

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 δD 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. Long term 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.

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.

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.

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

Introduction

In general a short introduction in using $\delta^{13}\text{C}$ and δD values is needed

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

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)

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

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 Prinzhover and Pernaton 1997. 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

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

Methods

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

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

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 223 and 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.

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.

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

Line 310 ¹⁴C values show old carbon, not clear that it is old methane

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.

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

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

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