

# Minimal geological methane emissions during the Younger Dryas–Preboreal abrupt warming event

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**Methane (CH<sub>4</sub>) is a powerful greenhouse gas and plays a key part in global atmospheric chemistry. Natural geological emissions (fossil methane vented naturally from marine and terrestrial seeps and mud volcanoes) are thought to contribute around 52 teragrams of methane per year to the global methane source, about 10 per cent of the total, but both bottom-up methods (measuring emissions)<sup>1</sup> and top-down approaches (measuring atmospheric mole fractions and isotopes)<sup>2</sup> for constraining these geological emissions have been associated with large uncertainties. Here we use ice core measurements to quantify the absolute amount of radiocarbon-containing methane (<sup>14</sup>CH<sub>4</sub>) in the past atmosphere and show that geological methane emissions were no higher than 15.4 teragrams per year (95 per cent confidence), averaged over the abrupt warming event that occurred between the Younger Dryas and Preboreal intervals, approximately 11,600 years ago. Assuming that past geological methane emissions were no lower than today<sup>3,4</sup>, our results indicate that current estimates of today's natural geological methane emissions (about 52 teragrams per year)<sup>1,2</sup> are too high and, by extension, that current estimates of anthropogenic fossil methane emissions<sup>2</sup> are too low. Our results also improve on and confirm earlier findings<sup>5–7</sup> that the rapid increase of about 50 per cent in mole fraction of atmospheric methane at the Younger Dryas–Preboreal event was driven by contemporaneous methane from sources such as wetlands; our findings constrain the contribution from old carbon reservoirs (marine methane hydrates<sup>8</sup>, permafrost<sup>9</sup> and methane trapped under ice<sup>10</sup>) to 19 per cent or less (95 per cent confidence). To the extent that the characteristics of the most recent deglaciation and the Younger Dryas–Preboreal warming are comparable to those of the current anthropogenic warming, our measurements suggest that large future atmospheric releases of methane from old carbon sources are unlikely to occur.**

The most comprehensive bottom-up assessment<sup>1</sup> of natural geological methane emissions considered contributions from mud volcanoes and other terrestrial macro-seeps, micro-seepage and marine seepage as well as geothermal and volcanic areas, indicating a range of 30–80 teragrams of methane per year (Tg CH<sub>4</sub> yr<sup>-1</sup>), with a best estimate of 53 ± 11 Tg CH<sub>4</sub> yr<sup>-1</sup>. A recent review of the global CH<sub>4</sub> budget that combined top-down and bottom-up methods found, however, that bottom-up approaches tend to over-estimate natural CH<sub>4</sub> sources<sup>11</sup>. Top-down approaches can, in principle, constrain the magnitude of different CH<sub>4</sub> sources by using isotopic data (<sup>δ</sup><sup>13</sup>C, <sup>14</sup>C and <sup>δ</sup>D). However, the isotopic signature of natural geological CH<sub>4</sub> is expected to be very similar to that of anthropogenic fossil CH<sub>4</sub> (ref. 2), and for <sup>14</sup>C there is an additional complication arising from <sup>14</sup>CH<sub>4</sub> that is emitted by nuclear power plants<sup>12</sup>. For this reason, isotopic studies of today's

atmosphere can only produce combined estimates of natural geological and anthropogenic fossil CH<sub>4</sub> emissions (refs 2, 12).

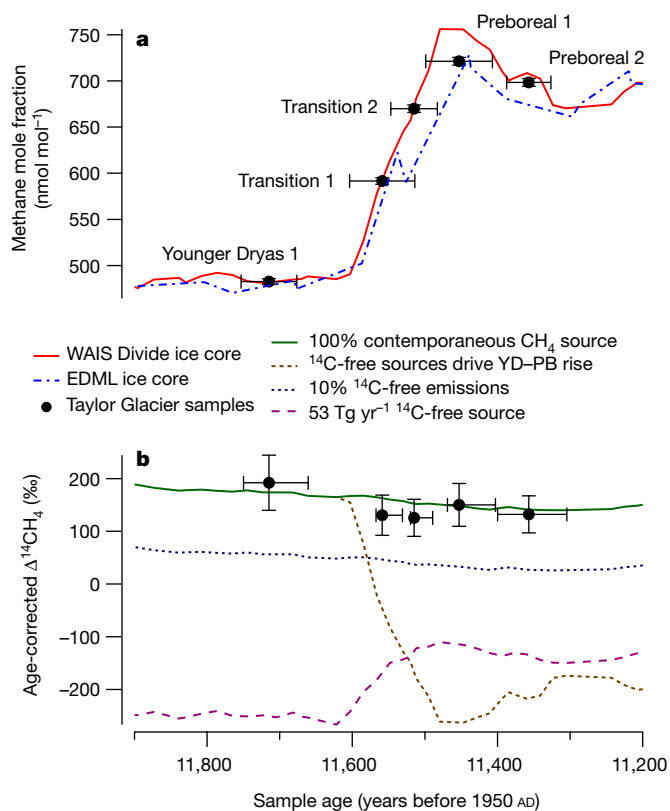
Polar ice contains samples of the preindustrial atmosphere and offers the opportunity to quantify geological CH<sub>4</sub> in the absence of anthropogenic fossil CH<sub>4</sub>. A recent study used a combination of revised source <sup>δ</sup><sup>13</sup>C isotopic signatures and published ice core <sup>δ</sup><sup>13</sup>CH<sub>4</sub> data to estimate natural geological CH<sub>4</sub> at 51 ± 20 Tg CH<sub>4</sub> yr<sup>-1</sup> (1σ range)<sup>2</sup>, in agreement with the bottom-up assessment of ref. 1. This estimate, however, used <sup>δ</sup><sup>13</sup>C data that were affected by interference from krypton during mass spectrometry (see Supplementary Information section 9). Further, <sup>δ</sup><sup>13</sup>C offers only a weak constraint, because of uncertainties in past CH<sub>4</sub> emissions from biomass burning and in the source <sup>δ</sup><sup>13</sup>C signatures (Supplementary Information section 9). In contrast, <sup>14</sup>CH<sub>4</sub> in the preindustrial atmosphere is the ideal tracer for constraining natural geological CH<sub>4</sub> because the <sup>14</sup>C signatures of most CH<sub>4</sub> sources are very well defined. The <sup>14</sup>C signature of CH<sub>4</sub> emitted from wetlands (the dominant natural CH<sub>4</sub> source), biomass burning, termites and ruminants follows the <sup>14</sup>C signature of contemporaneous atmospheric CO<sub>2</sub> (ref. 13), whereas <sup>14</sup>C of geological CH<sub>4</sub> is effectively zero because of the great age of fossil carbon. Methane emissions from marine methane hydrates are also devoid of <sup>14</sup>C (ref. 14). The <sup>14</sup>C content of emissions from thawing permafrost is variable but often depleted relative to that of atmospheric CO<sub>2</sub> (ref. 15). Because of these additional <sup>14</sup>C-depleted CH<sub>4</sub> emissions from hydrates and permafrost, a <sup>14</sup>CH<sub>4</sub> constraint would provide a conservative upper limit on the magnitude of geological CH<sub>4</sub> emissions.

There are two major challenges associated with reconstructing past atmospheric <sup>14</sup>CH<sub>4</sub>. First, atmospheric <sup>14</sup>CH<sub>4</sub> is present at an ultra-trace level in preindustrial air (at mole fractions of the order of 10<sup>-19</sup> mol mol<sup>-1</sup>), and an individual measurement requires about 1,000 kg of ancient glacial ice. In this study, we sampled very large volumes of ancient ice exposed near the surface of Taylor Glacier, Antarctica (Supplementary Information section 1 and Supplementary Figs 6 and 7). Second, there is interference from *in situ* cosmogenic production of <sup>14</sup>C in the ice<sup>5</sup>. <sup>14</sup>C is produced from <sup>16</sup>O directly in the ice lattice by energetic neutrons, negative muon capture and interaction with fast muons<sup>16</sup>. Most of this <sup>14</sup>C forms <sup>14</sup>CO<sub>2</sub> and <sup>14</sup>CO, but a small fraction forms <sup>14</sup>CH<sub>4</sub> (refs 16, 17).

The only prior attempt at measuring past atmospheric <sup>14</sup>CH<sub>4</sub> in glacial ice was unable to quantify geological CH<sub>4</sub> emissions owing to poor understanding of the *in situ* cosmogenic <sup>14</sup>CH<sub>4</sub> component<sup>5</sup>. To improve understanding of this component, a subsequent study targeted ice older than 50 kyr at Taylor Glacier<sup>16</sup>. The old age of the ice ensured that all <sup>14</sup>C originated exclusively from *in situ* cosmogenic production as the ice rose to the surface in the Taylor Glacier ablation zone.

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**Figure 1 | Results for large-volume samples from Taylor Glacier across the YD–PB transition. a, [CH<sub>4</sub>]; b,  $\Delta^{14}\text{CH}_4$ .** Individual sample names are shown in a. [CH<sub>4</sub>] from the WAIS Divide ice core is from ref. 30 with updated chronology as in ref. 31. [CH<sub>4</sub>] from the EPICA Dronning Maud Land (EDML) ice core is from ref. 32, with age scale shifted by –132 years to align the start of YD–PB [CH<sub>4</sub>] transition with the WAIS record. Differences in Preboreal [CH<sub>4</sub>] peak value between different ice core sites are most likely attributable to differences in signal smoothing in glacial firn between the sites (more smoothing at EDML and Taylor Glacier). Age-corrected  $\Delta^{14}\text{C}$  notation is as defined in ref. 33. For the line labelled ‘100% contemporaneous CH<sub>4</sub> source’, we assume that atmospheric  $\Delta^{14}\text{CH}_4$  is equal to atmospheric  $\Delta^{14}\text{CO}_2$  as in the IntCal13 compilation<sup>19</sup> at all times. For the line ‘<sup>14</sup>C-free sources drive YD–PB rise’, we assume that all of the YD–PB [CH<sub>4</sub>] increase is driven by <sup>14</sup>C-free sources. For the line labelled ‘10% <sup>14</sup>C-free emissions’, we assume that 10% of the global CH<sub>4</sub> emissions are <sup>14</sup>C-free. The line labelled ‘53 Tg yr<sup>-1</sup> <sup>14</sup>C-free source’ reflects a commonly used estimate of geological methane emissions<sup>1</sup>. Taylor Glacier [CH<sub>4</sub>] and  $\Delta^{14}\text{CH}_4$  mean values are shown after all corrections (see Supplementary Information sections 3 and 4) and with 1 $\sigma$  uncertainties indicated by the vertical error bars. Horizontal error bars in a represent the estimated age range of the large-volume samples (Supplementary Information section 2). Horizontal error bars in b represent the estimated mean age uncertainty with respect to the IntCal13 age scale (1 $\sigma$ ; Supplementary Information section 2).

This study found a constant <sup>14</sup>CH<sub>4</sub>/<sup>14</sup>CO ratio for a range of depths, demonstrating that *in situ* cosmogenic <sup>14</sup>CO could be accurately used to quantify and correct for the *in situ* cosmogenic <sup>14</sup>CH<sub>4</sub> component<sup>16</sup> (Supplementary Information section 4).

Figure 1 shows the new Taylor Glacier CH<sub>4</sub> mole fraction ([CH<sub>4</sub>]) and <sup>14</sup>CH<sub>4</sub> results for the Younger Dryas–Preboreal (YD–PB) transition after corrections for procedural effects and *in situ* cosmogenic <sup>14</sup>C (Supplementary Information sections 3 and 4). Taylor Glacier [CH<sub>4</sub>] agrees with existing Antarctic ice core records of [CH<sub>4</sub>], consistent with an earlier finding that CH<sub>4</sub> is well preserved in Taylor Glacier ice<sup>18</sup>. All five  $\Delta^{14}\text{CH}_4$  values agree with the IntCal13 palaeoatmospheric reconstruction of  $\Delta^{14}\text{CO}_2$  (green line)<sup>19</sup> within 1 $\sigma$  uncertainties. Table 1 shows the <sup>14</sup>C-free fraction of the total CH<sub>4</sub> source for the time interval of each of the samples estimated by comparing sample  $\Delta^{14}\text{CH}_4$  values with IntCal13  $\Delta^{14}\text{CO}_2$  (Supplementary Information section 4). We then used a Monte Carlo approach (Supplementary Information section 5) to estimate total global CH<sub>4</sub> emissions and <sup>14</sup>C-free emissions (Table 1). A simple two-box model confirms that the Antarctic location of Taylor Glacier does not result in detectable muting of a northern high-latitude source of <sup>14</sup>C-free CH<sub>4</sub> (Supplementary Information section 6).

During the YD–PB transition, <sup>14</sup>C-free emissions (including geological CH<sub>4</sub>) were in the range 0–18.1 Tg CH<sub>4</sub> yr<sup>-1</sup>, with an average 95% confidence upper limit of 15.4 Tg CH<sub>4</sub> yr<sup>-1</sup>. It has been proposed that natural geological CH<sub>4</sub> emissions were higher in the past than today, before anthropogenic petroleum extraction drained gas fields<sup>3</sup> and when lower sea-level stands exposed more methane seeps on continental margins<sup>4</sup>. Assuming that these considerations are correct, our results provide a conservative upper limit for today’s natural geological CH<sub>4</sub> emissions and indicate that its recent estimates<sup>1,2</sup> are too high by a factor of at least 3–4 (that is, by at least 35.6 Tg CH<sub>4</sub> yr<sup>-1</sup>). Because today’s top-down isotopic studies can constrain only the sum of natural geological and anthropogenic fossil CH<sub>4</sub> emissions, this would also mean that even the recently revised, higher, best-estimate value of 145 Tg CH<sub>4</sub> yr<sup>-1</sup> (ref. 2) for anthropogenic fossil CH<sub>4</sub> emissions is too low by 25% or more.

In addition to providing a constraint on natural geological CH<sub>4</sub> emissions, our results improve the understanding of the CH<sub>4</sub> budget during the gradual global warming of the last deglaciation as well as during past abrupt warming events (Dansgaard–Oeschger events). Several sources have been proposed as important drivers of the gradual deglacial and rapid Dansgaard–Oeschger increases in [CH<sub>4</sub>], including wetlands<sup>20</sup>, marine methane hydrates<sup>8</sup> and thermokarst lakes<sup>9</sup> as well as CH<sub>4</sub> trapped underneath ice sheets<sup>10</sup>. Understanding how these CH<sub>4</sub> sources responded during times of past warming is also relevant for today, because increased emissions from the same sources have been proposed for current and future warming<sup>21–24</sup>.

Prior studies that examined  $\delta^{13}\text{C}$  of CH<sub>4</sub> in ice cores indicated an important role for wetlands in both deglacial<sup>25,26</sup> and Dansgaard–Oeschger [CH<sub>4</sub>] increases<sup>6,25,26</sup>, and argued against a large methane hydrate contribution to the YD–PB [CH<sub>4</sub>] rise<sup>6</sup>. However,  $\delta^{13}\text{C}$  provides

**Table 1 | Confidence ranges (95%) for several quantities of interest as determined for each of the Taylor Glacier large-volume samples**

Sample	Sample mean age (yr BP)	<sup>14</sup> C-free fraction of total CH <sub>4</sub> source	Total global CH <sub>4</sub> emissions (Tg CH <sub>4</sub> yr <sup>-1</sup> )	<sup>14</sup> C-free emissions (Tg CH <sub>4</sub> yr <sup>-1</sup> )	<sup>14</sup> C-free emission increase* (Tg CH <sub>4</sub> yr <sup>-1</sup> )	<sup>14</sup> C-free fraction of CH <sub>4</sub> source increase*
Younger Dryas 1	11,715	0 to 0.071	113 to 195	0 to 10.5 (0)	–8.6 to 14.9	–0.24 to 0.40
Transition 1	11,559	0 to 0.092	142 to 245	0 to 17.4 (5.2)	–8.5 to 15.7	–0.13 to 0.23
Transition 2	11,515	0 to 0.082	166 to 281	0 to 18.1 (4.7)	–9.6 to 15.3	–0.12 to 0.19
Preboreal 1	11,453	0 to 0.068	177 to 302	0 to 15.7 (0)	–9.5 to 13.7	–0.14 to 0.20
Preboreal 2	11,357	0 to 0.069	166 to 288	0 to 15.3 (1.9)		

The confidence ranges were determined from the results of the Monte Carlo iterations used to calculate all of these quantities (Supplementary Information sections 4 and 5; see Supplementary Figs 1, 3 and 4 for probability distributions of quantities in columns 3 to 5). Only the positive (physical) parts of the 95% confidence ranges are shown for <sup>14</sup>C-free fraction of total CH<sub>4</sub> source and for <sup>14</sup>C-free emissions. For <sup>14</sup>C-free emissions, the mean of the probability distribution is also shown in parentheses (0 is shown if mean is <0). Negative values in the rightmost two columns are physical and represent a possible reduction in <sup>14</sup>C-free emissions during the YD–PB transition. Details on sample age ranges and uncertainties are found in Supplementary Table 1.

\*From Younger Dryas level.

relatively weak constraints on individual CH<sub>4</sub> sources because of overlapping source δ<sup>13</sup>C signatures<sup>25</sup> and temporal variations in δ<sup>13</sup>C of the wetland source<sup>26</sup> as well as uncertainties about CH<sub>4</sub> emissions from biomass burning (Supplementary Information section 9). Prior ice core studies of δD of CH<sub>4</sub> were able to rule out methane hydrates as the main source of [CH<sub>4</sub>] increase for several Dansgaard–Oeschger events, including the YD–PB transition<sup>7</sup>. But quantification of individual source magnitudes with δD remains challenging, because of uncertainties and possible temporal variation in individual source signatures<sup>7</sup>.

<sup>14</sup>CH<sub>4</sub> is unique in its ability to accurately quantify combined <sup>14</sup>C-free emissions from methane hydrates, thermokarst lakes and methane trapped under ice (which is also <sup>14</sup>C-depleted<sup>27</sup>) as a fraction of the total CH<sub>4</sub> source. The only prior study of palaeoatmospheric <sup>14</sup>CH<sub>4</sub> also sampled the YD–PB transition, but was hindered by poor understanding of the *in situ* cosmogenic <sup>14</sup>CH<sub>4</sub> component at that time<sup>5</sup>. That study suggested that wetlands were probably the main driver of the YD–PB increase in [CH<sub>4</sub>], with –7% to 65% (2σ range) of the overall [CH<sub>4</sub>] increase from the Younger Dryas to the peak mole fraction in the Preboreal possibly being due to <sup>14</sup>C-free sources. Our new <sup>14</sup>CH<sub>4</sub> results (Table 1) tighten the constraint on the <sup>14</sup>C-free fraction by a factor of 2, yielding –12% to 19% (95% confidence range). The YD–PB abrupt warming, which had a North Atlantic origin with hemisphere-scale effects<sup>28</sup>, seems to have resulted in the release of no more than 16 Tg CH<sub>4</sub> yr<sup>–1</sup> from old carbon reservoirs (Table 1). Our measurements thus confirm that wetlands were probably the main driver of the YD–PB increase in [CH<sub>4</sub>], consistent with prior isotope studies of CH<sub>4</sub> during the YD–PB warming<sup>5–7</sup>.

Our results present an opportunity to evaluate the potential of CH<sub>4</sub> release from <sup>14</sup>C-free sources in response not only to abrupt regional warming but also to gradual global warming and ice retreat. By the time of the YD–PB event, the retreat of the Northern Hemisphere ice sheets was already more than 50% complete (Supplementary Fig. 5), presumably allowing the release of hydrate<sup>10</sup> and geological<sup>27</sup> CH<sub>4</sub> that had been trapped under the ice prior to retreat. Global mean surface temperature had already been rising for several millennia and was about 2.9 °C warmer than at the Last Glacial Maximum (Supplementary Fig. 5). Given that intermediate-depth ocean waters also warmed, destabilization of methane hydrates should have been underway; destabilization in some regions is supported by geological evidence<sup>8</sup>. Thermokarst lake formation during the Younger Dryas was occurring in permafrost areas of Siberia, Alaska and northwest Canada, and may have intensified around the time of the YD–PB event<sup>9</sup>. Despite YD–PB conditions seeming conducive to methane release from these old carbon reservoirs, our results show that <sup>14</sup>C-free emissions were no higher than 15.4 Tg CH<sub>4</sub> yr<sup>–1</sup> (95% confidence) averaged over this event. This constraint also includes natural geological CH<sub>4</sub> emissions, leaving even less room for hydrate, thermokarst lake and under-ice CH<sub>4</sub> emissions.

The last deglaciation is only a partial analogue to ongoing anthropogenic warming. There are important differences, such as the climate background state, the rate of warming and the ultimate global mean temperature (the end point of deglacial warming is similar to the starting point of anthropogenic warming). There are also important similarities, such as polar amplification as well as the possible ultimate magnitude of anthropogenic warming. The differences between deglacial and modern warming preclude us from unequivocally ruling out the possibility of large-scale natural methane releases to the atmosphere from old carbon reservoirs in the future. Our results do, however, suggest that such releases are unlikely. This is consistent with recent atmospheric observations, which suggest that renewed growth of atmospheric CH<sub>4</sub> since 2006 is not driven by emissions from the Arctic<sup>29</sup>, where the most vulnerable old carbon reservoirs are located today. Instead, our results support the hypothesis that any future increases in natural CH<sub>4</sub> emissions to the atmosphere will be driven by contemporaneous sources such as wetlands.

**Data Availability** Data from this study are available via the US Antarctic Program Data Center (<http://www.usap-dc.org/view/dataset/601029>).

**Received 28 September 2016; accepted 21 June 2017.**

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**Supplementary Information** is available in the online version of the paper.

**Acknowledgements** This work was supported by US National Science Foundation Awards 0839031 (J.P.S.), 0838936 (E.B.) and 1245659 (V.V.P.), the National Oceanic and Atmospheric Administration Climate and Global Change Postdoctoral Fellowship (C.B.), the Packard Fellowship for Science and Engineering (V.V.P.), the Marsden Fund Council from New Zealand Government funding administered by the Royal Society of New Zealand (H.S.) and the ANSTO Isotopes in Climate Change and Atmospheric Systems project (A.M.S.). Further support came from NIWA under Climate and Atmosphere Research Programme CAAC1504 (2014/15 SCI). We acknowledge the financial support from the Australian Government for the Centre for Accelerator Science at ANSTO through the National Collaborative Research Infrastructure Strategy. We thank the US Antarctic Program for field support, US Ice Drilling and Development Office for ice drilling support, R. Beaudette for logistical assistance, the Institut Polaire Français Paul-Émile Victor for supporting X.F.'s field participation, J. Shakun for providing deglacial ice volume and temperature data, and M. Dyonisius, H. Graven, J. Miller, E. Dlugokencky, L. Murray, T. Weber, B. Hmiel and S. Schwietzke for comments.

**Author Contributions** V.V.P., J.P.S. and E.B. designed the study. V.V.P., J.P.S., D.B., T.B. and E.B. conducted field logistical preparations. V.V.P. led the Antarctic field

campaign, with D.B., H.S., C.B., A.S., X.F., L.M. and T.B. participating in sampling and field  $[\text{CH}_4]$  analyses. E.B. supervised analyses of  $[\text{CH}_4]$  in small ice samples in his laboratory. C.H. analysed  $[\text{CH}_4]$  and halocarbons in large air samples under the supervision of R.F.W. D.B. performed analyses of  $\delta^{15}\text{N}$ ,  $\delta\text{Xe}/\text{N}_2$  and  $\delta\text{Kr}/\text{N}_2$  with assistance from A.O. K.R. measured  $[\text{CO}]$  and  $\delta^{13}\text{CH}_4$ , and performed the extractions of  $\text{CH}_4$  and  $\text{CO}$  from sample air, with assistance from H.S. A.M.S. and Q.H. carried out graphitization and accelerator mass spectrometry  $^{14}\text{C}$  analyses. H.S. did the Monte Carlo calculations of  $\text{CH}_4$  emissions. V.V.P. performed the data corrections and analyses, determined sample ages and wrote the manuscript, with assistance from all other authors.

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**Reviewer Information** *Nature* thanks P. Hopcroft, R. Muscheler and the other anonymous reviewer(s) for their contribution to the peer review of this work.