

Author response:

We thank the Associate Editor for her comments and have edited the manuscript (yellow highlight) in accordance with the her suggestion. We clarify that we are not hypothesizing that contamination during or after sample collection is what occurred, but rather we are arguing that it is a valid option (along with environmental release), which procedural quality control measures would exclude or identify. We have also added an Abstract, cut from our original cover letter, which should also help to make this position clear while also summarizing the comment.

We have also added reference to the ^{14}C - CH_4 methodology for natural waters developed by Dean et al. (2017), which we neglected to include in the initial submission.

Lastly, in the third paragraph, we include a sentence cut from our response to RC1, which clearly points out that because a data table containing methane concentration, stable isotope, and radiocarbon information for each sample is not in the article, readers are again blocked from drawing independent conclusions related to this data.

Thank you,

Katy Sparrow and John Kessler

1 **Comment on “The origin of methane in the East Siberian Arctic Shelf unraveled with triple**
2 **isotope analysis,” by Sapart et al. (2017)**

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8 **Abstract**

9 In this comment, we outline two major concerns regarding some of the key data presented in this
10 paper. Both of these concerns are associated with the natural abundance radiocarbon-methane
11 ($^{14}\text{C-CH}_4$) data. First, no systematic methodology is presented, nor previous peer-reviewed
12 publication referenced, for how these samples were collected, prepared, and ultimately analyzed
13 for $^{14}\text{C-CH}_4$. Not only are these procedural details missing, but the critical evaluation of them
14 using gaseous and aqueous blanks and standards was omitted although these details are essential
15 for any reader to evaluate the quality of data and subsequent interpretations. Second, due to the
16 lack of methodological details, the source of the sporadic anthropogenic contamination cannot be
17 determined and thus it is premature for the authors to suggest it was in the natural environment
18 prior to sample collection. As the natural $^{14}\text{C-CH}_4$ data are necessary for the authors' stated
19 scientific objectives of understanding the origin of methane in the East Siberian Arctic Shelf, our
20 comment serves to highlight that the study's objectives have not been met.

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24 In the article titled, “The origin of methane in the East Siberian Arctic Shelf unraveled with triple
25 isotope analysis,” (5 May, p. 2283, doi:10.5194/bg-14-2283-2017), Célia Sapart and coauthors
26 present natural abundance radiocarbon-methane ($^{14}\text{C-CH}_4$) measurements from Laptev Sea
27 sediments and waters alongside methane concentration and methane stable isotope
28 measurements. The authors then draw conclusions about methane source-sink dynamics
29 operating in this arctic shelf sea based upon these methane data. Two concerns with the $^{14}\text{C-CH}_4$
30 data lead us to question whether these data should be used to interpret this natural system.

31 The first issue is that the method used to collect and prepare the $^{14}\text{C-CH}_4$ samples is inadequately
32 described by Sapart et al. and there is no quality control data presented. Radiocarbon-methane is
33 not a routine measurement in natural waters because of the challenges associated with sampling
34 and preparing a trace isotope of a trace gas. In the methods section of the article, the authors cite
35 two techniques that relate only to the ^{14}C -accelerator mass spectrometry (AMS) analysis, while
36 the methodologies used for the sample collection and preparation steps leading up to the ^{14}C
37 analyses of sediment and seawater samples are absent. The natural $^{14}\text{C-CH}_4$ content of a sample
38 can be affected by carbon and CH_4 added from the materials it encounters and by any contact
39 with the atmosphere, so quality control measures are necessary to ensure that a sample is not
40 significantly contaminated prior to analysis and that any minor contamination (i.e. blank
41 addition) is accounted for in the final results. In the supplement, the authors write that, “None of
42 the reference and blank measurements were abnormal,” without presenting any descriptions of or
43 data stemming from these tests. Refereed techniques for collecting and preparing $^{14}\text{C-CH}_4$
44 samples from natural waters (Dean et al., 2017; Elder et al., 2018; Kessler and Reeburgh, 2005;
45 Pack et al., 2015; Pohlman et al., 2000; Sparrow and Kessler, 2017) include detailed qualitative
46 and quantitative descriptions of the measures taken to validate their methodologies. These
47 measures include processing blank (methane-free) waters and treating methane-free gas and
48 methane of known $^{14}\text{C-CH}_4$ content in the same way as samples. As the $^{14}\text{C-AMS}$ measurement
49 error is typically very low relative to $^{14}\text{C-CH}_4$ collection and preparation procedures, we can only
50 assume that the error associated with the processes that most greatly affects the precision,
51 sensitivity, and accuracy of the reported $^{14}\text{C-CH}_4$ signature is unaccounted for by the authors.

52 The second issue that calls the integrity of this study’s $^{14}\text{C-CH}_4$ data into question is the existence
53 of super-modern sediment and water column samples (approaching 100 times above modern) in
54 the dataset. As the authors correctly reference, elevated $^{14}\text{C-CH}_4$ has previously been documented
55 in other ocean waters (Kessler et al., 2008), however, the values presented here are up to 27 times
56 higher than any previously reported elevated value. It is suggested in the main text and in the
57 supplement that the source of the “highly enriched ^{14}C ” is anthropogenic and that it existed in the
58 natural environment prior to sampling. We argue that it is premature to suggest an origin of this
59 enriched ^{14}C , either environmental release or contamination (incurred during sample collection,
60 processing, and/or analysis) when the $^{14}\text{C-CH}_4$ methodological details, with appropriate standards
61 and blanks, are absent from the article. The possibility that the enriched ^{14}C was derived from the
62 sampling equipment, vessel, and/or land-based laboratories was largely dismissed by the authors,
63 while we attest that it is a valid option. The authors discount the possibility that their samples
64 were contaminated during the sampling process, “because no radioactive tracers were used during
65 the sampling expeditions.” This argument is untenable because the half-life of ^{14}C is 5730 years,
66 meaning any surface contamination will persist for tens of thousands of years—well beyond the

67 specific project where it was used. In addition, the authors highlight that, for sediment samples,
68 “the higher ^{14}C values correspond to the lower CH_4 concentrations,” to suggest that a small
69 amount of radioactive contamination in the environment was added to a variable background of
70 naturally occurring CH_4 , which would most greatly affect the ^{14}C signature of the smallest sized
71 (lowest CH_4 concentration) samples. This may be true, but another scenario that is also valid
72 using the same logic is that the contamination was added during the ^{14}C - CH_4 sample collection
73 and/or preparation processes. This relationship was noted for sediment samples, but we are not
74 informed in the article or supplement on the relationship between CH_4 concentration and ^{14}C - CH_4
75 content for the seawater samples. The lack of a data table containing the specific triple-isotope
76 information for each CH_4 sample, in the article or in a data repository, has the effect of making
77 this study unnecessarily opaque for a reader attempting to draw conclusions for themselves. The
78 authors clearly state that additional experiments are necessary to determine the unknown origin of
79 this isotopic enrichment, however, without that complimentary data, or at least data that proves it
80 was in the sediments and waters prior to sample collection, its presence invalidates all ^{14}C - CH_4
81 data presented in this study from contributing to our understanding of methane dynamics in the
82 Arctic Ocean.

83 In a recently published study, we demonstrate how useful natural abundance ^{14}C - CH_4
84 measurements can be towards understanding the role of ancient sources of methane in arctic shelf
85 seas (Sparrow et al., 2018). Importantly, in this study, we find that the stable isotope ($\delta^{13}\text{C}$ - CH_4)
86 and dissolved CH_4 concentration data, together, would suggest an entirely different (and, we
87 argue, incorrect) interpretation of this system, which attests to the importance of ^{14}C - CH_4
88 measurements for investigations into the origins of methane. When conducting natural abundance
89 ^{14}C - CH_4 studies, it is imperative that we do so using peer review published methods with
90 appropriate radiocarbon blanks and standards; otherwise, interpretations made from ^{14}C - CH_4 data
91 are unverifiable and inconclusive.

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