



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

36 The first issue is that the method used to collect and prepare the  $^{14}\text{C}$ - $\text{CH}_4$  samples is inadequately  
37 described by Sapart et al. and there is no quality control data presented. Radiocarbon-methane is  
38 not a routine measurement in natural waters because of the challenges associated with sampling  
39 and preparing a trace isotope of a trace gas. In the methods section of the article, the authors cite  
40 two techniques that relate only to the  $^{14}\text{C}$ -accelerator mass spectrometry (AMS) analysis, while  
41 the methodologies used for the sample collection and preparation steps leading up to the  $^{14}\text{C}$   
42 analyses of sediment and seawater samples are absent. The natural  $^{14}\text{C}$ - $\text{CH}_4$  content of a sample  
43 can be affected by carbon and  $\text{CH}_4$  added from the materials it encounters and by any contact  
44 with the atmosphere, so quality control measures are necessary to ensure that a sample is not  
45 significantly contaminated prior to analysis and that any minor contamination (i.e. blank  
46 addition) is accounted for in the final results. In the supplement, the authors write that, “None of  
47 the reference and blank measurements were abnormal,” without presenting any descriptions of or  
48 data stemming from these tests. Refereed techniques for collecting and preparing  $^{14}\text{C}$ - $\text{CH}_4$   
49 samples from natural waters (Elder et al., 2018; Kessler and Reeburgh, 2005; Pack et al., 2015;  
50 Pohlman et al., 2000; Sparrow and Kessler, 2017) include detailed qualitative and quantitative  
51 descriptions of the measures taken to validate their methodologies. These measures include  
52 processing blank (methane-free) waters and treating methane-free gas and methane of known  
53  $^{14}\text{C}$ - $\text{CH}_4$  content in the same way as samples. As the  $^{14}\text{C}$ -AMS measurement error is typically  
54 very low relative to  $^{14}\text{C}$ - $\text{CH}_4$  collection and preparation procedures, we can only assume that the  
55 error associated with the processes that most greatly affects the precision, sensitivity, and  
56 accuracy of the reported  $^{14}\text{C}$ - $\text{CH}_4$  signature is unaccounted for by the authors.

57 The second issue that calls the integrity of this study’s  $^{14}\text{C}$ - $\text{CH}_4$  data into question is the existence  
58 of super-modern sediment and water column samples (approaching 100 times above modern) in  
59 the dataset. As the authors correctly reference, elevated  $^{14}\text{C}$ - $\text{CH}_4$  has previously been documented  
60 in other ocean waters (Kessler et al., 2008), however, the values presented here are up to 27 times  
61 higher than any previously reported elevated value. It is suggested in the main text and in the  
62 supplement that the source of the “highly enriched  $^{14}\text{C}$ ” is anthropogenic and that it existed in the  
63 natural environment prior to sampling, but the possibility that it was derived from the sampling  
64 equipment, vessel, and/or laboratory was not fully explored. The authors discount the possibility  
65 that their samples were contaminated during the sampling process, “because no radioactive  
66 tracers were used during the sampling expeditions.” This argument is untenable because the half-  
67 life of  $^{14}\text{C}$  is 5730 years, meaning any surface contamination will persist for tens of thousands of  
68 years—well beyond the specific project where it was used. In addition, the authors highlight that,  
69 for sediment samples, “the higher  $^{14}\text{C}$  values correspond to the lower  $\text{CH}_4$  concentrations,” to  
70 suggest that a small amount of radioactive contamination in the environment was added to a



71 variable background of naturally occurring CH<sub>4</sub>, which would most greatly affect the <sup>14</sup>C  
72 signature of the smallest sized (lowest CH<sub>4</sub> concentration) samples. This may be true, but another  
73 scenario that is also valid using the same logic is that the contamination was added during the  
74 <sup>14</sup>C-CH<sub>4</sub> sample collection and/or preparation processes. This relationship was noted for sediment  
75 samples, but we are not informed in the article or supplement on the relationship between CH<sub>4</sub>  
76 concentration and <sup>14</sup>C-CH<sub>4</sub> content for the seawater samples. The authors clearly state that  
77 additional experiments are necessary to determine the unknown origin of this isotopic  
78 enrichment, however, without that complimentary data, or at least data that proves it was in the  
79 sediments and waters prior to sample collection, its presence invalidates all <sup>14</sup>C-CH<sub>4</sub> data  
80 presented in this study from contributing to our understanding of methane dynamics in the Arctic  
81 Ocean.

82 In a recently published study, we demonstrate how useful natural abundance <sup>14</sup>C-CH<sub>4</sub>  
83 measurements can be towards understanding the role of ancient sources of methane in arctic shelf  
84 seas (Sparrow et al., 2018). Importantly, in this study, we find that the stable isotope (δ<sup>13</sup>C-CH<sub>4</sub>)  
85 and dissolved CH<sub>4</sub> concentration data, together, would suggest an entirely different (and, we  
86 argue, incorrect) interpretation of this system, which attests to the importance of <sup>14</sup>C-CH<sub>4</sub>  
87 measurements for investigations into the origins of methane. When conducting natural abundance  
88 <sup>14</sup>C-CH<sub>4</sub> studies, it is imperative that we do so using peer review published methods with  
89 appropriate radiocarbon blanks and standards; otherwise, interpretations made from <sup>14</sup>C-CH<sub>4</sub> data  
90 are unverifiable and inconclusive.

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## 106 References

- 107 Elder, C. D., Xu, X., Walker, J., Schnell, J. L., Hinkel, K. M., Townsend-Small, A., Arp, C. D.,  
108 Pohlman, J. W., Gaglioti, B. V., and Czimczik, C. I.: Greenhouse gas emissions from diverse  
109 Arctic Alaskan lakes are dominated by young carbon, *Nat. Clim. Change*, 8, 166-171,  
110 <https://doi.org/10.1038/s41558-017-0066-9>, 2018.
- 111 Kessler, J. D. and Reeburgh, W. S.: Preparation of natural methane samples for stable isotope and  
112 radiocarbon analysis, *Limnol. Oceanogr.: Methods*, 3, 408–418, doi:10.4319/lom.2005.3.408,  
113 2005.
- 114 Kessler, J. D., Reeburgh, W. S., Valentine, D. L., Kinnaman, F. S., Peltzer, E. T., Brewer, P. G.,  
115 Southon, J., and Tyler, S. C.: A survey of methane isotope abundance ( $^{14}\text{C}$ ,  $^{13}\text{C}$ ,  $^2\text{H}$ ) from five  
116 nearshore marine basins that reveals unusual radiocarbon levels in subsurface waters, *J. Geophys*  
117 *Res.: Oceans*, 113, C12021, doi:10.1029/2008JC004822, 2008.
- 118 Pack, M. A., Xu, X., Lupascu, M., Kessler, J. D., and Czimczik, C. I.: A rapid method for  
119 preparing low volume  $\text{CH}_4$  and  $\text{CO}_2$  gas samples for  $^{14}\text{C}$ -AMS analysis, *Org. Geochem.*, 78, 89–  
120 98, <http://dx.doi.org/10.1016/j.orggeochem.2014.10.010>, 2015.
- 121 Pohlman, J. W., Knies, D. L., Grabowski, K. S., DeTurck, T. M., Treacy, D. J., Coffin, R. B.:  
122 Sample distillation/graphitization system for carbon pool analysis by accelerator mass  
123 spectrometry (AMS), *Nucl. Instrum. Methods Phys. Res., Sect. B*, 172 (1–4), 428–433,  
124 doi:10.1016/S0168-583X(00)00153-1, 2000.
- 125 Sparrow, K. J. and Kessler, J. D.: Efficient collection and preparation of methane from low  
126 concentration waters for natural abundance radiocarbon analysis, *Limnol. Oceanogr.: Methods*,  
127 15, 601–617, doi:10.1002/lom3.10184, 2017.
- 128  
129 Sparrow, K. J., Kessler, J. D., Southon, J. R., Garcia-Tigreros, F., Schreiner, K. M., Ruppel, C.  
130 D., Miller, J. B., Lehman, S. J., and Xu, X.: Limited contribution of ancient methane to surface  
131 waters of the U.S. Beaufort Sea shelf, *Sci. Adv.*, 4, eaao4842, doi:10.1126/sciadv.aao4842, 2018.