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Title

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Permalink

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Journal

Nature, 548(7668)

ISSN

0028-0836

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Publication Date

2017-08-01

DOI

10.1038/nature23316

Peer reviewed

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

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Methane (CH₄) 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)¹ and top-down approaches (measuring atmospheric mole fractions and isotopes)² 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 (¹⁴CH₄) 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^{3,4}, our results indicate that current estimates of today's natural geological methane emissions (about 52 teragrams per year)^{1,2} are too high and, by extension, that current estimates of anthropogenic fossil methane emissions² are too low. Our results also improve on and confirm earlier findings^{5–7} 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 hydrates⁸, permafrost⁹ and methane trapped under ice¹⁰) 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 assessment¹ 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 CH₄ yr⁻¹), with a best estimate of 53 ± 11 Tg CH₄ yr⁻¹. A recent review of the global CH₄ budget that combined top-down and bottom-up methods found, however, that bottom-up approaches tend to over-estimate natural CH₄ sources¹¹. Top-down approaches can, in principle, constrain the magnitude of different CH₄ sources by using isotopic data (^δ¹³C, ¹⁴C and ^δD). However, the isotopic signature of natural geological CH₄ is expected to be very similar to that of anthropogenic fossil CH₄ (ref. 2), and for ¹⁴C there is an additional complication arising from ¹⁴CH₄ that is emitted by nuclear power plants¹². For this reason, isotopic studies of today's

atmosphere can only produce combined estimates of natural geological and anthropogenic fossil CH₄ emissions (refs 2, 12).

Polar ice contains samples of the preindustrial atmosphere and offers the opportunity to quantify geological CH₄ in the absence of anthropogenic fossil CH₄. A recent study used a combination of revised source ^δ¹³C isotopic signatures and published ice core ^δ¹³CH₄ data to estimate natural geological CH₄ at 51 ± 20 Tg CH₄ yr⁻¹ (1σ range)², in agreement with the bottom-up assessment of ref. 1. This estimate, however, used ^δ¹³C data that were affected by interference from krypton during mass spectrometry (see Supplementary Information section 9). Further, ^δ¹³C offers only a weak constraint, because of uncertainties in past CH₄ emissions from biomass burning and in the source ^δ¹³C signatures (Supplementary Information section 9). In contrast, ¹⁴CH₄ in the preindustrial atmosphere is the ideal tracer for constraining natural geological CH₄ because the ¹⁴C signatures of most CH₄ sources are very well defined. The ¹⁴C signature of CH₄ emitted from wetlands (the dominant natural CH₄ source), biomass burning, termites and ruminants follows the ¹⁴C signature of contemporaneous atmospheric CO₂ (ref. 13), whereas ¹⁴C of geological CH₄ is effectively zero because of the great age of fossil carbon. Methane emissions from marine methane hydrates are also devoid of ¹⁴C (ref. 14). The ¹⁴C content of emissions from thawing permafrost is variable but often depleted relative to that of atmospheric CO₂ (ref. 15). Because of these additional ¹⁴C-depleted CH₄ emissions from hydrates and permafrost, a ¹⁴CH₄ constraint would provide a conservative upper limit on the magnitude of geological CH₄ emissions.

There are two major challenges associated with reconstructing past atmospheric ¹⁴CH₄. First, atmospheric ¹⁴CH₄ is present at an ultra-trace level in preindustrial air (at mole fractions of the order of 10⁻¹⁹ mol mol⁻¹), 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 ¹⁴C in the ice⁵. ¹⁴C is produced from ¹⁶O directly in the ice lattice by energetic neutrons, negative muon capture and interaction with fast muons¹⁶. Most of this ¹⁴C forms ¹⁴CO₂ and ¹⁴CO, but a small fraction forms ¹⁴CH₄ (refs 16, 17).

The only prior attempt at measuring past atmospheric ¹⁴CH₄ in glacial ice was unable to quantify geological CH₄ emissions owing to poor understanding of the *in situ* cosmogenic ¹⁴CH₄ component⁵. To improve understanding of this component, a subsequent study targeted ice older than 50 kyr at Taylor Glacier¹⁶. The old age of the ice ensured that all ¹⁴C originated exclusively from *in situ* cosmogenic production as the ice rose to the surface in the Taylor Glacier ablation zone.

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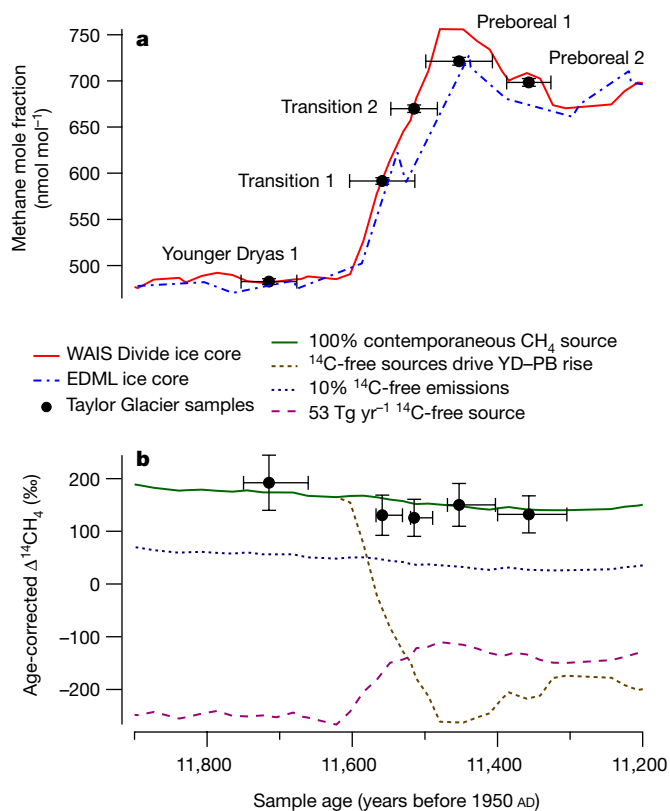


Figure 1 | Results for large-volume samples from Taylor Glacier across the YD–PB transition. a, [CH₄]; b, $\Delta^{14}\text{CH}_4$. Individual sample names are shown in **a**. [CH₄] from the WAIS Divide ice core is from ref. 30 with updated chronology as in ref. 31. [CH₄] from the EPICA Dronning Maud Land (EDML) ice core is from ref. 32, with age scale shifted by –132 years to align the start of YD–PB [CH₄] transition with the WAIS record. Differences in Preboreal [CH₄] 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 CH₄ source’, we assume that atmospheric $\Delta^{14}\text{CH}_4$ is equal to atmospheric $\Delta^{14}\text{CO}_2$ as in the IntCal13 compilation¹⁹ at all times. For the line ‘¹⁴C-free sources drive YD–PB rise’, we assume that all of the YD–PB [CH₄] increase is driven by ¹⁴C-free sources. For the line labelled ‘10% ¹⁴C-free emissions’, we assume that 10% of the global CH₄ emissions are ¹⁴C-free. The line labelled ‘53 Tg yr⁻¹ ¹⁴C-free source’ reflects a commonly used estimate of geological methane emissions¹. Taylor Glacier [CH₄] and $\Delta^{14}\text{CH}_4$ mean values are shown after all corrections (see Supplementary Information sections 3 and 4) and with 1 σ 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 σ ; Supplementary Information section 2).

This study found a constant ¹⁴CH₄/¹⁴CO ratio for a range of depths, demonstrating that *in situ* cosmogenic ¹⁴CO could be accurately used to quantify and correct for the *in situ* cosmogenic ¹⁴CH₄ component¹⁶ (Supplementary Information section 4).

Figure 1 shows the new Taylor Glacier CH₄ mole fraction ([CH₄]) and ¹⁴CH₄ results for the Younger Dryas–Preboreal (YD–PB) transition after corrections for procedural effects and *in situ* cosmogenic ¹⁴C (Supplementary Information sections 3 and 4). Taylor Glacier [CH₄] agrees with existing Antarctic ice core records of [CH₄], consistent with an earlier finding that CH₄ is well preserved in Taylor Glacier ice¹⁸. All five $\Delta^{14}\text{CH}_4$ values agree with the IntCal13 palaeoatmospheric reconstruction of $\Delta^{14}\text{CO}_2$ (green line)¹⁹ within 1 σ uncertainties. Table 1 shows the ¹⁴C-free fraction of the total CH₄ 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 CH₄ emissions and ¹⁴C-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 ¹⁴C-free CH₄ (Supplementary Information section 6).

During the YD–PB transition, ¹⁴C-free emissions (including geological CH₄) were in the range 0–18.1 Tg CH₄ yr⁻¹, with an average 95% confidence upper limit of 15.4 Tg CH₄ yr⁻¹. It has been proposed that natural geological CH₄ emissions were higher in the past than today, before anthropogenic petroleum extraction drained gas fields³ and when lower sea-level stands exposed more methane seeps on continental margins⁴. Assuming that these considerations are correct, our results provide a conservative upper limit for today’s natural geological CH₄ emissions and indicate that its recent estimates^{1,2} are too high by a factor of at least 3–4 (that is, by at least 35.6 Tg CH₄ yr⁻¹). Because today’s top-down isotopic studies can constrain only the sum of natural geological and anthropogenic fossil CH₄ emissions, this would also mean that even the recently revised, higher, best-estimate value of 145 Tg CH₄ yr⁻¹ (ref. 2) for anthropogenic fossil CH₄ emissions is too low by 25% or more.

In addition to providing a constraint on natural geological CH₄ emissions, our results improve the understanding of the CH₄ 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 [CH₄], including wetlands²⁰, marine methane hydrates⁸ and thermokarst lakes⁹ as well as CH₄ trapped underneath ice sheets¹⁰. Understanding how these CH₄ 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^{21–24}.

Prior studies that examined $\delta^{13}\text{C}$ of CH₄ in ice cores indicated an important role for wetlands in both deglacial^{25,26} and Dansgaard–Oeschger [CH₄] increases^{6,25,26}, and argued against a large methane hydrate contribution to the YD–PB [CH₄] rise⁶. 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)	¹⁴ C-free fraction of total CH ₄ source	Total global CH ₄ emissions (Tg CH ₄ yr ⁻¹)	¹⁴ C-free emissions (Tg CH ₄ yr ⁻¹)	¹⁴ C-free emission increase* (Tg CH ₄ yr ⁻¹)	¹⁴ C-free fraction of CH ₄ 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 ¹⁴C-free fraction of total CH₄ source and for ¹⁴C-free emissions. For ¹⁴C-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 ¹⁴C-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 CH₄ sources because of overlapping source δ¹³C signatures²⁵ and temporal variations in δ¹³C of the wetland source²⁶ as well as uncertainties about CH₄ emissions from biomass burning (Supplementary Information section 9). Prior ice core studies of δD of CH₄ were able to rule out methane hydrates as the main source of [CH₄] increase for several Dansgaard–Oeschger events, including the YD–PB transition⁷. But quantification of individual source magnitudes with δD remains challenging, because of uncertainties and possible temporal variation in individual source signatures⁷.

¹⁴CH₄ is unique in its ability to accurately quantify combined ¹⁴C-free emissions from methane hydrates, thermokarst lakes and methane trapped under ice (which is also ¹⁴C-depleted²⁷) as a fraction of the total CH₄ source. The only prior study of palaeoatmospheric ¹⁴CH₄ also sampled the YD–PB transition, but was hindered by poor understanding of the *in situ* cosmogenic ¹⁴CH₄ component at that time⁵. That study suggested that wetlands were probably the main driver of the YD–PB increase in [CH₄], with –7% to 65% (2σ range) of the overall [CH₄] increase from the Younger Dryas to the peak mole fraction in the Preboreal possibly being due to ¹⁴C-free sources. Our new ¹⁴CH₄ results (Table 1) tighten the constraint on the ¹⁴C-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 effects²⁸, seems to have resulted in the release of no more than 16 Tg CH₄ yr^{–1} from old carbon reservoirs (Table 1). Our measurements thus confirm that wetlands were probably the main driver of the YD–PB increase in [CH₄], consistent with prior isotope studies of CH₄ during the YD–PB warming^{5–7}.

Our results present an opportunity to evaluate the potential of CH₄ release from ¹⁴C-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 hydrate¹⁰ and geological²⁷ CH₄ 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 evidence⁸. 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 event⁹. Despite YD–PB conditions seeming conducive to methane release from these old carbon reservoirs, our results show that ¹⁴C-free emissions were no higher than 15.4 Tg CH₄ yr^{–1} (95% confidence) averaged over this event. This constraint also includes natural geological CH₄ emissions, leaving even less room for hydrate, thermokarst lake and under-ice CH₄ 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 CH₄ since 2006 is not driven by emissions from the Arctic²⁹, where the most vulnerable old carbon reservoirs are located today. Instead, our results support the hypothesis that any future increases in natural CH₄ 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.

1. Etiope, G., Lassey, K. R., Klusman, R. W. & Boschi, E. Reappraisal of the fossil methane budget and related emission from geologic sources. *Geophys. Res. Lett.* **35**, L09307 (2008).
2. Schwietzke, S. *et al.* Upward revision of global fossil fuel methane emissions based on isotope database. *Nature* **538**, 88–91 (2016).
3. Etiope, G., Milkov, A. V. & Derbyshire, E. Did geologic emissions of methane play any role in Quaternary climate change? *Global Planet. Change* **61**, 79–88 (2008).
4. Luyendyk, B., Kennett, J. & Clark, J. F. Hypothesis for increased atmospheric methane input from hydrocarbon seeps on exposed continental shelves during glacial low sea level. *Mar. Pet. Geol.* **22**, 591–596 (2005).
5. Petrenko, V. V. *et al.* ¹⁴CH₄ measurements in Greenland ice: investigating last glacial termination CH₄ sources. *Science* **324**, 506–508 (2009).
6. Schaefer, H. *et al.* Ice record of δ¹³C for atmospheric CH₄ across the Younger Dryas–Preboreal transition. *Science* **313**, 1109–1112 (2006).
7. Sowers, T. Late quaternary atmospheric CH₄ isotope record suggests marine clathrates are stable. *Science* **311**, 838–840 (2006).
8. Kennett, J. P., Cannariato, K. G., Hendy, I. L. & Behl, R. J. *Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis* (AGU, 2003).
9. Walter, K. M., Edwards, M. E., Grosse, G., Zimov, S. A. & Chapin, F. S. III. Thermokarst lakes as a source of atmospheric CH₄ during the last deglaciation. *Science* **318**, 633–636 (2007).
10. Weitemeyer, K. A. & Buffett, B. A. Accumulation and release of methane from clathrates below the Laurentide and Cordilleran ice sheets. *Global Planet. Change* **53**, 176–187 (2006).
11. Kirschke, S. *et al.* Three decades of global methane sources and sinks. *Nat. Geosci.* **6**, 813–823 (2013).
12. Lassey, K. R., Lowe, D. C. & Smith, A. M. The atmospheric cycling of radiomethane and the ‘fossil fraction’ of the methane source. *Atmos. Chem. Phys.* **7**, 2141–2149 (2007).
13. Wahlen, M. *et al.* Carbon-14 in methane sources and in atmospheric methane—the contribution from fossil carbon. *Science* **245**, 286–290 (1989).
14. Winckler, G. *et al.* Noble gases and radiocarbon in natural gas hydrates. *Geophys. Res. Lett.* **29**, 63–1–63–4 (2002).
15. Walter, K. M., Chanton, J. P., Chapin, F. S., Schuur, E. A. G. & Zimov, S. A. Methane production and bubble emissions from arctic lakes: isotopic implications for source pathways and ages. *J. Geophys. Res.* **113**, G00A08 (2008).
16. Petrenko, V. V. *et al.* Measurements of ¹⁴C in ancient ice from Taylor Glacier, Antarctica constrain *in situ* cosmogenic ¹⁴CH₄ and ¹⁴CO production rates. *Geochim. Cosmochim. Acta* **177**, 62–77 (2016).
17. Petrenko, V. V. *et al.* High-precision ¹⁴C measurements demonstrate production of *in situ* cosmogenic ¹⁴CH₄ and rapid loss of *in situ* cosmogenic ¹⁴CO in shallow Greenland firn. *Earth Planet. Sci. Lett.* **365**, 190–197 (2013).
18. Buizert, C. *et al.* Radiometric ⁸¹Kr dating identifies 120,000-year-old ice at Taylor Glacier, Antarctica. *Proc. Natl Acad. Sci. USA* **111**, 6876–6881 (2014).
19. Reimer, P. J. *et al.* Intcal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* **55**, 1869–1887 (2013).
20. Chappellaz, J. *et al.* Synchronous changes in atmospheric CH₄ and Greenland climate between 40 and 8 kyr BP. *Nature* **366**, 443–445 (1993).
21. Archer, D., Buffett, B. & Brovkin, V. Ocean methane hydrates as a slow tipping point in the global carbon cycle. *Proc. Natl Acad. Sci. USA* **106**, 20596–20601 (2009).
22. O’Connor, F. M. *et al.* Possible role of wetlands, permafrost, and methane hydrates in the methane cycle under future climate change: a review. *Rev. Geophys.* **48**, RG4005 (2010).
23. Wadham, J. L. *et al.* Potential methane reservoirs beneath Antarctica. *Nature* **488**, 633–637 (2012).
24. Walter, K. M., Smith, L. C. & Chapin, F. S. Methane bubbling from northern lakes: present and future contributions to the global methane budget. *Phil. Trans. R. Soc. A* **365**, 1657–1676 (2007).
25. Fischer, H. *et al.* Changing boreal methane sources and constant biomass burning during the last termination. *Nature* **452**, 864–867 (2008).
26. Möller, L. *et al.* Independent variations of CH₄ emissions and isotopic composition over the past 160,000 years. *Nat. Geosci.* **6**, 885–890 (2013).
27. Walter Anthony, K. M., Anthony, P., Grosse, G. & Chanton, J. Geologic methane seeps along boundaries of Arctic permafrost thaw and melting glaciers. *Nat. Geosci.* **5**, 419–426 (2012).
28. Clark, P. U. *et al.* Global climate evolution during the last deglaciation. *Proc. Natl Acad. Sci. USA* **109**, E1134–E1142 (2012).
29. Schaefer, H. *et al.* A 21st-century shift from fossil-fuel to biogenic methane emissions indicated by ¹³CH₄. *Science* **352**, 80–84 (2016).
30. Marcott, S. A. *et al.* Centennial-scale changes in the global carbon cycle during the last deglaciation. *Nature* **514**, 616–619 (2014).
31. Buizert, C. *et al.* The WAIS Divide deep ice core WD2014 chronology—Part 1: Methane synchronization (68–31 ka BP) and the gas age–ice age difference. *Clim. Past* **11**, 153–173 (2015).
32. Schilt, A. *et al.* Atmospheric nitrous oxide during the last 140,000 years. *Earth Planet. Sci. Lett.* **300**, 33–43 (2010).
33. Stuiver, M. & Polach, H. A. Discussion: reporting of ¹⁴C data. *Radiocarbon* **19**, 355–363 (1977).

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 CH_4 and CO from sample air, with assistance from H.S. A.M.S. and Q.H. carried out graphitization and accelerator mass spectrometry ^{14}C analyses. H.S. did the Monte Carlo calculations of 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.