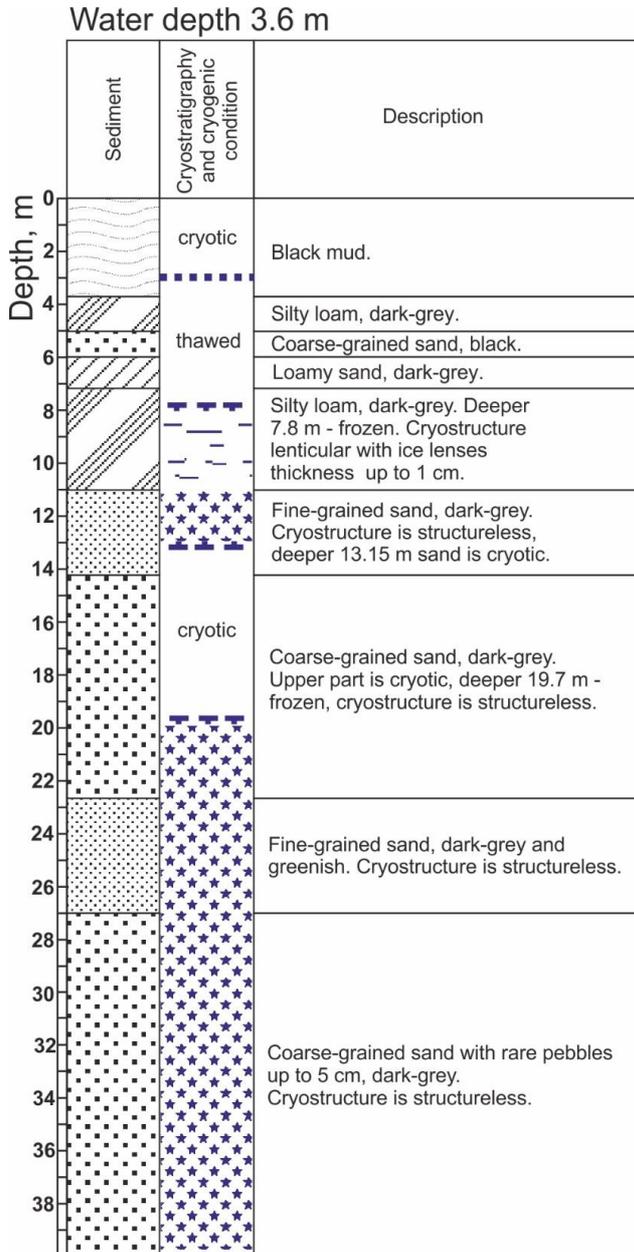
Water depth 4.1 m



135
136
137
138
139
140

Figure S3. Lithology and cryostratigraphy of the sediment core recovered from the borehole IID-13 in the near-shore zone of the ESAS. Ice-bonded permafrost table was not reached during the drilling. The sediments from 0 m to 51 m below the seafloor were cryotic from 0 to 6 m below the seafloor; thawed (that is unfrozen under temperatures >0°C) from 6 to 30 m below the seafloor and cryotic from 30 to 51 m below the seafloor. Legends, see Fig. S1.

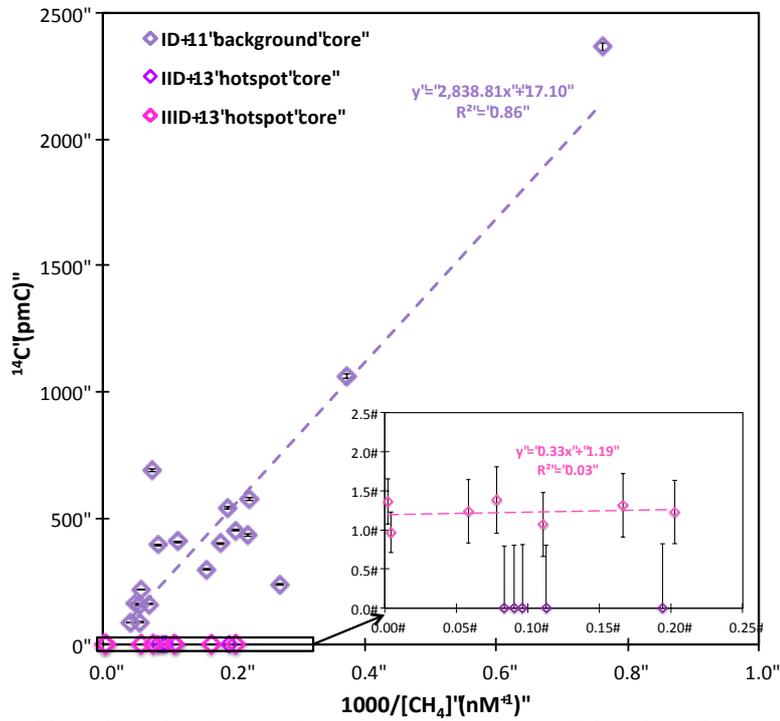
141



142
143
144
145
146
147

Figure S4. Lithology and cryostratigraphy of the sediment core recovered from the borehole VD-13 in the near-shore zone of the ESAS. Ice-bonded permafrost table was reached at 7.8m below the seafloor during the drilling. The sediments from 0 m to 3 m below the seafloor were cryotic; from 3 to 7.8 - frozen; within frozen sediments, the layer of cryotic sediments was observed from 13 to 19.5 m below the seafloor. Legends, see Fig. S1.

148
149



150
 151
 152
 153
 154
 155
 156
 157
 158
 159
 160
 161
 162
 163
 164
 165
 166
 167
 168
 169
 170
 171
 172
 173
 174
 175

Figure S5: Keeling plot: inverse CH₄ concentration versus ¹⁴C data for sediment samples in the partially thawed subsea permafrost. The diamonds are “deep” core sediment data and the dashed lines represent the linear regressions for the ID-11 (purple) and IID-13 (pink) cores. All values of the IID-13 core are close to zero so no linear regression line is depicted for this core. The intersections with the y-axis correspond to the ¹⁴C pmC values of the main CH₄ substrate.