

3. P. S. Berloff, J. C. McWilliams, A. Bracco, *J. Phys. Oceanogr.* **32**, 764 (2002).
4. J. B. Joergensen, J. Mann, S. Ott, H. L. Pécseli, J. Trulsen, *Phys. Fluids* **17**, 035111 (2005).
5. M. C. Wolf, R. Voigt, P. A. Moore, *J. Chem. Ecol.* **30**, 501 (2004).
6. P. Moore, J. Crimaldi, *J. Mar. Syst.* **49**, 55 (2004).
7. S. Edouard, B. Legras, F. Lefèvre, R. Eymard, *Nature* **384**, 444 (1996).
8. M. Nelkin, R. M. Kerr, *Phys. Fluids* **24**, 1754 (1981).
9. B. Sawford, *Annu. Rev. Fluid Mech.* **33**, 289 (2001).
10. L. F. Richardson, *Proc. R. Soc. London Ser. A* **110**, 709 (1926).
11. G. K. Batchelor, *Q. J. R. Meteorol. Soc.* **76**, 133 (1950).
12. P. K. Yeung, *Phys. Fluids* **6**, 3416 (1994).
13. S. Ott, J. Mann, *J. Fluid Mech.* **422**, 207 (2000).
14. G. Boffetta, I. M. Sokolov, *Phys. Rev. Lett.* **88**, 094501 (2002).
15. P. K. Yeung, M. S. Borgas, *J. Fluid Mech.* **503**, 93 (2004).
16. F. Nicolleau, G. Yu, *Phys. Fluids* **16**, 2309 (2004).
17. L. Biferale *et al.*, *Phys. Fluids* **17**, 115101 (2005).
18. A. La Porta, G. A. Voth, A. M. Crawford, J. Alexander, E. Bodenschatz, *Nature* **409**, 1017 (2001).
19. G. A. Voth, A. La Porta, A. M. Crawford, J. Alexander, E. Bodenschatz, *J. Fluid Mech.* **469**, 121 (2002).
20. M. Virant, T. Dracos, *Meas. Sci. Technol.* **8**, 1539 (1997).
21. N. T. Ouellette, H. Xu, E. Bodenschatz, *Exp. Fluids* **40**, 301 (2006).
22. A. N. Kolmogorov, *Dokl. Akad. Nauk SSSR* **30**, 301 (1941).
23. A. M. Obukhov, *Izv. Akad. Nauk SSSR* **5**, 453 (1941).
24. K. R. Sreenivasan, *Phys. Fluids* **7**, 2778 (1995).
25. P. K. Yeung, *Annu. Rev. Fluid Mech.* **34**, 115 (2002).
26. D. J. Thomson, B. J. Devenish, *J. Fluid Mech.* **526**, 277 (2005).
27. S. Kurien, K. R. Sreenivasan, *Phys. Rev. E* **64**, 056302 (2001).
28. R. A. Shaw, *Annu. Rev. Fluid Mech.* **35**, 183 (2003).
29. Z. Warhaft, J. L. Lumley, *J. Fluid Mech.* **88**, 659 (1978).
30. This research was supported by the Physics Division of NSF and by the Max Planck Society. We thank L. Collins, G. Falkovich, J. Hunt, J. Schumacher, D. Vincenzi, and Z. Warhaft for helpful discussions and suggestions over the course of this work.

24 October 2005; accepted 5 January 2006  
10.1126/science.1121726

## Late Quaternary Atmospheric CH<sub>4</sub> Isotope Record Suggests Marine Clathrates Are Stable

Todd Sowers

One explanation for the abrupt increases in atmospheric CH<sub>4</sub> that occurred repeatedly during the last glacial cycle involves clathrate destabilization events. Because marine clathrates have a distinct deuterium/hydrogen (D/H) isotope ratio, any such destabilization event should cause the D/H ratio of atmospheric CH<sub>4</sub> ( $\delta D_{CH_4}$ ) to increase. Analyses of air trapped in the ice from the second Greenland ice sheet project show stable and/or decreasing  $\delta D_{CH_4}$  values during the end of the Younger and Older Dryas periods and one stadial period, suggesting that marine clathrates were stable during these abrupt warming episodes. Elevated glacial  $\delta D_{CH_4}$  values may be the result of a lower ratio of net to gross wetland CH<sub>4</sub> emissions and an increase in petroleum-based emissions.

The ice core record of atmospheric CH<sub>4</sub> changes covering the past 650,000 years exhibits two primary frequencies. Over long time scales (greater than 10,000 years) atmospheric CH<sub>4</sub> changes have a substantial amount of variance concentrated in the precessional bandwidth (19,000 and 23,000 years) (1, 2) that is considered to be an integral part of tropical climate throughout the late Pleistocene. One hypothesis that accounts for this observation involves an energized hydrologic cycle during periods of elevated low-latitude insolation. The invigorated hydrologic cycle promotes an increase in wetland extent driving a concomitant increase in CH<sub>4</sub> emissions that raise atmospheric CH<sub>4</sub> levels during warm periods. Embedded within the precession signal are millennial- and century-scale variations that are tightly coupled to Greenland temperature (3, 4). In general, increasing atmospheric CH<sub>4</sub> levels are synchronous with, or slightly lag (by a few decades), the surface temperature increase over Greenland (5). Assessing the nature of these abrupt CH<sub>4</sub> events is important for understanding how ecosystems and

climate are connected and in estimating the degree to which future CH<sub>4</sub> levels may contribute to changes in Earth's radiation budget.

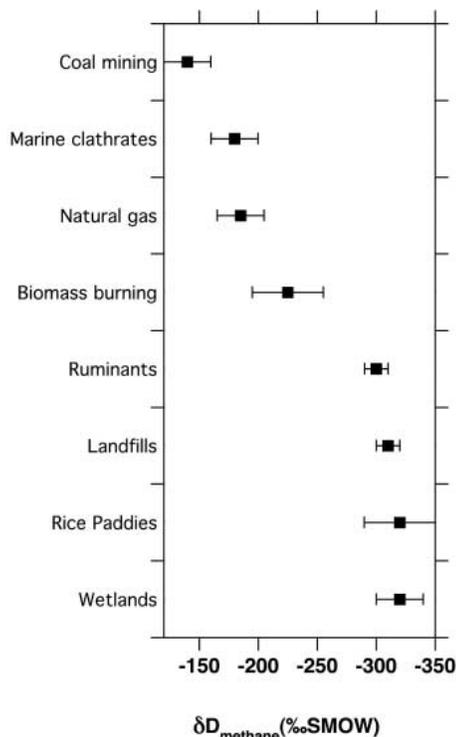
There are two competing explanations for the abrupt CH<sub>4</sub> increases. One hypothesis holds that the terrestrial biosphere is capable of rapidly increasing CH<sub>4</sub> emissions in response to abrupt changes in the hydrologic cycle that are teleconnected to surface temperatures over Greenland (3, 4). The other explanation involves the sudden release of marine clathrates situated along the continental margin where episodic destabilization events may have been triggered by enhanced ventilation (warming) of upper thermocline waters (6). The majority of the released CH<sub>4</sub> ultimately travels across the air-sea interface leading to atmospheric CH<sub>4</sub> increases.

Model estimates of changes in the primary CH<sub>4</sub> sink (tropospheric hydroxyl radical) during the last glacial termination suggest that the observed CH<sub>4</sub> variations must be due in large part to changes in the sources as opposed to changes in the rate of removal (7). The isotopic composition of atmospheric CH<sub>4</sub> therefore provides additional information on the relative contribution of the various sources. Variations in the D/H ratio of atmospheric CH<sub>4</sub> ( $\delta D_{CH_4}$ ) can be used to infer variable clathrate contributions on the basis of their elevated  $\delta D$

values compared with all terrestrial CH<sub>4</sub> sources (Fig. 1). Methane clathrates within the continental margin sediments are formed almost exclusively by CO<sub>2</sub> reduction or thermal cracking of longer chain hydrocarbons, whereas terrestrial CH<sub>4</sub> emissions are primarily aceticlastic in nature (8, 9). During CO<sub>2</sub> reduction, all the methyl hydrogen atoms come directly from porewater H<sub>2</sub> that is in isotopic equilibrium with the porewater (10). The resulting  $\delta D_{CH_4}$  values are lower than the porewater  $\delta D_{H_2O}$  due to a  $\sim 180$  per mil (‰) biologically induced isotope effect associated with CO<sub>2</sub> reduction (9, 11). Marine clathrate  $\delta D_{CH_4}$  values from 13 near-shore sites scattered throughout the Northern Hemisphere are surprisingly constant ( $-189 \pm 27\%$ ; error is SD) given the diverse nature of the geologic and sedimentologic settings and the varying proportions of microbial and thermogenic CH<sub>4</sub> at each site (12, 13). In contrast, CH<sub>4</sub> production in terrestrial ecosystems is dominated by acetogenesis (acetate fermentation) where three-fourths of the hydrogen atoms in the emitted methane originate from the methyl group associated with the acetate substrate. The remaining hydrogen comes from the local water with the resulting terrestrial  $\delta D_{CH_4}$  values generally ranging from  $-250$  to  $-380\%$ , with the local  $\delta D_{CH_4}$  value strongly influenced by the  $\delta D$  of precipitation (8, 9).

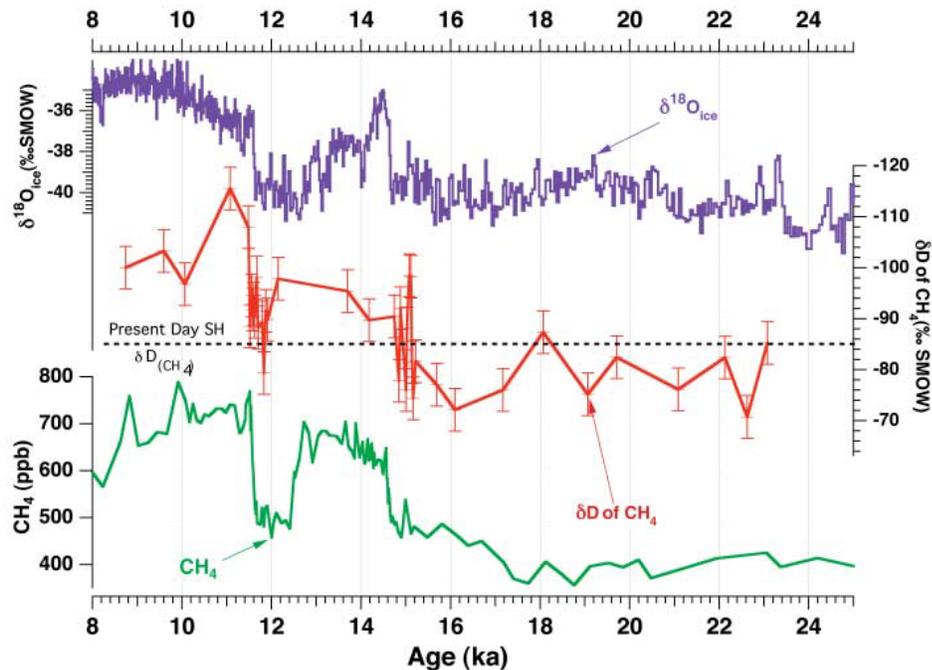
An atmospheric  $\delta D_{CH_4}$  record (Fig. 2) was generated from the second Greenland ice sheet project (GISP II) ice core using a previously described technique with an external precision of  $\pm 4.2\%$  (14). The general picture of  $\delta D_{CH_4}$  variations associated with the deglaciation shows a progressive decrease in  $\delta D_{CH_4}$  as the concentration of CH<sub>4</sub> increases, opposite to that predicted by increasing clathrate contributions due to warming associated with the termination. During the last glacial maximum (LGM),  $\delta D_{CH_4}$  values were generally  $\sim 5\%$  higher than the Bolling/Allerod values [15 to 13 thousand years ago (ka)] and  $\sim 20\%$  higher than early Holocene values. There are three factors that can be reasonably constrained as contributing to the elevated  $\delta D_{CH_4}$  values during the LGM. All three factors are temperature dependent, so

Department of Geosciences and the Earth and Environmental Systems Institute, Pennsylvania State University, University Park, PA 16802, USA. E-mail: sowers@geosc.psu.edu



**Fig. 1.** Characteristic  $\delta D_{CH_4}$  values for various present-day  $CH_4$  sources. All the data except the value for the marine clathrates (13) are from (26–28). Present day atmospheric  $\delta D_{CH_4}$  estimates are  $\sim -90 \pm 5\%$  (29). The enriched atmospheric value is the result of a large KIE (+250‰) associated with the primary sink (tropospheric OH) (14). Error bars for each source correspond to the tabulated range of values. SMOW, standard mean ocean water.

estimates have been made on the basis of two different tropical LGM temperature estimates (Table 1). First, colder temperatures during this period would have increased atmospheric  $\delta D_{CH_4}$  through the temperature-dependent kinetic isotope effect (KIE) associated with the primary removal process, OH oxidation in the troposphere. The magnitude of this effect is +3.4‰ on the basis of the laboratory-determined temperature dependence (15), assuming tropospheric temperatures were 5°C colder during the LGM. Secondly,  $\delta D$  changes in mean ocean water arising from changes in continental ice volume impart a direct effect on atmospheric  $\delta D_{CH_4}$  by altering the  $\delta D$  of porewater  $H_2$  that is utilized by  $CO_2$  reducing methanogens (oceanic and terrestrial). A less direct effect occurs as the oceanic  $\delta D_{H_2O}$  change is propagated through the hydrologic cycle and incorporated in terrestrial organic hydrocarbons (16, 17), the primary substrate for the fermentative methanogens. The mean ocean  $\delta D_{H_2O}$  change [7.5‰ (18)] is transferred through the LGM global hydrologic cycle (19, 20), causing changes in  $\delta D_{CH_4}$  values for terrestrial  $CH_4$  that range from -5 to 5‰, depending on the assumed LGM tropical temperatures (8, 9). Finally, a 10% decrease in



**Fig. 2.** Results from the last glacial termination as recorded in the GISP II ice core. The upper purple curve is the isotopic temperature (30). The red curve is from the current  $\delta D_{CH_4}$  analyses with  $1\sigma$  (4.2‰) error bars. The bottom  $CH_4$  concentration curve (green) is from Brook *et al.* (3). ppb, parts per billion. The increased sample resolution associated with the abrupt  $CH_4$  concentration increases associated with the onset of the Bolling/Allerod and the end of the Younger Dryas periods are shown in expanded view in Fig. 3. The present-day  $\delta D_{CH_4}$  value for the Southern Hemisphere (SH) is shown as a horizontal dashed line for reference.

**Table 1.** Constraining factors influencing  $\delta D_{CH_4}$  during the LGM.

Factor	$\Delta\delta D_{CH_4}$ (LGM to Holocene) (‰)	
	CLIMAP SST*	5°C Tropical cooling
10% decrease in $C_3/C_4$ ratio during LGM†	-1.9	0
KIE for OH oxidation	0	3.4
$\Delta$ Sea level‡	5.1	0 to -5
Total change	+3.2	3.4 to -1.6

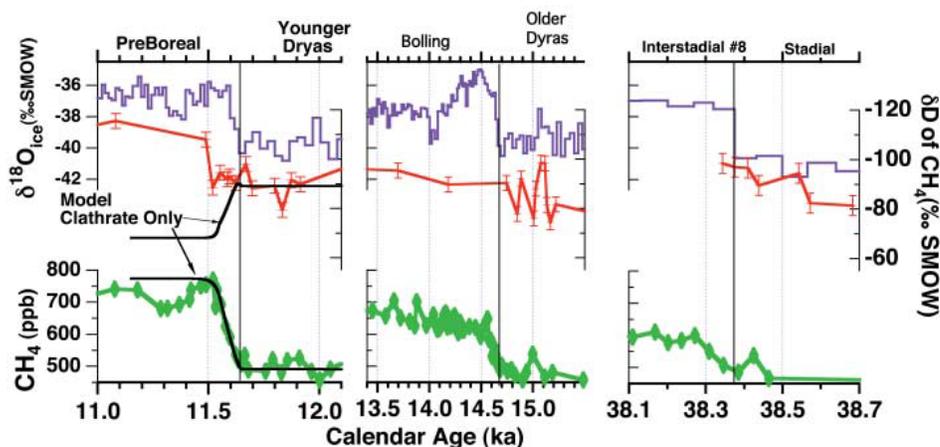
\*CLIMAP Climate: Long-Range Investigation, Mapping, and Prediction; SST, sea surface temperature. †Assuming the D/H ratio in  $C_3$  and  $C_4$  plants differs by  $\sim 15\%$  [ $C_3$  plants have higher  $\delta D$  values (31)], then a 10% reduction in the  $C_3/C_4$  ratio of wetland plants during the LGM (21) would have raised atmospheric  $\delta D_{CH_4}$  values by  $\sim 1.9\%$  relative to Holocene values. Assume additional 5°C cooling during LGM yields no change in  $C_3/C_4$  ratio. ‡Seawater  $\delta D_{H_2O}$  during LGM = 7.5‰ standard mean ocean water (18). General circulation model simulations suggest little change in  $\delta D_{H_2O}$  precipitation using CLIMAP SST (19, 20) but a slight decrease in  $\delta D_{H_2O}$  precipitation for 5°C tropical cooling (19). Finally, assume  $\delta D_{CH_4}/\delta D_{H_2O} = 0.675$  (8).

the ratio of  $C_3$ - to  $C_4$ -type plants during the LGM (21) would have lowered atmospheric  $\delta D_{CH_4}$  values by 0 to 1.9‰ relative to Holocene values. Together these three factors account for a small portion of the observed 20‰  $\delta D_{CH_4}$  shift between the LGM and early Holocene, implying that other factors must be considered.

There are at least three additional factors contributing to the atmospheric  $\delta D_{CH_4}$  change associated with the termination that are difficult to quantify. First, elevated  $\delta D_{CH_4}$  values during the LGM may be the result of a decrease in the ratio of net to gross (N/G)  $CH_4$  production. It has been fairly well documented through inhibitor studies that as much as 50% of the  $CH_4$  produced at depth in soils is consumed by

microbially mediated methane oxidation near the soil-atmosphere interface (22). The  $\delta D_{CH_4}$  values for the emitted  $CH_4$  are strongly dependent on the N/G ratio because of the large KIE associated with methane oxidation [-95 to -285‰ (23)]. For example, lowering N/G by 11% during the LGM (with the  $\delta D_{CH_4}$  of gross  $CH_4$  assigned as -300‰ and the KIE for methane oxidation as -95‰) would raise atmospheric  $\delta D_{CH_4}$  by 10‰. The sense of this change is consistent with observations that the methane-producing communities are more sensitive to temperature changes than methane-oxidizing communities (24).

Two additional factors contributing to the elevated  $\delta D_{CH_4}$  values during the LGM involve an increase in the relative proportion



**Fig. 3.** Expanded views of three abrupt  $\text{CH}_4$  concentration events recorded in the GISP II ice core. The isotopic temperature record (30) and atmospheric  $\text{CH}_4$  concentration record (3) are plotted for reference. The red curves are from the current  $\delta\text{D}_{\text{CH}_4}$  analyses with  $1\sigma$  errors at each measured depth. The results from the one-box clathrate-only model are shown for the Younger Dryas simulation with black curves. All data in all three panels are plotted on the same y axes for comparison.

of petroleum-based and/or biomass-burning  $\text{CH}_4$  emissions, both of which have elevated D/H ratios (Fig. 1). Model simulations of biomass burning, however, suggest lowered  $\text{CH}_4$  emissions during the LGM (25). If, as recently suggested (12, 13),  $\text{CH}_4$  from petroleum seeps contributed a larger proportion of global sources during the LGM compared with early Holocene periods, then we would expect higher atmospheric  $\delta\text{D}_{\text{CH}_4}$  values during the LGM. Assuming global  $\text{CH}_4$  emissions during the LGM were 111 Tg/year (3) and the characteristic  $\delta\text{D}_{\text{CH}_4}$  value for the terrestrial biosphere was  $-300\text{‰}$ , then a  $10\text{‰}$   $\delta\text{D}_{\text{CH}_4}$  signal can be accounted for by increasing the fraction of  $\text{CH}_4$  emissions based on petroleum and/or biomass burning by 9% during the LGM (compared with early Holocene emissions).

The high-resolution  $\delta\text{D}_{\text{CH}_4}$  records during the end of the Younger and Older Dryas periods (11.5 and 14.7 ka, respectively) and the onset of interstadial 8 (IS8) (38.5 to 38 ka) provide important constraints for assessing clathrate stability during these periods (Fig. 3). With the exception of one short period of increasing  $\delta\text{D}_{\text{CH}_4}$  between 15.2 and 15.0 ka, the atmospheric  $\delta\text{D}_{\text{CH}_4}$  record from GISP II shows relatively stable or slightly decreasing  $\delta\text{D}_{\text{CH}_4}$  values during periods of increasing  $\text{CH}_4$  concentration. This trend is not consistent with either a gradual or an episodic release of clathrates, suggesting that marine clathrates were stable throughout the last glacial termination as well as during periods of abrupt warming.

To estimate the magnitude of the atmospheric  $\delta\text{D}_{\text{CH}_4}$  shift associated with a hypothetical clathrate destabilization event, a simple one-box model of the atmosphere was developed using the  $\text{CH}_4$  concentration history from the end of the Younger Dryas period to constrain total  $\text{CH}_4$  emissions (3). The model consists of two sources and a single sink term. Terrestrial

$\text{CH}_4$  emissions, the lifetime of atmospheric  $\text{CH}_4$ , the  $\delta\text{D}_{\text{CH}_4}$  value for terrestrial  $\text{CH}_4$  emissions ( $-300\text{‰}$ ), and the KIE associated with the sink ( $+165\text{‰}$ ) were all held constant throughout the simulation. Then, beginning at model year 11.64 ka, we introduced clathrate-derived  $\text{CH}_4$  ( $\delta\text{D}_{\text{CH}_4} = -189\text{‰}$ ) at a rate of 0.8 Tg/year for the next 100 model years, after which clathrate emissions were held constant at 80 Tg/year. The model predicted evolution of  $\text{CH}_4$  concentration and  $\delta\text{D}_{\text{CH}_4}$  are included in Fig. 3 for comparison with the GISP II data from the Younger Dryas. Assuming clathrate  $\text{CH}_4$  was the only new  $\text{CH}_4$  source at the end of the Younger Dryas, the predicted  $\delta\text{D}_{\text{CH}_4}$  change was  $+21\text{‰}$ . The relatively constant  $\delta\text{D}_{\text{CH}_4}$  values throughout the transition to elevated  $\text{CH}_4$  levels suggest little change in the relative proportion of all individual emissions with near-constant characteristic  $\delta\text{D}_{\text{CH}_4}$  values.

The transition from the Older Dryas to Bolling period (15 to 14 ka) provides a very different view of the factors influencing  $\delta\text{D}_{\text{CH}_4}$  (Fig. 3). During the 300-year period immediately preceding the abrupt increase in atmospheric  $\text{CH}_4$  loading,  $\delta\text{D}_{\text{CH}_4}$  initially decreases by  $15\text{‰}$  followed by a rapid  $10\text{‰}$  increase, during which time atmospheric  $\text{CH}_4$  levels remained effectively constant. Obviously, many more data are needed to document this oscillation but, with the limited data in hand, it appears that a rapid shift in the characteristic  $\delta\text{D}_{\text{CH}_4}$  values of various sources is needed in the absence of substantial global emission changes during a period of relative climate stability.

The general trend of decreasing  $\delta\text{D}_{\text{CH}_4}$  throughout the termination, combined with relatively stable  $\delta\text{D}_{\text{CH}_4}$  values during periods of rapidly increasing  $\text{CH}_4$ , suggests that marine clathrates are stable during this period and specifically during abrupt warming events. The

elevated LGM  $\delta\text{D}_{\text{CH}_4}$  values are likely to be related to a number of factors, the most important being decreased N/G ratios and an increase in petroleum-based  $\text{CH}_4$  emissions during the glacial period. Further insight into these factors will derive from future measurements of  $\delta^{13}\text{C}_{\text{CH}_4}$  that are in progress.

#### References and Notes

- J. Chappellaz, J.-M. Barnola, D. Raynaud, Y. S. Korotkevich, C. Lorius, *Nature* **345**, 127 (1990).
- R. Spahni *et al.*, *Science* **310**, 1317 (2005).
- E. Brook, T. Sowers, J. Orchard, *Science* **273**, 1087 (1996).
- J. Chappellaz *et al.*, *Nature* **366**, 443 (1993).
- J. P. Severinghaus, T. Sowers, E. J. Brook, R. B. Alley, M. L. Bender, *Nature* **391**, 141 (1998).
- J. P. Kennett, K. G. Cannariato, I. L. Hendy, R. J. Behl, *Methane Hydrates in Quaternary Climate Change* (American Geophysical Union, Washington, DC, 2003).
- P. Martinierie, G. P. Brasseur, C. Granier, *J. Geophys. Res.* **100**, 14291 (1995).
- S. Waldron, J. M. Lansdown, E. M. Scott, A. E. Fallick, A. J. Hall, *Geochim. Cosmochim. Acta* **63**, 2237 (1999).
- M. J. Whiticar, E. Faber, M. Schoell, *Geochim. Cosmochim. Acta* **50**, 693 (1986).
- D. L. Valentine, A. Chidthaisong, A. Rice, W. S. Reeburgh, S. C. Tyler, *Geochim. Cosmochim. Acta* **68**, 1571 (2004).
- M. Balabane, E. Galimov, M. Hermann, R. Letolle, *Org. Geochem.* **11**, 115 (1987).
- B. Luyendyk, J. P. Kennett, J. F. Clark, *Mar. Pet. Geol.* **22**, 591 (2005).
- A. V. Milkov, *Org. Geochem.* **36**, 681 (2005).
- Materials and methods are available as supporting material on Science Online.
- T. Gierczak, R. D. Talukdar, S. C. Herndon, G. L. Vaghjiani, A. R. Ravishankara, *J. Phys. Chem.* **101**, 3125 (1997).
- D. Sachse, J. Radke, G. Gleixner, *Geochim. Cosmochim. Acta* **69**, 4877 (2004).
- S. Epstein, C. J. Yapp, J. H. Hall, *Earth Planet. Sci. Lett.* **30**, 241 (1976).
- D. P. Schrag *et al.*, *Quaternary Sci. Rev.* **21**, 331 (2002).
- C. D. Charles, D. Rind, R. Healy, R. S. Webb, *Clim. Dyn.* **17**, 489 (2001).
- J. Jouzel, G. Hoffmann, R. D. Koster, V. Masson, *Quaternary Sci. Rev.* **19**, 363 (2000).
- G. J. Collatz, J. A. Berry, J. S. Clark, *Oecologia* **114**, 441 (1998).
- W. S. Reeburgh, in *The Atmosphere*, R. F. Keeling, Ed. (Elsevier-Perigamon, Oxford, 2004), vol. 4, pp. 65–90.
- M. J. Whiticar, *Chem. Geol.* **161**, 291 (1999).
- S. C. Moosavi, P. M. Crill, *J. Geophys. Res.* **103**, 29093 (1998).
- K. Thonicke, I. C. Prentice, C. Hewitt, *Global Biogeochem. Cycles* **19**, GB3008 (2005).
- P. Quay *et al.*, *Global Biogeochem. Cycles* **13**, 445 (1999).
- A. K. Snover, P. D. Quay, *Global Biogeochem. Cycles* **14**, 25 (2000).
- A. K. Snover, P. D. Quay, W. M. Hao, *Global Biogeochem. Cycles* **14**, 11 (2000).
- A. Rice, A. A. Gotoh, H. O. Aijie, S. C. Tyler, *Anal. Chem.* **73**, 4104 (2001).
- P. M. Grootes, M. Stuiver, J. W. C. White, S. Johnsen, J. Jouzel, *Nature* **366**, 552 (1993).
- Y. Chikaraishi, H. Naraoka, *Phytochemistry* **63**, 361 (2003).
- The research was supported by NSF (ATM-0117291 and OPP-0125900). I thank R. Alley, J. Kennett, and three anonymous reviewers for carefully reviewing the manuscript.

#### Supporting Online Material

www.sciencemag.org/cgi/content/full/311/5762/838/DC1  
Materials and Methods

Table S1

References

11 October 2005; accepted 17 January 2006  
10.1126/science.1121235