www.sciencemag.org/cgi/content/full/310/5752/1317/DC1

Supporting Online Material for

Atmospheric Methane and Nitrous Oxide of the Late Pleistocene from Antarctic Ice Cores

Renato Spahni, Jérôme Chappellaz, Thomas F. Stocker,* Laetitia Loulergue, Gregor Hausammann, Kenji Kawamura, Jacqueline Flückiger, Jakob Schwander, Dominique Raynaud, Valérie Masson-Delmotte, Jean Jouzel

*To whom correspondence should be addressed: stocker@climate.unibe.ch

Published 25 November 2005, *Science* **310**, 1317 (2005)
DOI: 10.1126/science.1120132

This PDF file includes:

Materials and Methods
Figs S1 to S3
References

SUPPORTING ONLINE MATERIAL

for

Atmospheric Methane and Nitrous Oxide of the Late Pleistocene from Antarctic Ice Cores

R. Spahni, J. Chappellaz, T. F. Stocker, L. Loulergue,
G. Hausammann, K. Kawamura, J. Flückiger, J. Schwander,
D. Raynaud, V. Masson-Delmotte, J. Jouzel

1. November 2005

Materials and Methods

Measurement Methods

The air from samples of about 40g (Bern) and 50g (LGGE) of polar ice cores is extracted with a melt-refreezing method, and the extracted gas is then analyzed for N_2 + O_2 + Ar, CH_4 (Bern, LGGE) and N_2O (Bern) by gas chromatography (*1, 2*). Two standard gases (408 ppbv CH_4/201 ppbv N_2O, 1050 ppbv CH_4/304 ppbv N_2O) have been used at Bern and one (499 ppbv CH_4) at LGGE. The mean analytical uncertainty (1σ) is 10 ppbv for CH_4 (*1*) and 3.7 ppbv for N_2O (*3*). The concentrations are not corrected for gravitational settling in the firn column which corresponds to only about 1% of the measured levels. Further details about the method, tests and calibration are given by Chappellaz et al. (*1*) and Flückiger et al. (*2, 3*).

Offset corrections

A) Dome C CH_4

The agreement between the Dome C CH_4 measurements performed at Bern and LGGE is generally good, but the Bern data are consistently higher by 6 ppbv because of a different contamination correction. In order to construct a continuous record consistent with earlier Dome C measurements (*2, 4*), we added 6 ppbv to all concentrations measured at LGGE along the Dome C record.

B) Dome C – Vostok CH_4

On average between MIS 5.4 and MIS 7.3, where the Dome C and the Vostok CH_4 records provide a similar time resolution, the offset between uncorrected LGGE Dome C measurements and published Vostok results is 17 ppbv. The Vostok measurements were all performed in the 90s with the previous LGGE gas extraction system. This 17 ppbv difference is also the difference between contamination corrections applied with this older extraction system (37 ppbv) and with the new one (20 ppbv). The most plausible explanation for the offset thus lies in the contamination correction, which was probably overestimated with blank tests performed with the older extraction system. The presented Vostok CH_4 data in this paper is not corrected for this offset.

C) Dome C N_2O

Due to a N_2O measurement offset in the Bern Lab that occurred before the edc99 ice core was analyzed, we have to correct these data by a constant value of +10 ppbv, which was determined by resampling Holocene ice from the Dome C ice core and the EPICA Dronning Maud Land ice core (EDML, 75°00' S, 00°04' E, 2892 m.a.s.l.) and comparing the new results to earlier Holocene measurements *(2)*. The corrrection of 10 ppbv over 0-10 kyr BP was calculated as mean offset between splines with a cut off period of 3000 yr *(5)* through the new EDML and earlier Dome C data sets. Affected is the whole N_2O data set measured along the edc99 ice core (measurements below 776 m) covering the time period prior to 38.9 kyr BP. The corrected N_2O data set agrees well with earlier published results from the last glacial epoch and the previous interglacial ((*3, 6, 7*) and Fig. 1).

N_2O artifacts localization

Figures S1 and S2 are reproduced from J. Flückiger (*8*) and demonstrate the higher N_2O variability during climatic cold periods, e.g. the last glacial maximum, with higher dust concentrations in the ice core in the corresponding depth interval. Figure S3 shows the locations of higher dust concentrations and thus intervals of N_2O artifacts in the Dome C ice core.

Figures and legends

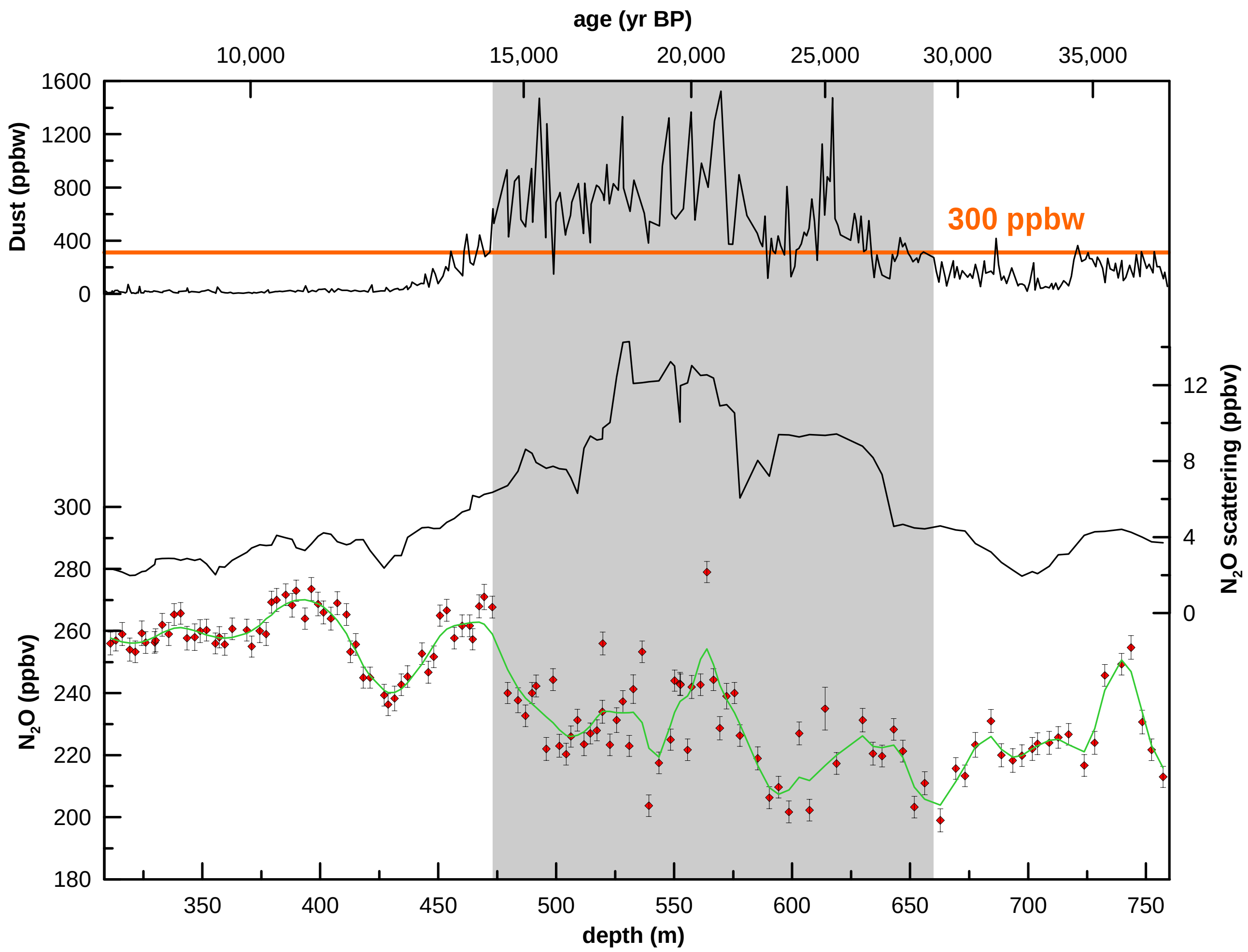

Fig. S1. Dome C dust concentration (top) (*9*), N_2O scattering (middle), and N_2O (red diamonds) against depth ((*2, 10, 11*) and Fig. 1). The smoothed spline for N_2O (green line) was calculated according to (*5*) with a cut off period of 2000 years on the Dome C EDC2 timescale (*12*). The one sigma N_2O scattering of the difference between the N_2O concentration and the spline is calculated continously over 9 datapoints (*8*). The shaded area highlights the depth range of the highly scattered N_2O data. The high scattering coincide with high impurity concentrations as indicated by the dust concentraion. This depth interval has to be excluded and cannot be interpreted in terms of the atmospheric trend of N_2O. Dust concentration above a conservativ threshold of 300 ppbw cuts out the same shaded area.

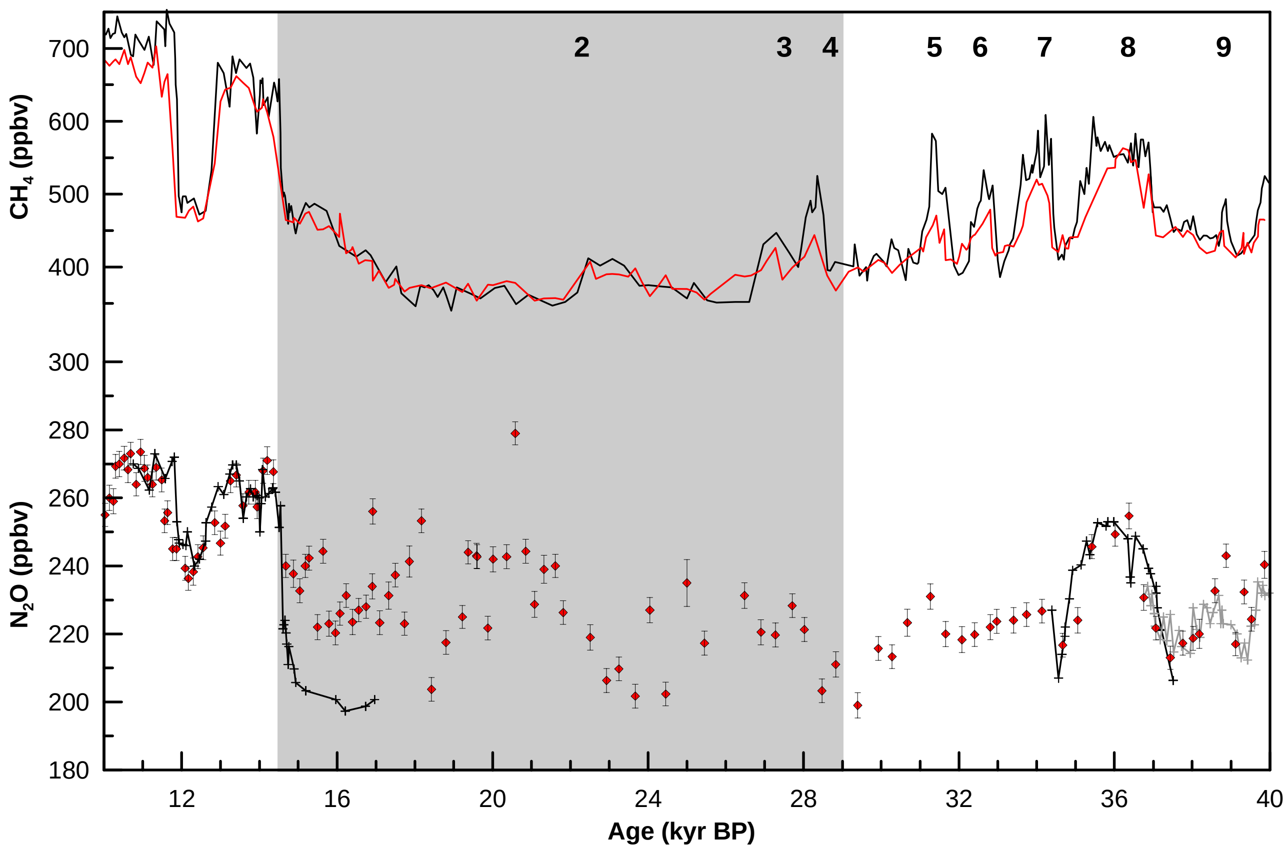

Fig. S2. Shown are CH_4 records from Dome C (red line) ((*4*) and Fig. 1) and GRIP/NGRIP (black line) (*3, 13, 14*) together with N_2O records from Dome C (red diamonds), GRIP (black crosses) (*15*) and NGRIP (grey crosses) (*3*). For the Dome C N_2O data the one sigma uncertainty is given. Not shown are GRIP and NGRIP N_2O data points that are assumed to be artifacts. All data are shown on the EDC2 time scale. The GRIP and NGRIP data was matched to the EDC2 timescale by visual matching of the corresponding CH_4 records. The numbers of the D/O events are given according to (*16*) at the top of the figure. The shaded area covers the same depth range as in Fig. S1.

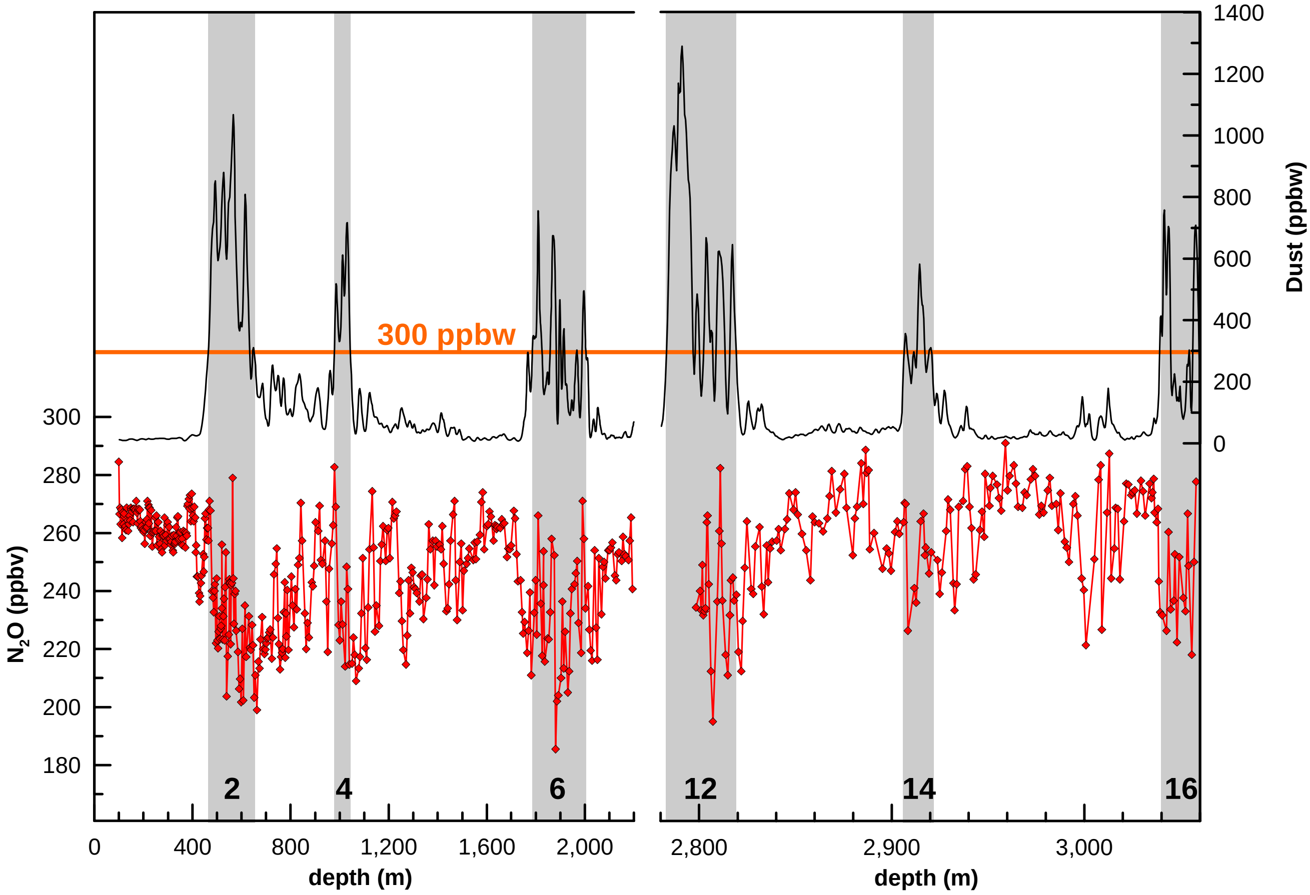

Fig. S3. Dome C N_2O (taken from Fig. 1, Fig. 2) (red curves) and dust (*9, 17*) (black curves, splined with cut off period of 2000 yr (*5*)) records plotted against depth. The 300 ppbw dust level (orange line) separates depth intervals (grey shaded) possibly containing N_2O artifacts in the ice, which are excluded for the interpretation of the data.

References

1. J. Chappellaz *et al.*, *J. Geophys. Res.* **102**, 15987 (1997).
2. J. Flückiger *et al.*, *Global Biogeochem. Cycles* **16** (2002).
3. J. Flückiger *et al.*, *Global Biogeochem. Cycles* **18** (2004).
4. E. Monnin *et al.*, *Science* **291**, 112 (2001).
5. I. G. Enting, *J. Geophys. Res.* **92**, 10977 (1987).
6. T. Sowers, R. B. Alley, J. Jubenville, *Science* **301**, 945 (2003).
7. T. Sowers, *J. Geophys. Res.* **106**, 31903 (2001).
8. J. Flückiger, *Thesis, University of Bern* (2004).
9. B. Delmonte *et al.*, *Earth Sci. Rev.* **66**, 63 (2004).
10. B. Stauffer *et al.*, *Ann. Glaciol.* **35**, 202 (2002).
11. B. Stauffer, J. Flückiger, E. Monnin, T. Nakazawa, S. Aoki, *Mem. National Inst. Polar Res.* **57**, 139 (2003).
12. EPICA Community Members, *Nature* **431**, 147 (2004).
13. T. Blunier *et al.*, *Nature* **394**, 739 (1998).
14. J. Chappellaz *et al.*, *Nature* **366**, 443 (1993).
15. J. Flückiger *et al.*, *Science* **285**, 227 (1999).
16. W. Dansgaard *et al.*, *Nature* **364**, 218 (1993).
17. F. Lambert, *in preparation* (2005).