

Notes on Sapart et al. *The origin of methane in the East Siberian Arctic Shelf unraveled with triple isotope analysis*

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.

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.

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.

l. 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).

l. 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.

ll. 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".

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

ll.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?

l. 78: change "and" to "or"

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.

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

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.

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

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?

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.

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.

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

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

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.

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 ¹⁴C.

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.

L 206: There is no section 3.1.

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

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?

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.

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.

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

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.

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 deep-production hypothesis, and a short discussion could be extracted from the SI and incorporated here in the main text.

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.

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

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.

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 δ -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.

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?

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

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.

ll. 295-297: The Overduin paper reports similar concentrations in the thawed 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.

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.

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

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?

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.

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

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.

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

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.

I. 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.

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

II. 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).

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

I. 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.

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

II. 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.

II. 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.

II. 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.

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?

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.

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

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.

Supplementary Information:

This entire first section is not useful. Probably best if the core descriptions were removed and perhaps moved to the main text. 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. If the permafrost was formed subaerially then it is likely that the ice will have very low salinities. This is certainly indicated by the δ -D values of the deeper CH₄.

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.

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).

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.

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