

## CLIMATOLOGY

## Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf

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In response to warming climate, methane can be released to Arctic Ocean sediment and waters from thawing subsea permafrost and decomposing methane hydrates. However, it is unknown whether methane derived from this sediment storehouse of frozen ancient carbon reaches the atmosphere. We quantified the fraction of methane derived from ancient sources in shelf waters of the U.S. Beaufort Sea, a region that has both permafrost and methane hydrates and is experiencing significant warming. Although the radiocarbon-methane analyses indicate that ancient carbon is being mobilized and emitted as methane into shelf bottom waters, surprisingly, we find that methane in surface waters is principally derived from modern-aged carbon. We report that at and beyond approximately the 30-m isobath, ancient sources that dominate in deep waters contribute, at most,  $10 \pm 3\%$  of the surface water methane. These results suggest that even if there is a heightened liberation of ancient carbon-sourced methane as climate change proceeds, oceanic oxidation and dispersion processes can strongly limit its emission to the atmosphere.

## INTRODUCTION

Methane ( $\text{CH}_4$ ) emissions from Arctic Ocean shelf seas are anomalously large relative to those of the global mean ocean (1–4), but the source of these emissions remains largely unknown. Permafrost, which contains perennially frozen ancient carbon (C) (5), and  $\text{CH}_4$  hydrate, an ice-like form of  $\text{CH}_4$  that is principally ancient and older than surrounding sediment (6), are often invoked as likely sources because both constitute large C reservoirs and can be converted to  $\text{CH}_4$  gas as a result of warming climate. Although the global atmospheric  $\text{CH}_4$  inventory is increasing, arctic  $\text{CH}_4$  growth rates are comparable to or less than the global average (7) and appear to be derived mainly from biogenic sources (2, 8, 9). Ancient C stores, including arctic permafrost and hydrates, were recently determined to have contributed  $\leq 19\%$  of the  $\text{CH}_4$  released to the atmosphere during the Younger Dryas–Preboreal abrupt warming event (10), an analog to climate change today. Because of residual, fundamental unknowns about  $\text{CH}_4$  emissions from permafrost and hydrates, this potentially catastrophic climatological feedback has been absent from most Earth system models (5, 11).

Previous studies of  $\text{CH}_4$  dynamics in Arctic Ocean continental margins have measured atmospheric  $\text{CH}_4$  mole fractions ( $[\text{CH}_4]$ ), dissolved  $[\text{CH}_4]$ , and dissolved stable C isotopes ( $\delta^{13}\text{C}-\text{CH}_4$ ) to document emissions from the seafloor to the water column and from the water column to the atmosphere (1–4, 12–16). Because no study has conclusively fingerprinted the source of this  $\text{CH}_4$ , it is unknown what fraction emitted to the atmosphere from the shallow arctic shelf seas is derived from ancient C sources. These ancient C  $\text{CH}_4$  sources are terrestrial and

subsea permafrost via the biological transformation of thawed organic C (5), subsea permafrost-associated  $\text{CH}_4$  hydrates (6), and geologic  $\text{CH}_4$ . Methane sources to seawater derived from modern-aged C include the atmosphere (17) and in situ production from more modern-aged substrates (12, 18).

Ancient and modern C-sourced  $\text{CH}_4$  can be readily distinguished with natural abundance  $^{14}\text{C}-\text{CH}_4$  measurements, as radioactive decay leaves ancient C sources substantially depleted in  $^{14}\text{C}$  with respect to modern C sources. Thermonuclear weapons and nuclear power generation have introduced anthropogenic  $^{14}\text{C}$  into atmospheric and oceanic  $\text{CH}_4$  (17, 19). We collected dissolved  $^{14}\text{C}-\text{CH}_4$  samples to test the hypotheses that (i) ancient C sources contribute  $\text{CH}_4$  to Arctic Ocean continental shelf waters and (ii) the contribution of ancient C sources to surface water and atmospheric  $\text{CH}_4$  in this environment diminishes as proximity to these sources decreases (that is, as water depth and distance from shore increase). Without newly developed techniques (Materials and Methods) (20), testing these hypotheses would not have been possible due to the challenge of collecting sufficient quantities of  $\text{CH}_4$  for natural abundance  $^{14}\text{C}-\text{CH}_4$  analysis in surface waters (1, 3, 4, 12, 13, 15, 16).

## RESULTS AND DISCUSSION

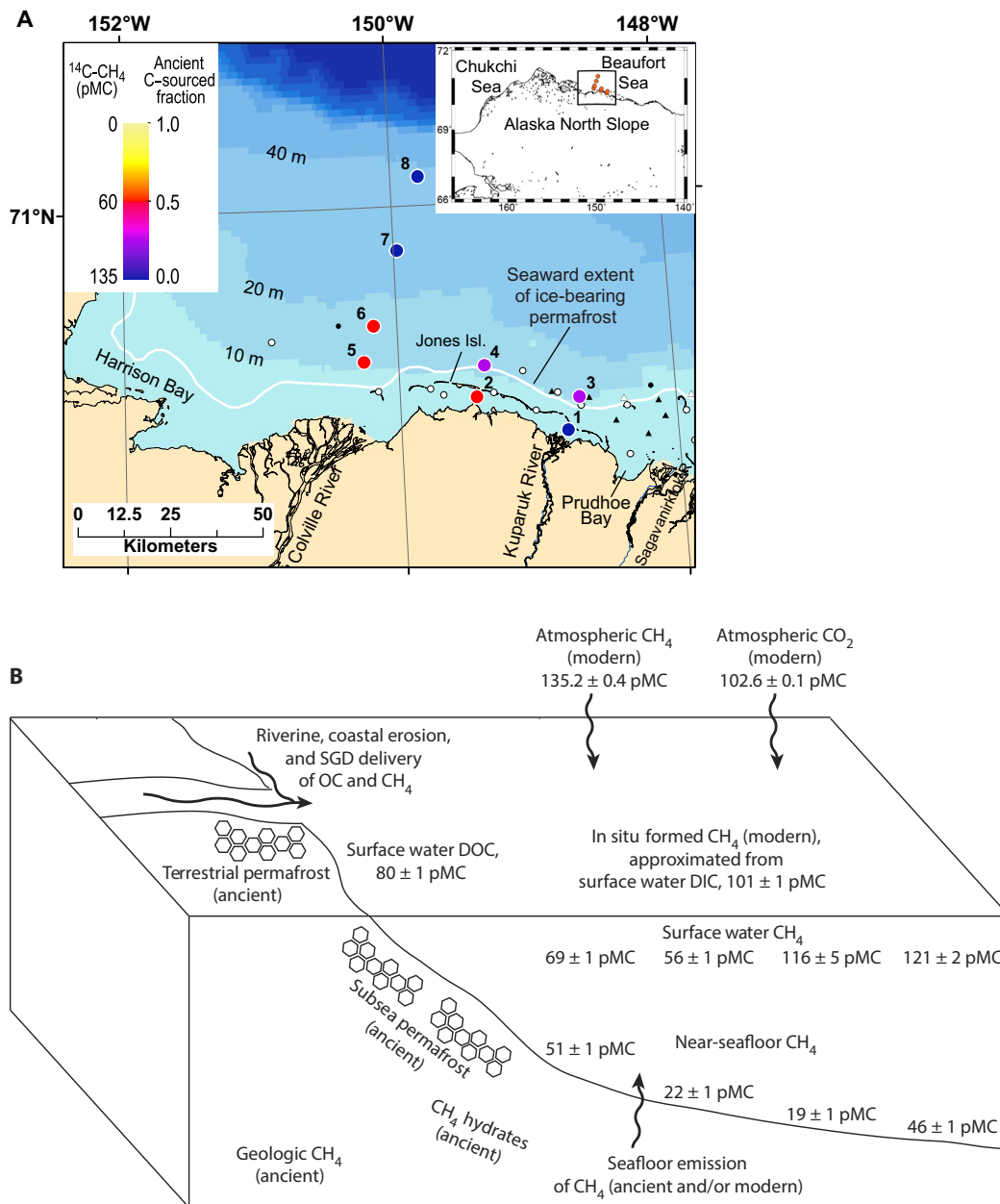
The continental shelf offshore Prudhoe Bay, AK, in the U.S. Beaufort Sea was chosen as an ideal site to assess the input of ancient C-sourced  $\text{CH}_4$  to surface waters (Fig. 1A). Figure 1B illustrates the components of the Prudhoe Bay system schematically, including  $^{14}\text{C}$  measurements of dissolved  $\text{CH}_4$  and possible ancient and modern endmembers. The seaward extent of persistent subsea ice-bonded permafrost in this shelf sea, which was unglaciated land during the Late Pleistocene, has been determined from seismic reflection analysis (21) and verified with direct evidence from borehole well data (Fig. 1A) (22). Gas hydrates may occur within and beneath permafrost in this passive margin shelf (22) and may dissociate to release  $\text{CH}_4$  even after the permafrost matrix has thawed (6). Terrestrial peat and permafrost soils (5, 23, 24), including yedoma permafrost (25), are other potential sources of ancient  $\text{CH}_4$  delivered to the shelf by rivers [mainly the Colville and Mackenzie rivers (24)], coastal erosion, and submarine groundwater discharge

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**Fig. 1. Surface water  $^{14}\text{C}\text{-CH}_4$  data and potential  $\text{CH}_4$  endmembers in the U.S. Beaufort Sea shelf study area. (A)** Station map showing both the  $^{14}\text{C}\text{-CH}_4$  data in units of percent Modern Carbon (pMC), with the atmosphere in 1950 defined as 100 pMC (33, 34), as well as the calculated fraction of ancient C-sourced  $\text{CH}_4$  ( $f_c$ ) (Eqs. 1 to 5) in surface waters at each station. The white curve is the bulk sediment velocity contour (2000 m/s) used to delineate the seaward boundary of the sedimentary section that contains substantial (up to 29%) ice-bearing permafrost in the upper ~600 m (21). White circles and triangles respectively show boreholes (hundreds of meters deep) and geotechnical borings (<100 m) that contain permafrost based on an analysis of well logs and recovery of permafrost samples, respectively (22). Black circles and triangles respectively indicate no permafrost inferred or found in deep boreholes and geotechnical borings (22). **(B)** System schematic showing  $^{14}\text{C}$  values of dissolved  $\text{CH}_4$  (stations 5 to 8) and possible ancient and modern endmembers that were also measured here. SGD, submarine groundwater discharge; OC, organic carbon; DOC, dissolved organic carbon.

(26) (Fig. 1B). Rates of both terrestrial permafrost degradation near the Colville River and erosion along the area's permafrost-dominated coastline have been increasing in recent years (27, 28). Atmospheric  $\text{CH}_4$  in this system (and globally, as described above) has a  $^{14}\text{C}$  activity above modern because the atmosphere is both the site of natural  $^{14}\text{C}$  production and influenced by  $^{14}\text{C}$ -enriched  $\text{CH}_4$  produced by nuclear reactors (17). A second modern  $\text{CH}_4$  source in the system is in situ

aerobic methanogenesis associated with the production and decomposition of phytoplankton biomass (12, 18), which we assume is similar to the measured  $^{14}\text{C}$  content of dissolved inorganic carbon (DIC) in surface waters (Fig. 1B). Anaerobic methanogenesis from the metabolism of recently fixed organic matter in sediment (29) is also a potential source of modern methane, but the substrate must be modern and not from one of the ancient C sources highlighted above. For this reason,

we assume that this third potential modern CH<sub>4</sub> source has a <sup>14</sup>C content similar to that of DIC in surface waters (Fig. 1B).

Although these disparate sources can contribute CH<sub>4</sub> to the Beaufort Sea shelf (Fig. 1B), a plot of <sup>14</sup>C-CH<sub>4</sub> versus the reciprocal of molar [CH<sub>4</sub>], a so-called Keeling plot (30, 31), displays surprising linearity for a complex system ( $R^2 = 0.75$ ) (Fig. 2). The relationship is statistically significant ( $P < 0.01$ ) and suggests that the observed (“obs”) system can be largely described as a mixture of modern background (“bkg”) and an ancient source (“s”); this result does not exclude the possibility that multiple sources of CH<sub>4</sub> may contribute to the source and/or the background values, but it does suggest that potential CH<sub>4</sub> endmembers can be linearly combined to establish a pseudo-two-component mixture

$$c_{\text{obs}} = c_{\text{bkg}} + c_s \quad (1)$$

$$^{14}\text{C}_{\text{obs}}c_{\text{obs}} = ^{14}\text{C}_{\text{bkg}}c_{\text{bkg}} + ^{14}\text{C}_s c_s \quad (2)$$

where “c” is [CH<sub>4</sub>] and “<sup>14</sup>C” is <sup>14</sup>C-CH<sub>4</sub> content. Combining and rearranging Eqs. 1 and 2 yields a linear equation (Eq. 3), whose y intercept indicates the <sup>14</sup>C-CH<sub>4</sub> content of the source (<sup>14</sup>C<sub>s</sub>) when an infinite amount of source is added (Fig. 2B) (30).

$$^{14}\text{C}_{\text{obs}} = c_{\text{bkg}}(^{14}\text{C}_{\text{bkg}} - ^{14}\text{C}_s)(1/c_{\text{obs}}) + ^{14}\text{C}_s \quad (3)$$

Because the values of both <sup>14</sup>C<sub>obs</sub> and 1/c<sub>obs</sub> contain uncertainty, a standard Model I, linear least squares regression, is inappropriate to determine the y intercept; instead, a Model II, geometric mean regression, is often preferred (31, 32). This analysis is used here (Fig. 2B) and suggests that <sup>14</sup>C<sub>s</sub> equals  $-5.60 \pm 11.22$  percent Modern Carbon (pMC) relative to the 1950 atmosphere, which is defined as 100 pMC (33, 34). Negative values of pMC have no meaning, so <sup>14</sup>C<sub>s</sub> likely ranges from 0 to 5.62 pMC, indicating that ancient sources of CH<sub>4</sub> (zero to low <sup>14</sup>C content,

<<100 pMC) (Fig. 1B) are being added to the background CH<sub>4</sub> in these waters. Although this analysis cannot distinguish between different ancient sources of CH<sub>4</sub>, it does suggest that at least one, if not several, of the ancient sources is contributing CH<sub>4</sub> to this region, confirming previous conjectures (5, 6, 13–16). The background CH<sub>4</sub> to which these ancient sources are added is likely composed of more modern CH<sub>4</sub> ( $\geq 100$  pMC) from the atmosphere ( $135.2 \pm 0.4$  pMC;  $n = 3$ ), in situ aerobic (water column) and anaerobic (sediment) methanogenesis ( $101 \pm 1$  pMC;  $n = 6$ ), or some combination of the three (Fig. 1B).

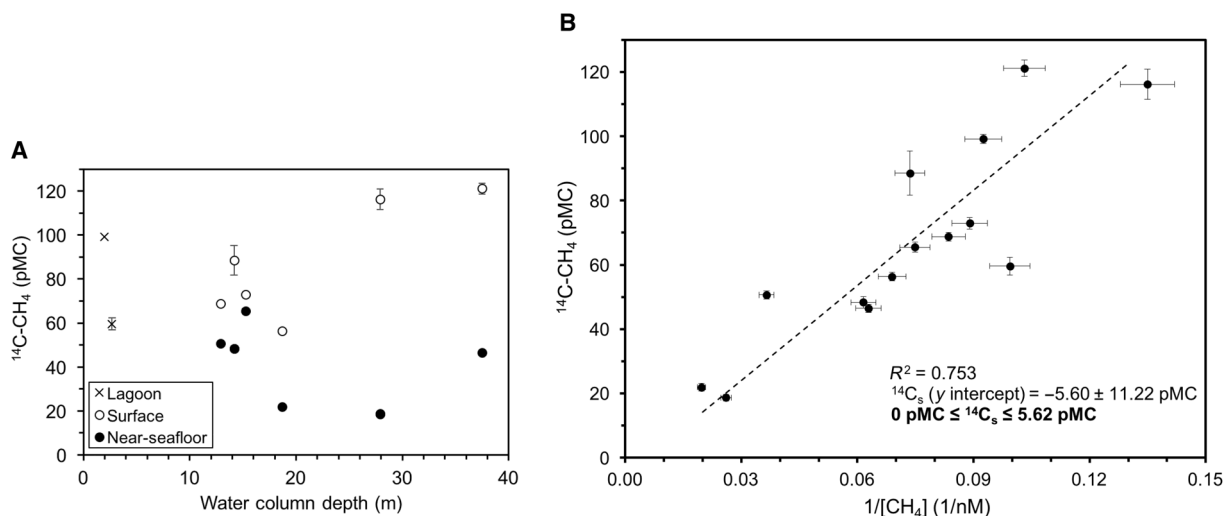
We calculate the fraction of each dissolved CH<sub>4</sub> sample that was derived from the ancient C source ( $f_s$ ) with an isotopic mass balance

$$^{14}\text{C}_{\text{obs}} = ^{14}\text{C}_h(f_h) + ^{14}\text{C}_p(f_p) + ^{14}\text{C}_a(f_a) + ^{14}\text{C}_i(f_i) \quad (4)$$

$$1 = f_h + f_p + f_a + f_i \quad (5)$$

where the radiocarbon content of each CH<sub>4</sub> endmember is represented by the subscripts “h” (hydrate or geologic CH<sub>4</sub>; 0 pMC), “p” (permafrost CH<sub>4</sub>; 5.62 pMC), “a” (atmospheric CH<sub>4</sub>; 135.2 pMC), and “i” (in situ produced CH<sub>4</sub>; 101 pMC) (Fig. 1). Because this isotopic mass balance contains two equations and four unknowns ( $f_h, f_p, f_a,$  and  $f_i$ ), we begin by defining  $f_a$  and  $f_i$  by systematically varying them from 0 to 1 in increments of 0.001, considering all possible combinations. Then, values of  $f_h$  and  $f_p$  are calculated using Eqs. 4 and 5 for each unique combination of  $f_a$  and  $f_i$ . When either  $f_h$  or  $f_p$  is determined to be less than 0 or greater than 1, all values are discarded for that linear combination. The resulting values of  $f_h$  and  $f_p$  are summed to more generally represent  $f_s$  because <sup>14</sup>C<sub>h</sub> and <sup>14</sup>C<sub>p</sub> are assumed on the basis of the results of the Keeling plot (Fig. 2B) and not directly measured; the average and standard deviation of  $f_s, f_a,$  and  $f_i$  are then calculated (Table 1 and Fig. 1A).

In the back-barrier lagoon (stations 1 and 2), where sediment overlies intact subsea permafrost (Fig. 1A) (21, 22), just one “lagoon” <sup>14</sup>C-CH<sub>4</sub> sample was collected per station because of the shallow water depth (<3 m) (Fig. 2A). At each of the six deeper-water stations



**Fig. 2.** <sup>14</sup>C-CH<sub>4</sub> data from each station and Keeling plot analysis. (A) Dissolved <sup>14</sup>C-CH<sub>4</sub> data for stations 1 to 8, plotted by the water depth of the station. The data include lagoon samples (x), surface samples (white circles), and near-seafloor samples (black circles). Error bars that are not visible are smaller than the markers. Uncertainty for <sup>14</sup>C-CH<sub>4</sub> data incorporates the collection, preparation, and measurement uncertainties (20). (B) A Keeling plot (Eq. 3) incorporating [CH<sub>4</sub>] and <sup>14</sup>C-CH<sub>4</sub> measurements from stations 1 to 8 suggests that the system can be viewed as a pseudo-two-component mixture and that the <sup>14</sup>C-CH<sub>4</sub> source signature (<sup>14</sup>C<sub>s</sub>) likely ranges from 0 to 5.62 pMC.

**Table 1. Calculated fractions of ancient and modern C-sourced CH<sub>4</sub> in each sample.**

Station	Water depth (m)	Distance offshore (km)	Sample type	Ancient C-sourced CH <sub>4</sub> fraction, $f_s$	Atmospheric-sourced CH <sub>4</sub> fraction, $f_a$	In situ produced CH <sub>4</sub> fraction, $f_i$
1	2	3	Lagoon	0.18 ± 0.06	0.47 ± 0.18	0.35 ± 0.25
2	3	2	Lagoon	0.50 ± 0.04	0.23 ± 0.12	0.27 ± 0.17
3	14	12	Surface	0.26 ± 0.06	0.37 ± 0.18	0.37 ± 0.24
			Near-seafloor	0.60 ± 0.04	0.18 ± 0.10	0.22 ± 0.13
4	15	10	Surface	0.39 ± 0.05	0.29 ± 0.15	0.33 ± 0.20
			Near-seafloor	0.45 ± 0.05	0.25 ± 0.14	0.30 ± 0.18
5	13	18	Surface	0.42 ± 0.05	0.27 ± 0.14	0.31 ± 0.19
			Near-seafloor	0.58 ± 0.04	0.19 ± 0.10	0.23 ± 0.14
6	19	27	Surface	0.53 ± 0.04	0.21 ± 0.12	0.26 ± 0.16
			Near-seafloor	0.83 ± 0.02	0.07 ± 0.04	0.10 ± 0.06
7	28	48	Surface	0.10 ± 0.03	0.72 ± 0.10	0.18 ± 0.13
			Near-seafloor	0.86 ± 0.02	0.06 ± 0.04	0.08 ± 0.05
8	38	69	Surface	0.07 ± 0.03	0.79 ± 0.07	0.14 ± 0.10
			Near-seafloor	0.61 ± 0.03	0.17 ± 0.10	0.22 ± 0.13

(stations 3 to 8), two <sup>14</sup>C-CH<sub>4</sub> samples were collected: a “surface” sample acquired at 2 m below the sea surface and a “near-seafloor” sample collected 3 to 8 m from the seafloor (table S1 and Fig. 2A).

The δ<sup>13</sup>C-CH<sub>4</sub> and [CH<sub>4</sub>] data associated with each <sup>14</sup>C-CH<sub>4</sub> sample are presented in table S1. The average values for the surface samples [−58 ± 6‰, 11 ± 3 nmol/liter (nM);  $n = 6$ ] are more enriched in <sup>13</sup>C and have lower concentrations than those of the near-seafloor samples (−63 ± 6‰, 27 ± 15 nM;  $n = 6$ ). These observations are also true of each station’s surface and near-seafloor pair (fig. S1). Because <sup>12</sup>CH<sub>4</sub> is oxidized faster than <sup>13</sup>CH<sub>4</sub>, these trends support the traditional view of oceanic CH<sub>4</sub> dynamics, in which CH<sub>4</sub> is emitted from anoxic seafloor sediments and oxidized throughout its ascent in the water column (35).

In sharp contrast, the values of  $f_s$  computed from the <sup>14</sup>C-CH<sub>4</sub> data allow an entirely different interpretation of this system. The lagoon sample collected at station 1 is composed mainly of modern background CH<sub>4</sub> ( $f_s = 0.18 ± 0.06$ ), whereas the sample collected from station 2 is of intermediate origin ( $f_s = 0.50 ± 0.04$ ), a roughly equivalent mixture of ancient C source and modern background. The mean value of  $f_s$  in the near-seafloor samples ranges from 0.45 to 0.86 ( $n = 6$ ), whereas the mean value of  $f_s$  in the surface samples ranges from 0.07 to 0.53 ( $n = 6$ ). The surface samples are all dominantly modern background CH<sub>4</sub> except for the sample collected at station 6, which has an intermediate origin ( $f_s = 0.53 ± 0.04$ ).

At stations 3, 5, 7, and 8, CH<sub>4</sub> in the near-seafloor sample is derived mainly from ancient C sources in contrast to CH<sub>4</sub> derived mainly from modern background in the surface water sample. This decoupling is most evident at mid-outer shelf stations 7 and 8 (at water depths of 28 and 38 m, respectively), where little to no CH<sub>4</sub> is sourced from ancient C in surface waters, whereas CH<sub>4</sub> found near the seafloor is mainly sourced from ancient C (Table 1). These analyses suggest that (i) ancient C sources supply CH<sub>4</sub> to shelf waters and (ii) ancient C sources contrib-

ute little to no CH<sub>4</sub> to surface waters (and therefore to the atmosphere) with increasing water depth and thus confirms our hypotheses.

These results demonstrate that ancient C-sourced CH<sub>4</sub> offshore Prudhoe Bay is largely not reaching the atmosphere beyond, approximately, the 30-m isobath. Our findings are consistent with other Arctic Ocean studies that have found CH<sub>4</sub> removal processes to be highly efficient in sediment (36) and relatively shallow water columns (<100 m depth) (15, 16). The evidence of strong CH<sub>4</sub> removal mechanisms operating in the Arctic from these studies suggests that an enhancement of ancient C mobilization due to climate change would not necessarily increase CH<sub>4</sub> emission to the atmosphere from the Arctic Ocean. In addition to potential changes in the magnitude of CH<sub>4</sub> sources in a warmer, increasingly ice-free Arctic Ocean (37), we must also consider that the rate of CH<sub>4</sub> removal processes, such as aerobic CH<sub>4</sub> oxidation by microorganisms in the water column (6, 35), could also change. Thus, to accurately constrain the mobilization of ancient C and the subsequent emission of CH<sub>4</sub>, we recommend that natural abundance <sup>14</sup>C-CH<sub>4</sub> analyses should be conducted in future studies of CH<sub>4</sub> dynamics.

## MATERIALS AND METHODS

### Sample collection

Our study was carried out aboard the R/V *Ukpik* from 30 August to 5 September 2015, coincident with the period of the year that typically has the minimum extent of sea ice. Because the surface water [CH<sub>4</sub>] in the Prudhoe Bay area is lower than the limit of previous <sup>14</sup>C-CH<sub>4</sub> techniques (16 nM for a small sample accelerator mass spectrometry analysis) (38), a new dissolved <sup>14</sup>C-CH<sub>4</sub> sampling and preparation method was developed and used in this study (20). Using this method, seawater was continuously pumped onboard and the dissolved gases were continuously extracted from the water. In the Prudhoe Bay sample set,

the average seawater sample volume was  $32,000 \pm 4000$  liters ( $n = 14$ ), and the average extracted gas volume was  $350 \pm 50$  liters ( $n = 14$ ). The extracted gas was compressed into a 2-liter cylinder for transport to the home laboratory, where it was prepared for  $^{14}\text{C}$  and stable isotope analyses. Although the cylinder is only pressurized to a maximum of 2100 psi, equivalent to 240 liters, it was necessary to extract 350 to 400 liters of gas to (i) flush the compressor pump and cylinder with sample and (ii) account for some small, unresolved loss of sample (that is, a leak) in the compression process.

Atmospheric  $\text{CH}_4$  for  $^{14}\text{C}$ - $\text{CH}_4$  analyses was sampled in Utqiagvik (formerly, Barrow), AK, on three separate days across 3 months (August to October 2015, bounding our cruise dates) and is reported as mean  $\pm 1$  SD ( $n = 3$ ); the samples were collected when winds were coming from the north, so these measurements represent a circum-Arctic average, to some extent. Atmospheric  $\text{CO}_2$  for  $^{14}\text{C}$ - $\text{CO}_2$  analyses was also sampled in Utqiagvik, AK, on three separate days across 3 weeks (August to September 2015, bounding our cruise dates) and is reported as mean  $\pm 1$  SD ( $n = 3$ ). DIC and DOC samples for  $^{14}\text{C}$ -DIC and  $^{14}\text{C}$ -DOC analyses were collected contemporaneously with  $^{14}\text{C}$ - $\text{CH}_4$  sampling on our research cruise; these measurements are reported as the mean  $\pm 1$  SD of surface water samples (2 m depth) at stations 3 to 8 ( $n = 6$ ).

A discrete vial for  $[\text{CH}_4]$  analysis was collected at each sample collection depth using a single Niskin bottle following standardized procedures (39). In total, 16 samples were collected from the 14 sample collection depths because two duplicate vials were collected. Each sample was collected by transferring the seawater in the Niskin bottle to a 60-ml glass vial, which was flushed with seawater, filled, and sealed with a stopper and crimp cap. Then, a 10-ml gaseous headspace of ultrahigh-purity nitrogen was injected into each vial from a syringe while 10 ml of seawater from the vial was removed with a second syringe. Each sample was then sterilized with 25  $\mu\text{l}$  of supersaturated mercuric chloride solution to prevent microbial perturbation of the original  $[\text{CH}_4]$  and stored stopper side down to prevent any diffusion of headspace gas across the seal.

The  $[\text{CH}_4]$  analyses were performed 2 months after the cruise in the home laboratory using an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID). The GC analysis of the headspace of each vial was performed in two consecutive runs. The  $[\text{CH}_4]$  of the headspace was calculated by fitting the measured peak area to a four-point calibration curve created on the same day by analyzing a suite of  $\text{CH}_4$  gas standards  $\{[\text{CH}_4] = 0, 1, 10, \text{ and } 100 \text{ parts per million (ppm)}\}$  that bound all of the measured values. The measured headspace  $[\text{CH}_4]$  of each vial was translated to a dissolved  $[\text{CH}_4]$  value (40) with knowledge of the sample incubator temperature and the salinity of the sampled seawater, the latter of which was measured with a water quality sonde in the field (YSI, 600R series). An uncertainty of 5.2% is associated with each measurement (39).

To evaluate the degree of  $\text{CH}_4$  saturation in the sampled seawater from the dissolved  $[\text{CH}_4]$  data, it was necessary to calculate the  $[\text{CH}_4]$  that would be found if each water sample had come to full equilibrium with the atmosphere (that is, the “equilibrium solubility”). The local atmosphere was sampled from bow air that was pumped to an onboard cavity ring-down spectrometer (CRDS; G2401, Picarro). The atmospheric  $[\text{CH}_4]$  ( $2.000 \pm 0.002$  ppm;  $n = 79$ ) was used along with the temperature- and salinity-dependent  $\text{CH}_4$  solubility (40) to calculate the  $\text{CH}_4$  equilibrium solubility of each sample. The degree of  $\text{CH}_4$  saturation is reported for all surface water samples in table S1. Samples that have  $\text{CH}_4$  concentrations greater than the seawater’s

equilibrium solubility concentration have  $\text{CH}_4$  saturation values of  $>100\%$  (that is, supersaturated), representing that the net flux of  $\text{CH}_4$  is from sea to air.

### $^{14}\text{C}$ - $\text{CH}_4$ and $\delta^{13}\text{C}$ - $\text{CH}_4$ sample preparation

The extracted gas cylinder samples were prepared for  $^{14}\text{C}$ - $\text{CH}_4$  and  $\delta^{13}\text{C}$ - $\text{CH}_4$  analyses on a newly developed shore-based vacuum line (20). From 15 collected samples, 17 samples were then prepared and analyzed for  $^{14}\text{C}$ - $\text{CH}_4$  and  $\delta^{13}\text{C}$ - $\text{CH}_4$ , as two preparation duplicates were made by preparing a single extracted gas sample cylinder twice. Only 16 of these 17 prepared samples were analyzed (and discussed here) because a sample collected at one lagoon station (original station ID T5S29: 70.489°N, 149.114°W) was suspected to have been contaminated by carbon monoxide-C during the sample preparation process. The samples were prepared in a random order across 5 weeks. Vacuum line quality control assessments described by Sparrow and Kessler (20) were performed daily during the preparation period using gas standards with  $[\text{CH}_4]$  of 0, 5, and 250 ppm.

The vacuum line technique achieves high-efficiency purification, oxidation, and collection of the sample  $\text{CH}_4$ . The aliquots collected for the isotopic analyses are the  $\text{CH}_4$  oxidation products,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , which are produced when the sample  $\text{CH}_4$  is oxidized on a heated platinumized quartz wool catalyst. Although the gas sample volumes are large ( $\leq 240$  liters), a high flow rate (2 liters/min) through the vacuum line allows multiple sample preparations per day. The total process blank of the procedure is small (5.0  $\mu\text{g}$  of  $\text{CH}_4$ -C), composing 1.2% of the average collected and prepared sample ( $424 \pm 163$   $\mu\text{g}$ ;  $n = 16$ ). The  $^{14}\text{C}$ - $\text{CH}_4$  blanks of the vacuum line have acceptably low radiocarbon content ( $0.22 \pm 0.07$  pMC;  $n = 8$ ) relative to the  $^{14}\text{C}$ -dead (0 pMC)  $\text{CH}_4$  from which they are prepared, enabling radiocarbon dating of the dissolved  $\text{CH}_4$ -C to the analytical limit of accelerator mass spectrometry ( $\sim 50,000$  years Before Present).

The  $^{14}\text{C}$ - $\text{CH}_4$  data were analyzed and corrected for isotopic fractionation (33, 34) at the W. M. Keck Carbon Cycle Accelerator Mass Spectrometry (CCAMS) Laboratory at the University of California, Irvine. The uncertainties for  $^{14}\text{C}$ - $\text{CH}_4$  data (both  $^{14}\text{C}$ - $\text{CH}_4$  content and conventional  $^{14}\text{C}$  age of  $\text{CH}_4$ ) reported in Fig. 1A, fig. S1, and table S1 are calculated from the root mean square of the collection, preparation, and measurement uncertainties (20). Except for two smaller-sized samples (100 and 150  $\mu\text{g}$  of  $\text{CH}_4$ -C),  $\delta^{13}\text{C}$ - $\text{CH}_4$  data were also analyzed at the Keck CCAMS facility to a precision of  $<0.1\%$  relative to standards traceable to Pee Dee Belemnite using a Thermo Finnigan Delta Plus stable isotope ratio mass spectrometer (IRMS) with GasBench inlet. The  $\delta^{13}\text{C}$ - $\text{CH}_4$  measurements for the two samples that had insufficient  $\text{CH}_4$ -C for a separate IRMS aliquot were measured via CRDS (G2201-i, Picarro), analyzed directly from the sample cylinders; reported value is the 3-min average ( $n \approx 120$ ), and uncertainty is the standard error.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/1/eaao4842/DC1>

fig. S1. Dissolved  $\text{CH}_4$  concentration and isotopic data plotted by station depth.

table S1. Dissolved  $^{14}\text{C}$ - $\text{CH}_4$ ,  $\delta^{13}\text{C}$ - $\text{CH}_4$ , and  $[\text{CH}_4]$  data with relevant sample information.

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K.J.S. and analyzed by J.R.S. Samples for  $^{14}\text{C}$ -DIC,  $^{14}\text{C}$ -DOC, atmospheric  $^{14}\text{C}$ - $\text{CH}_4$ , and atmospheric  $^{14}\text{C}$ - $\text{CO}_2$  analyses were prepared by F.G.-T. and X.X., K.M.S., J.B.M. and S.J.L., and X.X., respectively. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. government. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. The water column data are also available at doi:10.18739/A2B69R. Additional information is available from the authors upon request.

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## Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf

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