$^{14}CH_4$ Measurements in Greenland Ice: Investigating Last Glacial Termination CH_4 Sources

Vasilii V. Petrenko,[1*†] Andrew M. Smith,[2] Edward J. Brook,[3] Dave Lowe,[4] Katja Riedel,[4] Gordon Brailsford,[4] Quan Hua,[2] Hinrich Schaefer,[4] Niels Reeh,[5] Ray F. Weiss,[1] David Etheridge,[6] Jeffrey P. Severinghaus[1]

The cause of a large increase of atmospheric methane concentration during the Younger Dryas–Preboreal abrupt climatic transition (~11,600 years ago) has been the subject of much debate. The carbon-14 (^{14}C) content of methane ($^{14}CH_4$) should distinguish between wetland and clathrate contributions to this increase. We present measurements of $^{14}CH_4$ in glacial ice, targeting this transition, performed by using ice samples obtained from an ablation site in west Greenland. Measured $^{14}CH_4$ values were higher than predicted under any scenario. Sample $^{14}CH_4$ appears to be elevated by direct cosmogenic ^{14}C production in ice. ^{14}C of CO was measured to better understand this process and correct the sample $^{14}CH_4$. Corrected results suggest that wetland sources were likely responsible for the majority of the Younger Dryas–Preboreal CH_4 rise.

Ice core records from Greenland and Antarctica show large and rapid variations in atmospheric methane (CH_4) concentrations ([CH_4]) in response to climate change (1). One such rapid [CH_4] increase occurred at the Younger Dryas (YD)–Preboreal (PB) [~11,600 years before present (B.P.), in which 0 B.P. = 1950 A.D.] abrupt warming event during the last deglaciation (Fig. 1). The causes of these rapid [CH_4] fluctuations have been the subject of intense debate. Several modeling studies suggest that glacial-interglacial changes in the atmospheric concentration of OH radicals (the main CH_4 sink) were small (2, 3). It is thus likely that the observed rapid [CH_4] increases were driven mostly by increases in CH_4 sources.

Several hypotheses regarding such sources have been proposed, including increased emissions from wetlands (4), marine clathrates (5, 6), and, more recently, thermokarst lakes (7). The possibility of CH_4 clathrate reservoir instability in response to climatic warming is particularly troubling in the light of present anthropogenic warming. If only 10% of CH_4 from the modern clathrate reservoir (which has ~5000 Pg of C) were to be released to the atmosphere in a few years, the radiative forcing would be equivalent to a 10-fold increase in [CO_2] (8).

In an attempt to better understand past changes in the CH_4 budget, two records of carbon-13/carbon-12 ratio ($\delta^{13}C$) (9, 10) and one record of deuterium/hydrogen ratio (δD) (11) of CH_4 from ice cores spanning the last glacial termination have recently been produced. Unfortunately, $\delta^{13}CH_4$ of many major CH_4 sources is similar (12), imperfectly known (13), and influenced by climatic conditions (14), limiting the utility of $\delta^{13}CH_4$ for testing different hypotheses for the rapid [CH_4] increases. δD of CH_4 is a more promising tracer for this purpose, because the δD of clathrate CH_4 is much higher than that of wetland emissions (11). The Greenland Ice Sheet Project 2 (GISP2) ice core record (Fig. 1) showed no significant change in δD of CH_4 through the YD-PB transition, which is evidence against major clathrate involvement (11).

The best tracer for distinguishing between the clathrate and wetland hypotheses is arguably $^{14}CH_4$. The ultimate source of C for wetland-produced CH_4 is essentially contemporaneous atmospheric CO_2 (15). If wetlands were the only source of the rapid [CH_4] rise, there should be either no change or an increase in $^{14}CH_4$ after the abrupt warming event. In contrast, CH_4 clathrates are geologically old and contain little or no measurable ^{14}C (16). If clathrates were the only source of the [CH_4] rise, $^{14}CH_4$ over the transition would decrease (Fig. 1). In addition, paleoatmospheric $^{14}CH_4$ measurements should allow for straightforward quantification of the strength of the geologic CH_4 source, which may be an important term in the global CH_4 budget (17).

We used a surface outcrop named Pakitsoq on the west Greenland ice margin (18–20) to obtain ~1000-kg-sized glacial ice samples containing ancient air from the YD-PB transition and yielding ~ 20 μg of CH_4 carbon per sample for ^{14}C measurements. Air was melt-extracted from sample ice in the field (20, 21). We dated the sampled ice and occluded air using a combination of $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, $\delta^{18}O$ of ice ($\delta^{18}O_{ice}$), and [CH_4] measurements (21), which uniquely identified the age of the sampled section. Sample CH_4 was separated from bulk air by means of combustion to CO_2 on platinized quartz wool followed by cryogenic trapping (20, 22). CH_4-derived CO_2 was converted to graphite and measured for ^{14}C by means of accelerator mass spectrometry (20, 22).

$^{14}CH_4$ results are presented in Fig. 1 and table S1. Surprisingly, all values are higher than ^{14}C of contemporaneous CO_2; that is, above the highest expected paleoatmospheric $^{14}CH_4$. Procedural ^{14}C contamination was shown through extensive testing to be very small (<3% of sample

[1]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA. [2]Australian Nuclear Science and Technology Organisation (ANSTO), Private Mail Box 1, Menai, NSW 2234, Australia. [3]Department of Geosciences, Oregon State University, Corvallis, OR 97331, USA. [4]National Institute of Water and Atmospheric Research Ltd., Post Office Box 14901, Kilbirnie, 301 Evans Bay Parade, Wellington, New Zealand. [5]DTU Space, National Space Institute, Technical University of Denmark, Ørsteds Plads, Building 348, DK-2800 Kongens Lyngby, Denmark. [6]Commonwealth Scientific and Industrial Research Organisation, Marine and Atmospheric Research, Private Mail Box 1, Aspendale, VIC 3195, Australia.

*Present address: Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA.
†To whom correspondence should be addressed. E-mail: vasilii.petrenko@colorado.edu

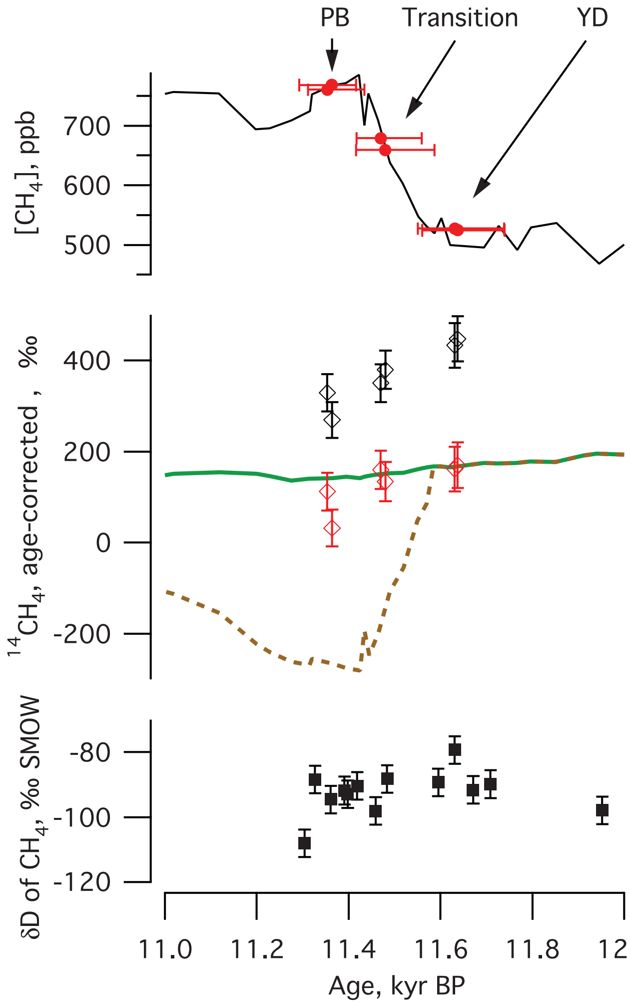
^{14}C content) and has been corrected for (22). Therefore, at least one other mechanism must exist that elevates $^{14}CH_4$ in Pakitsoq ice.

$[CH_4]$ in Pakitsoq samples from the YD-PB transition agrees within uncertainties with expected values based on the GISP2 $[CH_4]$ record (table S1) (21). The mechanism that elevates sample $^{14}CH_4$ must therefore do so without significantly affecting sample $[CH_4]$. We carefully considered the following possibilities (20): (i) biological CH_4 production from CO_2 or methylphosphonate in the ice [ruled out because the substrate ^{14}C is insufficiently high (table S3)], (ii) cosmogenic $^{14}CH_4$ production in the deglacial atmosphere (ruled out for not having been observed today), (iii) addition of ^{14}C from ^{14}C-rich CO during sample air processing (ruled out through testing), (iv) CH_4 production from ^{14}C-rich CO during air extraction from ice (an unlikely reaction under extraction conditions), and (v) biological CH_4 production directly from ^{14}C-rich CO in the ice (unlikely because it is an unknown reaction pathway with an insufficient ^{14}C yield). We found that the only feasible mechanism is in situ cosmogenic production of $^{14}CH_4$ molecules in the ice.

Cosmogenic production of ^{14}C in glacial ice by way of neutron-induced spallation of ^{16}O atoms is well known, although all of the produced ^{14}C has been thought to form ^{14}CO or $^{14}CO_2$ (23). However, laboratory experiments in which water or ice were subjected to intensive irradiation by protons to produce hot ^{11}C atoms or by energetic $^{14}C^+$ or $^{14}CO^+$ beams found that a small fraction of the hot C atoms formed CH_4; other simple organics were also formed (24, 25). This suggests the hypothesis that a small amount of $^{14}CH_4$ is also formed in natural ice via hot-atom chemistry after the nuclear reactions.

To better understand cosmogenic ^{14}C production in Pakitsoq ice, we measured ^{14}C of CO in remaining sample air (20). We found values in the range of 2 to 9 ^{14}CO molecules per gram of ice from cosmogenic production for most samples (table S4). Although considerable uncertainties exist regarding cosmogenic ^{14}CO production rates in ice, our results agree well with theoretical calculations of ablation-zone cosmogenic ^{14}CO production at Pakitsoq (20). We therefore applied a correction to sample $^{14}CH_4$ to account for cosmogenic production in the ablation zone (20). The correction uses a model to predict the total amount of cosmogenic ^{14}C produced in the ablation zone for each sample, which depends mainly on sample depth below the surface. The correction also assumes that the fraction of cosmogenic ^{14}C that forms $^{14}CH_4$ is the same for all samples. This allows for precise estimates of the ratios of cosmogenic $^{14}CH_4$ content between different samples (the uncertain parameters in the model affect the absolute values but not the ratios). The absolute magnitude of this correction is then adjusted so that the corrected $^{14}CH_4$ value for the YD sample average falls on the wetland/clathrate hypothesis line in Fig. 1. Individual corrected absolute $^{14}CH_4$ values are thus meaningless, but this approach allows meaningful comparisons between samples.

Although the applied correction represents the most likely scenario according to available evidence, it is imperfectly understood and therefore somewhat speculative. Corrected $^{14}CH_4$ values within each pair of replicate samples are still in agreement within ^{14}C measurement uncertainties [for age-corrected Δ^{14}C values, the average offset between replicates is 38 per mil (‰) versus an average measurement uncertainty of 44‰ (table S1)]. This is consistent



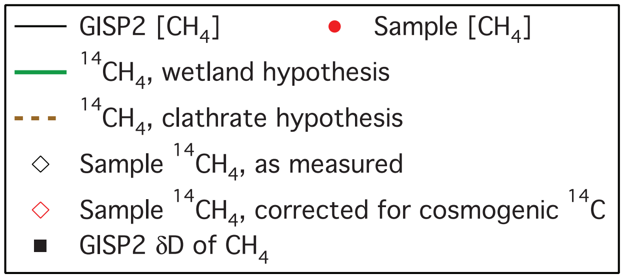


Fig. 1. $^{14}CH_4$ for the YD-PB transition. ^{14}C uncertainties are 1 SD (s). For data corrected for cosmogenic ^{14}C, uncertainties are valid for inter-sample comparisons only, not for absolute ^{14}C values. For the wetland hypothesis, 100% biospheric CH_4 emissions are assumed for all times, with $^{14}CH_4$ of emissions equal to contemporaneous $^{14}CO_2$ as specified by the INTCAL04 radiocarbon calibration (29). For the clathrate hypothesis, it is assumed that the ^{14}C of released clathrate CH_4 is −1000‰ and that all of the CH_4 rise during the transition is due to clathrate emissions. Clathrate emissions are then assumed to decrease linearly to 0 over 1000 years. The transient $^{14}CH_4$ increase at 11.44 thousand years B.P. in the clathrate model line corresponds to the simultaneous transient drop in $[CH_4]$. All $[CH_4]$ values are on the National Oceanic and Atmospheric Administration's NOAA04 scale (30). Sample and GISP2 (1) $[CH_4]$ have been corrected for gas dissolution during air melt-extraction (20). GISP2 dD of CH_4 is from (11). All records are plotted on the gas age scale for GISP2, as in (10). Horizontal error bars represent the maximum possible range of air ages included in the samples (table S1). SMOW, standard mean ocean water; ppb, parts per billion mole fraction.

with the applied corrections accurately representing the real processes that elevated sample $^{14}CH_4$.

Corrected $^{14}CH_4$ results with their propagated uncertainties are presented in Fig. 1 and table S1. For the assessment of possible clathrate contribution to the [CH_4] increase, it is useful to consider the changes in $^{14}CH_4$ during the YD-PB transition in terms of the implied changes in the strength of the fossil (^{14}C-free) CH_4 source (ΔQ_{fossil}) (Table 1). The calculation of ΔQ_{fossil} is dependent on the initial Q_{fossil} value assumed for the YD. The corrected results presented in Fig. 1 assumed a Q_{fossil} of zero for YD for simplicity. However, there is now evidence for substantial ^{14}C-free geologic CH_4 emissions (26). We used the atmospheric d$^{13}CH_4$ record from Greenland ice (10) to estimate the maximum YD geologic CH_4 source at 50 Tg/year (20) and included a scenario with a Q_{fossil} of 50 Tg/year for the YD in Table 1.

Considering these end-member scenarios, the full suggested range of possible ΔQ_{fossil} between the intervals represented by YD and transition samples is –4 to + 7 Tg/year (as compared with a 38 Tg/year total CH_4 source increase). This argues against a substantial involvement of clathrate or other geologic CH_4 in the first half of the YD-PB transition and is consistent with evidence from dD (11). The results suggest a ΔQ_{fossil} of +7 to +30 Tg/year (as compared with a 64 Tg/year total CH_4 source increase) for the full YD-PB transition, pointing to wetland CH_4 emissions with contemporaneous $^{14}CH_4$ as the likely main source of the YD-PB [CH_4] rise. For the YD Q_{fossil} = 50 Tg/year scenario, the results further suggest that most of the fossil source increase took place in the later part of the transition. This scenario implies that wetland sources respond to the warming quickly, whereas ^{14}C-depleted sources have a time lag of at least ~100 years, which is consistent with estimated minimum response times for thermokarst lake (20) and clathrate emissions (8, 20).

The +7 to +30 Tg/year increase in Q_{fossil} suggested by the $^{14}CH_4$ results for the full YD-PB transition can be explained by either thermokarst lake or clathrate/geologic CH_4 emissions, or some combination of the two, as follows. Measured thermokarst lake emissions today have a mean $\Delta^{14}CH_4$ of ~–740‰ (27). If we assume the same overall $\Delta^{14}CH_4$ for thermokarst lake emissions for the PB (20) and a maximum YD-PB thermokarst lake emission rate increase of ~15 Tg/year (7), then thermokarst lakes can explain a ΔQ_{fossil} of up to 12 Tg/year (20).

The YD-PB record of dD of CH_4 (11) can be used to illustrate some possible constraints on the magnitude of clathrate/geologic contributions to the CH_4 rise. dD of CH_4 in natural gas is very similar to the estimated clathrate value [–189 T 27‰ (11)], whereas dD of wetland CH_4 is around –320 T 20‰ (9, 11). Results of a simple one-box model and isotopic mass balance calculations (20) show that for the case of zero Q_{fossil} for the YD, the dD record allows for only 1 Tg/year of clathrate/geologic emissions in the PB. However, if a Q_{fossil} of 50 Tg/year is assumed for the YD, then a YD-PB increase of up to 28 Tg/year of clathrate/geologic emissions is possible. These limits decrease if we assume that all of the fossil source increase is due to marine clathrates (rather than a combination of marine clathrate and terrestrial geologic sources, for example) (20). This is because CH_4 released from marine clathrates is partially oxidized in the sediments and the water column, resulting in even higher dD values for clathrate-derived CH_4 released to the atmosphere (28).

In summary, our $^{14}CH_4$ results, although somewhat uncertain because of the applied correction for cosmogenic ^{14}C, suggest that wetlands were the likely main driver of the YD-PB [CH_4] increase and that clathrates did not play a large role. This is in agreement with findings from previous ice core CH_4 isotopic studies (10, 11).

Table 1. Inferred changes in the total CH_4 source (Q_{total}) and the fossil CH_4 source (Q_{fossil}) during the YD-PB transition. Q_{total} for the YD is as in (1); Q_{total} for the transition and PB was calculated based on the YD value and the average sample [CH_4] and assuming no changes in the CH_4 atmospheric lifetime. Q_{fossil} for the YD was assumed to be either zero (third column) or 50 Tg/year (fourth column); for other intervals it was calculated as

$$Q_{fossil}\ ¼\ Q_{total}\quad 1 - \frac{^{14}CH_{4sample}}{^{14}CH_{4wetland}}$$

$^{14}CH_{4wetland}$ is the expected value for wetland CH_4 emissions, set equal to contemporaneous $^{14}CO_2$ (29). Calculations were made with the corrected $^{14}CH_4$ results, averages of replicate samples, in pMC units and decay-corrected for the sample age. For the case of YD Q_{fossil} = 50 Tg/year, the cosmogenic ^{14}C corrections were recalculated accordingly for all samples.

Intervals compared	DQ_{total}, Tg/year	ΔQ_{fossil}, Tg/year*	ΔQ_{fossil}, Tg/year†
Younger Dryas (141 Tg/yr) transition	+38	−4 − +5	−3 − +7
Transition Preboreal	+26	+2 − +22	+12 − +33
Younger Dryas Preboreal	+64	+7 − +18	+18 − +30

*Assuming Q_{fossil} = 0 Tg/year for YD; 1 s range. †Assuming Q_{fossil} = 50 Tg/year for YD; 1 s range.

References and Notes

1. E. J. Brook, S. Harder, J. Severinghaus, E. J. Steig, C. M. Sucher, Global Biogeochem. Cycles 14, 559 (2000).
2. A. M. Thompson, J. A. Chappellaz, I. Y. Fung, T. L. Kucsera, Tellus 45B, 242 (1993).
3. P. Martinerie, G. P. Brasseur, C. Granier, J. Geophys. Res. 100, 14291 (1995).
4. J. Chappellaz et al., Nature 366, 443 (1993).
5. J. P. Kennett, K. G. Cannariato, I. L. Hendy, R. J. Behl, Science 288, 128 (2000).
6. E. G. Nisbet, Can. J. Earth Sci. 27, 148 (1990).
7. K. M. Walter, M. E. Edwards, G. Grosse, S. A. Zimov, F. S. Chapin III, Science 318, 633 (2007).
8. D. Archer, Biogeosciences 4, 521 (2007).
9. H. Fischer et al., Nature 452, 864 (2008).
10. H. Schaefer et al., Science 313, 1109 (2006).
11. T. Sowers, Science 311, 838 (2006).
12. P. Quay et al., Global Biogeochem. Cycles 13, 445 (1999).
13. A. V. Milkov, Org. Geochem. 36, 681 (2005).
14. H. Schaefer, M. J. Whiticar, Global Biogeochem. Cycles 22, GB002889 (2008).
15. M. Wahlen et al., Science 245, 286 (1989).
16. G. Winckler et al., Geophys. Res. Lett. 29, 1423 (2002).
17. K. A. Kvenvolden, B. W. Rogers, Mar. Pet. Geol. 22, 579 (2005).
18. V. V. Petrenko, J. P. Severinghaus, E. J. Brook, N. Reeh, H. Schaefer, Quat. Sci. Rev. 25, 865 (2006).
19. N. Reeh, H. Oerter, A. Letreguilly, H. Miller, H. W. Hubberten, Global Planet. Change 90, 373 (1991).
20. Materials and methods are available as supporting material on Science Online.
21. V. V. Petrenko et al., J. Glaciol. 54, 233 (2008).
22. V. V. Petrenko et al., Radiocarbon 50, 53 (2008).
23. D. Lal, A. J. T. Jull, D. J. Donahue, D. Burtner, K. Nishiizumi, Nature 346, 350 (1990).
24. I. M. Evans, thesis, University of Cambridge, Cambridge, UK (1970).
25. K. Rossler, H. J. Jung, B. Nebeling, Adv. Space Res. 4, 83 (1984).
26. G. Etiope, Atmos. Environ. 38, 3099 (2004).
27. K. M. Walter, J. P. Chanton, F. S. Chapin, E. A. G. Schuur, S. A. Zimov, J. Geophys. Res. 113, JG000569 (2008).
28. M. J. Whiticar, Chem. Geol. 161, 291 (1999).
29. P. J. Reimer et al., Radiocarbon 46, 1029 (2004).
30. E. J. Dlugokencky et al., J. Geophys. Res. 110, JD006035 (2005).
31. This work was supported by NSF grants OPP0221470 (to J.P.S.) and OPP0221410 (to E.J.B.), a Packard Fellowship (to J.P.S.), an American Chemical Society grant PRF 42551-AC2 (to H.S. and E.J.B.), the ANSTO Cosmogenic Climate Archives of the Southern Hemisphere project, the New Zealand Foundation of Science and Technology (contract C01X0703), and the Australian Climate Change Science Program. We thank D. Ferretti and P. Franz for making d$^{13}CH_4$ measurements; the Keeling laboratory for the use of a CO_2 extraction line; G. Emanuel for advice with $^{14}CO_2$ processing; M. Headly for Kr/Ar and Xe/Ar measurements; D. Lal for valuable discussions; A. Williams, V. Levchenko, R. Moss, T. Bromley, and R. Martin for assistance with sample processing; J. Melton, M. Arsenault, P. Rose, N. Ness, and K. Ranke for help with field sampling; and Z. Wang and J. Mak for ^{13}C of CO measurements. The manuscript was improved by suggestions from E. Nesbit and one anonymous reviewer.

Supporting Online Material
www.sciencemag.org/cgi/content/full/324/5926/506/DC1
Materials and Methods
Tables S1 to S6
References

24 November 2008; accepted 5 March 2009
10.1126/science.1168909