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Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Holocene

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Abstract. High-resolution records of atmospheric methane over the last 11,500 years have been obtained from two Antarctic ice cores (D47 and Byrd) and a Greenland core (Greenland Ice Core Project). These cores show similar trapping conditions for trace gases in the ice combined with a comparable sampling resolution; this together with a good relative chronology, provided by unequivocal CH_4 features, allows a direct comparison of the synchronized Greenland and Antarctic records, and it reveals significant changes in the interpolar difference of CH_4 mixing ratio with time. On the average, over the full Holocene records, we find an interpolar difference of 44±7 ppbv. A minimum difference of 33±7 ppbv is observed from 7 to 5 kyr B.P. whereas the maximum gradient (50±3 ppbv) took place from 5 to 2.5 kyr B.P. A gradient of 44±4 ppbv is observed during the early Holocene (11.5 to 9.5 kyr B.P). We use a three-box model to translate the measured differences into quantitative contributions of methane sources in the tropics and the middle to high latitudes of the northern hemisphere. The model results support the previous interpretation that past natural CH_4 sources mainly lay in tropical regions, but it also suggests that boreal regions provided a significant contribution to the CH_4 budget especially at the start of the Holocene. The growing extent of peat bogs in boreal regions would also have counterbalanced the drying of the tropics over the second half of the Holocene. Finally, our model results suggest a large source increase in tropical regions from the late Holocene to the last millennium, which may partly be caused by anthropogenic emissions.

1. Introduction

Atmospheric CH_4 has increased globally over the past 200 years due to anthropogenic activities [*Etheridge et al.*, 1992, and references therein]. In 1992 and 1993 the rate of increase slowed for reasons that are still uncertain [*Dlugokencky et al.*, 1994; *Lowe et al.*, 1994]. In particular, it is difficult to ascertain the potential role of natural fluctuations (e.g. changes in the wetland emissions) in such short-term variability and also in future natural emissions of methane. On the other hand, studies of past atmospheric CH_4 fluctuations from polar ice cores allow us to decipher and to quantify the relationship between the past climate change and the natural CH_4 cycle [*Raynaud and Chappellaz*, 1993].

Recently, the resolution obtained on past CH_4 changes from ice core studies has been largely improved from the central Greenland Greenland Ice Core Project (GRIP) and Greenland Ice Sheet Project 2 (GISP2) ice cores [*Chappellaz et al.*, 1993b; *Blunier et al.*, 1995; *Brook et al.*, 1996]. Variations in CH_4 over Greenland during the Holocene (last 11,500 years) are now resolved at better than 100 years on the average. This allows a detailed comparison with other paleodata and a better insight into the causes of past CH_4 changes.

On the basis of the Greenland CH_4 record alone, we suggested that variations in the tropical wetland extent controlled the global CH_4 budget up to ~5 kyr B.P. and that boreal wetland growth since then caused CH_4 to increase to its preindustrial level [*Blunier et al.*, 1995]. Still, the CH_4 mixing ratio information alone is not sufficient to ascertain the relative role of the tropics and the boreal regions on past natural CH_4 changes. Quantitative constraint can be brought by additional ice core analyses: in principle, the isotopic composition of CH_4 ($^{13}C/^{12}C$ and D/H) can be combined with the distinctive isotopic signature of different sources and sinks of methane. However such measurements on air entrapped in ice cores remain a technical challenge [*Craig et al.*, 1988]. On the other hand, as we apply in this study, the comparison of Greenland and Antarctic CH_4 records over the same timescale allows the interpolar difference of CH_4 to be monitored. This difference, which amounts to about 140 ppbv today [*Dlugokencky et al.*, 1994], results from the heterogeneous distribution of CH_4 sources and sinks with latitude, combined with an atmospheric residence time of methane, which is 1 order of magnitude longer than the interhemispheric exchange time.

The CH_4 records, used to depict variations in the interpolar CH_4 difference, must satisfy several criteria: (1) the relative dating of the ice cores must be precise enough; (2) the measurements must be based on reliable standards, and their reproducibility must be good enough to reveal statistically significant changes; (3) the smoothing of

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atmospheric variations due to gas trapping in the ice must be of the same order for all the ice cores used.

The third criterion refers to the fact that the air slowly diffuses through the porous firn layers at the top of ice sheets and that air bubbles close off inside a depth range at the firn/ice transition. In consequence, the air in the bubbles does not have a discrete age but rather an age distribution, and the atmospheric temporal trends of trace gases are smoothed in the ice core records [*Schwander*, 1996]. Thus when comparing gas signals obtained from sites with different gas-trapping conditions, differences can appear when the atmospheric signal changes quickly enough with time. In this study, we use two Antarctic ice cores, D47 and Byrd, whose gas-trapping conditions are comparable to our Greenland reference from GRIP (Table 1). We present new CH_4 measurements from the Antarctic ice cores that cover the Holocene period, and we compare the results with a refined GRIP CH_4 profile. The high resolution of our records, which fulfil the three criteria mentioned above, allows us to highlight four different time periods when the CH_4 interpolar difference significantly changed. A three-box model is used to interpret this analytical signal in terms of changes in the CH_4 source strengths in the tropical regions and middle to high latitudes of the northern hemisphere during the Holocene.

2. Experimental Techniques

The basic principles of measurements are the same as the ones used for previously published methane records [*Raynaud et al.*, 1988; *Chappellaz et al.*, 1990, 1993b; *Blunier et al.*, 1993, 1995]. The main differences include the use of a new extraction line at Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) (Grenoble) and of a wet extraction technique on some of the samples at Bern. At LGGE (Grenoble) an ice sample (~40-50 g) is melted under vacuum in a glass container sealed with indium and then refrozen from the bottom with an alcohol bath at -50°C to expel gases dissolved in the water (extraction efficiency of 99%). The gas sample is then expanded into an evacuated sample loop and injected into the gas chromatograph (Varian 3300) with a six-port Valco valve. N_2 + O_2 + Ar and CH_4 are separated on a Porapak-N column (3m, 1.8 mm ID) and detected with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID), respectively. Calibration is performed against a standard gas (Air Liquide) with 499 ppbv of CH_4 in air. The samples presented here were measured with a new extraction line that can handle seven glass containers (instead of one in the previous line) and includes a multiposition Valco valve, reducing the measuring time and the volume of the expansion line.

Table 1. Present-Day Characteristics of Three Ice Cores Used in This Study

	Greenland Ice Core Project	D47	Byrd
Location and altitude	72°34'N 37°37'W 3238 m	67°23'S 137°33'E 1550 m	80°01'S 119°31'W 1530 m
Year of drilling	1990-1992	1988-1989	1968
Mean annual temperature, °C	-32	-25	-28
Accumulation rate, centimeter of ice per year	23	30	11.9
Air/ice difference in age, years	210	165	305
Age width, years	15*	10-15*	20-25*

* Based on the firn study at Summit, Greenland [*Schwander et al.*, 1993].

Blanks of the experimental procedure, determined by adding the 499 ppbv gas standard to artificial bubble-free ice, amount to 20±13 (2σ) ppbv and are substracted from all results. This is comparable to but less scattered than a blank series run on the previous line using a 1200 ppbv gas standard (18±26 ppbv). The better reproducibility may be due to an identical duration of melting and refreezing for the seven samples of the new line [*Chappellaz*, 1990]. Overall, the external precision at LGGE (blank plus chromatography) becomes ±20 (2σ) ppbv (±37 ppbv previously).

In Bern, dry and wet extraction systems were used. For dry extractions [*Fuchs et al.*, 1993] the ice sample (~12-20 g) is crushed by a milling cutter driven by a helium-flushed rotary feedthrough, inside a stainless steel container sealed with indium. The escaping gas is helium-flushed and trapped on a Porapak-Q column at -196°C. The injection occurs by desorption at 50°C. N_2 + O_2 + Ar and CH_4 are separated on a Carboxen-1000 column (50 cm, 1.5 mm ID) and detected by a TCD and a FID, respectively. Blanks amount to 19±8 ppbv. Calibration is done against a standard gas with 980±20 ppbv of CH_4. The external precision (excluding the standard gas uncertainty), from replicate and blank measurements, is ±20 ppbv (2σ).

For the wet extraction in Bern the system developed in Grenoble was used. The only differences were a container sealed with viton and a lower refreezing temperature (-60°C). Blanks amount to 21±17 (2σ) ppbv and are thus comparable to the Grenoble blanks. The external precision (excluding the standard gas uncertainty) is ±20 ppbv (2σ).

The uncertainties concerning the internally used standard gases have been checked recently through an intercalibration with the National Oceanographic and Atmospheric Administration (NOAA) scale [*Sowers et al.*, 1997]. Our standards are 1±2(1σ)% and 2±1(1σ)% higher than the NOAA standard for Bern and Grenoble, respectively. The difference between Bern and Grenoble standards thus amounts to 1.0±2.2(1σ)% and is not significant. In addition, applying such correction causes a significant disagreement between Bern and Grenoble results on the same ice samples. As a consequence, the results presented here are not on the NOAA scale but on the Grenoble and Bern internal scales, leading to the best agreement between the two laboratories.

3. Greenland Record

The GRIP core drilled at Summit presents the most favorable characteristics (Table 1) in Greenland with respect to the objective of the study (high temporal resolution, no summer melting, good dating). The timescale [*Johnsen et al.*, 1995] is slightly modified from the GRIP original dating of *Dansgaard et al.* [1993]; it gives the best fit to the Holocene stratigraphic markers (S. Johnsen, personal communication, 1996). The ice-dating precision is better than ±50 years over the Holocene; the GRIP chronology thus serves as a reference in the following. The gas/ice age difference is calculated with a densification model [*Barnola et al.*, 1991] using past temperature and accumulation rate of *Johnsen et al.* [1995]. Today's difference amounts to 210 years [*Schwander et al.*, 1993]; over the Holocene it varies little between 200 and 240 years.

3.1. Original Data

The previous GRIP Holocene series [*Blunier et al.*, 1995] revealed a systematic difference of 30 ppbv between the Bern and the LGGE results, not related to the standard gas difference mentioned above, and whose cause was originally unknown. The results were thus arbitrarily corrected by -15 and + 15 ppbv for Bern and Grenoble, respectively. New analyses revealed that the entire 30 ppbv shift was due to a drift in one container of the Bern standard gas. In this work, we thus decrease all GRIP results of *Blunier et al.* [1995] by 15 ppbv. Note that the first GRIP series, presented by *Chappellaz et al.* [1993b] and corrected by *Blunier et al.* [1995], thus comes back to the original values and that the Bern standard drift affects only the results published by *Blunier et al.* [1995]. In the first series the mixing ratios measured in Bern by dry extraction were also significantly higher than the wet extraction results in the depth range 1220-1320 m. We attributed this to effects resulting from the air-bubble to air-hydrate transformation, which takes place in that depth range. Consequently, new measurements were performed exclusively with the wet extraction technique, extracting all gases from air bubbles and air hydrates, while the dry extraction method favors extraction from air bubbles.

3.2. New Data

The mean sampling resolution of the original GRIP Holocene CH_4 profile was 85 years back to 8.0 kyr B.P. [*Blunier et al.*, 1995] and 165 years from 8.0 to 11.5 kyr B.P. [*Chappellaz et al.*, 1993b]. We analyzed 24 new depth levels, bringing down the sampling resolution to 80 years between 8.0 and 11.5 kyr B.P. We also remeasured 22 depth levels from the first series to exclude any drift in the analytical apparatus (standard gas or blank variations) since the completion of the original profile. Such drift would have biased the interpolar comparison of CH_4 levels. The difference between the first series (decreased by 15 ppbv) and the new results on the same depth levels amounts, on the average, to 3 ± 25 (2σ) ppbv and is statistically not significant (Figure 1). One depth level at 1398 m makes exception as it differs by 90 ppbv. In the first CH_4 series this was the only sample having the characteristic smell of the drilling fluid (kerosene) after extracting the gas, so it was probably contaminated. We only use the 1398 m result from the new series in agreement with neighboring samples.

The refined sampling resolution between 8.0 and 11.5 kyr B.P. (Figure 2) reveals new features in the Holocene CH_4 record: the CH_4 dip centered around 8.2 kyr B.P. is sharper (duration of ~200 years) and smaller (~60 ppbv) than observed before; it appears in the middle of a general downward trend of atmospheric methane extending from ~9.2 to 5.2 kyr B.P. Also, two other significant sharp minima (amplitude of ~50 ppbv) comparable to the one at 8.2 kyr appear at 9.3 and 11.4 kyr B.P. In opposition to the 8.2-kyr event they have no counterpart in other GRIP signals, like the isotopic or solid conductivity profiles.

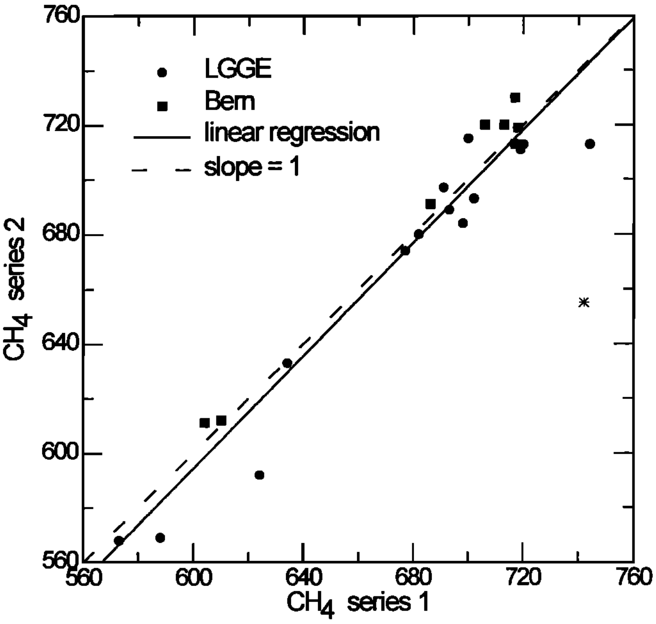

Figure 1. Comparison on specific Greenland Ice Core Project (GRIP) depth levels of the mean CH_4 mixing ratios obtained during previous measurement series (series 1, *Chappellaz et al.* [1993b] and *Blunier et al.* [1995]) and in the new set presented in this paper (series 2). The asterisk indicates a sample contaminated by the drilling fluid in series 1 (see text).

4. Antarctic Record

The Antarctic CH_4 record is obtained from two ice cores: D47, drilled on coastal Adelie Land, and Byrd in West Antarctica. The D47 core spans only the latest two thirds of the Holocene. The Byrd core reaches back to the last glacial period but presents a large brittle zone in the depth range roughly corresponding to the ice time-period 9 to 2.5 kyr B.P. (gas age 8.7-2.2 kyr B.P). In this brittle zone no reliable CH_4 results could be obtained. Combining the two ice cores allows us to build a nearly complete Holocene Antarctic CH_4 record except for the time-period 7.0-8.7 kyr B.P. Gas trapping conditions at the two sites are similar to Summit in Greenland (Table 1). The smoothing of atmospheric CH_4 variations is thus comparable at the three sites; the CH_4 records in the ice should depict similar temporal trends, even under transient conditions. The series of measurements on both D47 and Byrd were performed during the same time period as the additional CH_4 measurements on the GRIP core, which are in excellent agreement with earlier measurements (see above). In consequence, no significant experimental bias questions a comparison among the three CH_4 records.

4.1. D47

D47 is located on the margin of the East Antarctic ice sheet where rapid ice flow takes place. The original ice dating using an ice-flow model was constrained with a series of fine isotope profiles depicting a varying length of seasonal

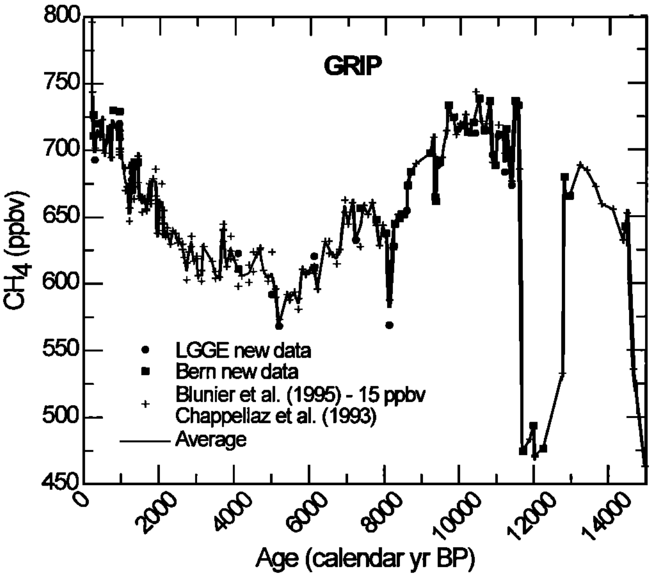

Figure 2. GRIP CH_4 profile over the last 15 kyr.

variations with depth [*Ciais*, 1991]. The model age for the upper part of the core was adjusted slightly based on two volcanic horizons [*Barnola et al.*, 1995], leading to an uncertainty of ±50 years around 1000 A.D. For older ice the uncertainty increases, and the age of the bottom of the core is estimated to be 7.5±0.75 kyr B.P. [*Ciais et al.*, 1994].

Seventy-two depth levels (111 samples) were analyzed for methane. The resulting profile as a function of depth (Figure 3) shows a characteristic downward trend of CH_4 down to ~780 m, already observed on GRIP, which corresponds to the later half of the Holocene; below ~780 m, CH_4 increases again. The CH_4 minimum, dated at 5.2 kyr B.P. in the GRIP chronology, makes an excellent time marker to constrain the age of the deepest part of D47. We thus redated D47 using the ice-flow model forced with the two volcanic horizons above 1000 A.D. and the CH_4 minimum at 5.2 kyr B.P. In that way we obtain a chronology for the trapped gases at D47, with an estimated uncertainty of ~100 years relative to the GRIP chronology. The air/ice difference in age, calculated with a densification model [*Barnola et al.*, 1991], increases with time due to the lower accumulation rate corresponding to ice originating from inland. This age difference amounts to 165 years in the upper part of the record and increases to 250 years in the deepest strata. Taking it into account, we obtain a chronology for the ice and an age of ice at the bottom of D47 of 7.3 kyr B.P. (in good agreement with the estimate of *Ciais et al.* [1994]).

The mean sampling resolution of the D47 CH_4 profile is 100 years (maximum 210 years), close to the GRIP sampling resolution. The two CH_4 profiles, shown on a common timescale in Figure 4a, reveal a remarkable overall coherency over the last 7.0 kyr. Combined with the large number of measurements, this allows us to calculate a reliable interpolar mixing ratio difference.

4.2. Byrd

Various attempts have been made to date the Byrd core drilled in 1968 [*Sowers and Bender*, 1995; *Hammer et al.*, 1994, and references therein]. The most precise timescale over the Holocene part of the core is obtained from the observation of seasonal variations of acidity [*Hammer et al.*, 1994]. Unfortunately, these observations could not be performed on the entire core length and are especially missing in the depth range 300-880 m where the ice is very brittle. The ice dating precision is thus not better than ±500 years at the start of the Holocene.

The air/ice difference in age has been calculated using a dynamic model [*J. Schwander et al.*, Age scale of the air in the Summit ice — Implication for glacial-interglacial temperature change, submitted to *Journal of Geophysical Research*, 1997], including a firn densification model

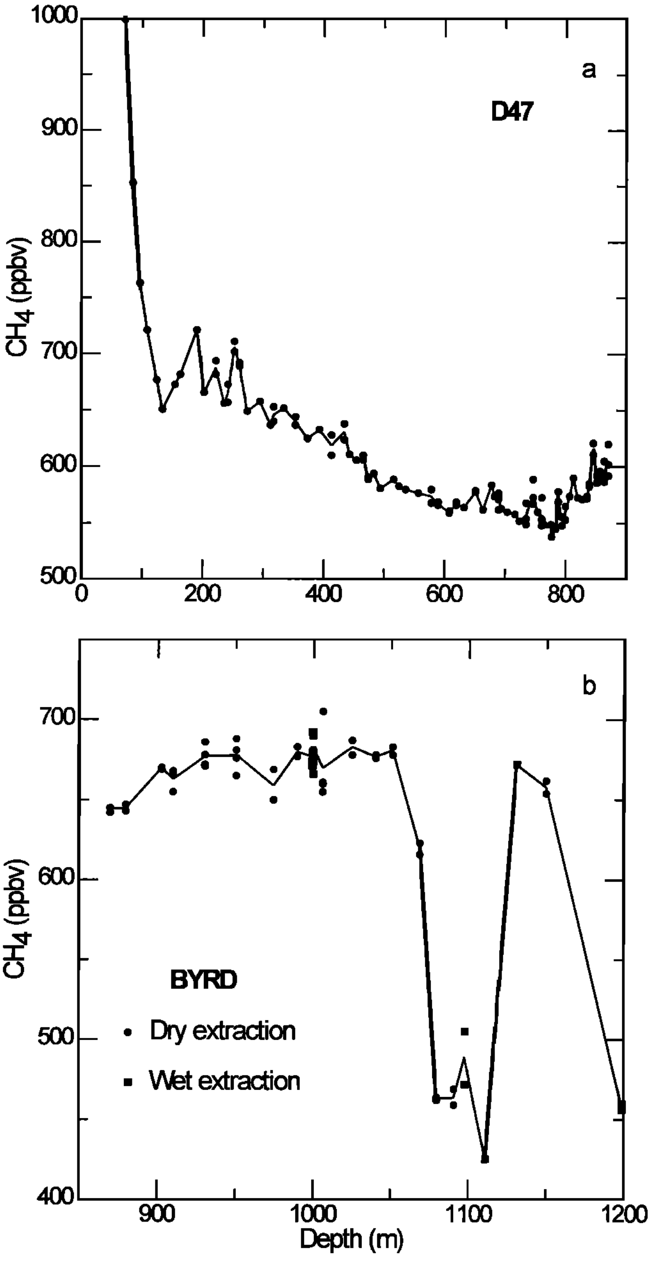

Figure 3. Antarctic CH_4 profiles as a function of depth. (a) CH_4 results from the D47 ice core. Note the clear CH_4 minimum around 780 m of depth, which is dated at 5.2 kyr B.P. in the GRIP chronology. (b) CH_4 results from the Byrd ice core. The low CH_4 levels between 1080 and 1100 m of depth correspond to the Younger Dryas event at the end of the last deglaciation.

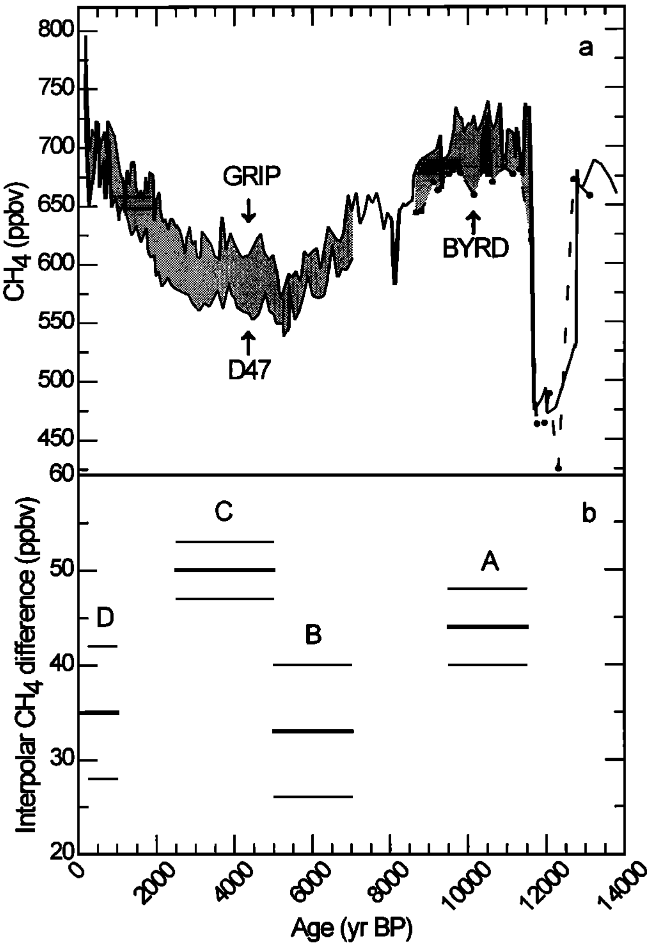

Figure 4. (a) Comparison of the Greenland and Antarctic mean CH_4 mixing ratios over the last 14 kyr. Note that none of the Antarctic records encompasses the period including the 8.2 kyr event. The hatched area reveals the interpolar difference of mixing ratio and its variations over the Holocene. (b) Interpolar CH_4 difference and 1σ error bars for four selected time intervals (A to D) during the Holocene.

[*Barnola et al.*, 1991], temperature dependence of the close-off density, and calculation of the age of the air at the close-off density based on present-day investigations at Summit [*Schwander et al.*, 1993]. Holocene temperature and accumulation were assumed constant at -28°C and 11.9 cm of ice equivalent/year [*Hammer et al.*, 1994]. This gives an age difference of 305 years. For the last climatic transition the temperature was calculated from the $\delta^{18}O$ signal using a $\delta^{18}O$/temperature relationship of 0.99‰/°C [*Robin*, 1983]. The accumulation rate was estimated on the basis of measurements of annual layers by Electrical Conductivity Method (ECM) [*Hammer et al.*, 1994]. The uncertainty for the age difference is ±50 years allowing a ±10% variation in the accumulation rate and a ±2°C variation in temperature.

We present results in the depth range 870-1150 m (Figure 3), obtained with the dry and wet extraction methods. Since the core was drilled more than 20 years before the analyses, almost all air-hydrates will have decomposed and formed air cavities [*Uchida et al.*, 1994]. Therefore we do not expect differences between wet and dry extraction results. This is confirmed by multiple measurements at 1000-m depth showing that the two methods lead within the error limits to the same results. Above 870 m in the brittle zone, replicates at the same depth level reveal a scatter of up to 150 ppbv, attributed to contamination by drilling fluid that permeated into cracks which formed immediately after core recovery [*Gow*, 1971]. Sixteen depth levels (29 samples) between 870 and 1070 m were analyzed, covering the early Holocene from 8.7 to 11.5 kyr B.P. with a sampling resolution of 100 to 350 years. Another six depth levels (10 samples) down to 1150 m allowed us to reveal the Younger Dryas CH_4 minimum and the high mixing ratios of the Bolling/Allerod, making a validation of the Byrd chronology with respect to the GRIP dating [*T. Blunier et al.*, Timing of the Antarctic cold reversal and the atmospheric CO_2 increase with respect to the Younger Dryas event, submitted to *Geophysical Research Letters*, 1997].

Although the Byrd record does not reach a sampling resolution comparable to the GRIP one over the first 3000 years of the Holocene, the general shape of the profile (Figure 4a) is in good agreement with the CH_4 trend depicted by the Greenland core.

5. Greenland/Antarctic CH_4 Difference

Uncertainties in the relative dating of the three ice cores combined with an overall precision of the measurements of 20 ppbv at the 2σ level do not allow us to calculate an interpolar gradient for time intervals equivalent to the mean sampling resolution of our profiles (80 to 350 years). Nevertheless we can depict the difference for specific time intervals, including a significant number of measurements, and thus examine variations of the gradient between time intervals. We also have to consider that the data set is not evenly spaced in time. Thus for calculating a mean concentration, each data point $C(t_i)$ has to be weighted by the time interval that it represents, i.e., $(t_{i+1} - t_{i-1})/2$. Mean mixing ratios and their standard errors for each time period were calculated for Greenland and Antarctica using equations (1) and (2).

$$\overline{C}=\frac{\Sigma_i C(t_i).(t_{i+1}-t_{i-1})}{\Sigma_i (t_{i+1}-t_{i-1})} \tag{1}$$

$$\sigma=\sqrt{\frac{\Sigma_i (C_i-\overline{C})^2.(t_{i+1}-t_{i-1})}{(i-1).\Sigma_i (t_{i+1}-t_{i-1})}} \tag{2}$$

The interhemispheric differences and the corresponding confidence limits were then calculated using equations (3) and (4).

$$\overline{\Delta C}=\overline{C_{\text{north}}}-\overline{C_{\text{south}}} \tag{3}$$

$$\overline{\sigma}=\sqrt{\sigma^2_{\text{north}}+\sigma^2_{\text{south}}} \tag{4}$$

First we consider the full period in the Holocene when both polar records are available, i.e., from 0.25 to 7 kyr B.P. and from 9.5 to 11.5 kyr B.P. It represents about 75% of the Holocene. The mean interpolar difference is 44±7 (1σ) ppbv (Table 2). Second, we select four time intervals with different mixing ratio levels (Figure 4b). Right after the Younger Dryas (11.5-9.5 kyr B.P.), the interpolar difference is 44±4 ppbv. During the CH_4 decrease to the middle of the Holocene (7-5 kyr) the difference is only 33±7 ppbv. The

Table 2. Characteristics of Greenland and Antarctic CH_4 Records Over Selected Time Intervals of the Holocene and for the Last Glacial Maximum

Time Interval (kyr B.P.)	0.25 - 1	2.5 - 5	5 - 7	9.5- 11.5	0.25-7 9.5-11.5	LGM
Greenland number of depth levels	31	29	18	26	120	10*
Mean CH_4 mixing ratio, ppbv	710	617	608	718	654	364
Standard deviation of the mean, ppbv	2	2	5	3	5	7
Antarctica number of depth levels	20	19	18	9	84	-
Mean CH_4 mixing ratio, ppbv	675	567	575	674	610	-
Standard deviation of the mean, ppbv	6	2	5	3	6	-
Interpolar difference and 1σ uncertainty, ppbv	35±7	50±3	33±7	44±4	44±7	0-18†

* GRIP data in the time period 16.7-20.3 kyr B.P. [*Chappellaz et al.*, 1993b].

† Based on preliminary Antarctic data.

largest CH_4 difference of 50±3 ppbv is observed in the second half of the Holocene (5-2.5 kyr) when the mixing ratios were relatively constant. Over the fourth time interval (1-0.25 kyr B.P.), corresponding to an increased CH_4 level, we observe a reduced gradient of 35±7 ppbv.

Previous measurements of the interpolar difference were published for this fourth period. The pioneering work of *Rasmussen and Khalil* [1984] reports an interhemispheric difference of 70±19 (1σ) ppbv between 0.25 and 3.05 kyr B.P. A more recent work reports a difference of 55±15 (1σ) ppbv in the 0.1-0.7 kyr B.P. interval [*Nakazawa et al.*, 1993]. We recalculate the interpolar difference of Khalil and Rasmussen for the time period 1-0.25 kyr B.P. with equations (1) and (2) by eliminating some data points suspected of being contaminated [*Khalil and Rasmussen*, 1989] and by using updated calculations of the air/ice age difference for the relevant ice cores [*Schwander and Stauffer*, 1984]. It reduces the gradient from 70±19 to 47±17 ppbv and brings it in closer agreement with our value. The larger gradient of *Nakazawa et al.* [1993] probably results from their limited number of samples and the short overlapping time period of their two polar records (~150 years).

6. Interpretation: A Three-Box Model

Changes in the interpolar CH_4 difference can result from variations of three parameters: (1) the source latitudinal distribution, (2) the sink latitudinal distribution, and (3) the interhemispheric transport. We use a latitudinal three-box model (adapted from the four-box model of *Khalil and Rasmussen* [1983]) to take into account the effect of each parameter. The three boxes of the model are the regions 90°-30°N (N), 30°N-30°S (T), and 30°-90°S (S). Separating the tropical sources into two boxes, north and south of the equator, would have been meaningless since we have only two geographical points as a constraint and neither of them in the tropics. The mass balance equations for our model is

$$\frac{dC}{dt}=S-\Omega.C \qquad (5)$$

with

$$\Omega=\begin{pmatrix} \lambda_N+n_N & -n_N/2 & 0 \\ -n_N & \lambda_T+(n_N+n_S)/2 & -n_S \\ 0 & -n_S/2 & \lambda_S+n_S \end{pmatrix} \qquad (6)$$

S is the CH_4 source term; n_N and n_S represent the inverse transport time from box N to box T and box S to box T, respectively; λ_x is the inverse lifetime in box x.

The box model is initialized by using the modern CH_4 distribution for the years 1984-1990 [*Steele et al.*, 1992] together with a source estimate of 440 Tg/year [*Thompson et al.*, 1993]. The source distribution was taken from the best scenario (scenario 7) of *Fung et al.* [1991].

The total sink term of 440 Tg/yr is split as 16%, 73%, and 11% in boxes N, T, and S respectively, after *Fung et al.* [1991]. This operation reduces the number of free parameters from 5 to 3. Lifetimes and transport times were varied in order to best approximate the CH_4 measurements. The resulting lifetimes were found to be 18.7, 8.1, and 26.8 years for box N, T, and S, respectively, with an average global lifetime of 11.9 years. The resulting transport times of about 9 months between two neighboring boxes were tested against ^{85}Kr data [*Jacob et al.*, 1987] and appeared to be realistic.

7. Calculation of Sources for Four Selected Time Intervals

One fundamental requirement of our model is to deduce the mean mixing ratio in each box from the measured mixing ratios in Greenland and Antarctica. The present-day latitudinal profile of atmospheric CH_4 [*Dlugokencky et al.*, 1994] demonstrates that mixing ratios measured in Greenland do not represent the mean mixing ratio in box N. Today, the Greenland-box N difference is equal to ~13% of the Greenland-Antarctic difference. Since the present-day anthropogenic sources are essentially located in the middle to high northern latitudes, we expect that the mean mixing ratio in box N during the pre-industrial Holocene was closer to the Greenland value. We assume that the Greenland-box N difference was always proportional to the interpolar difference, and we decrease arbitrarily the factor of proportionality from 13 to 7% for the preindustrial time. In contrast to box N the mixing ratio in box S is nearly constant. Thus the Antarctic mixing ratio represents well the mean mixing ratio in box S.

Finally, since we have no measurement of atmospheric CH_4 in box T, we adjusted it in order to get a source of 15 Tg/yr in box S, consistent with source estimates for this region [*Fung et al.*, 1991].

The sink term in the CH_4 budget is dominated by the OH oxidation in the troposphere [*Fung et al.*, 1991, and references therein]. It is generally suggested that the OH concentration was 10 to 30% higher during the preindustrial

Holocene than today [*Thompson*, 1992]. We have thus increased the global sink term by 20% to account for this effect. We assume that the increase in the sink term is latitudinally uniform. The box lifetimes become 15.6, 6.8, and 22.4 years for box N, T, and S, respectively, with an average global lifetime of 9.9 years. In addition, the mean annual transport times were kept identical to the modern initialization, assuming that the atmospheric circulation on a global scale did not change enough over the Holocene to modify them. In other words, among the three parameters listed at the start of section 6, we make the assumption that only the source latitudinal distribution is responsible for the observed variations of the interpolar CH_4 difference.

The model uncertainty was estimated by (1) using the calculated uncertainty of the mean mixing ratios for each of the four time intervals and (2) assuming a Greenland/box N CH_4 difference between 0 and 13% of the interpolar difference. Depending on the time interval considered, the second source of uncertainty represents between 15 and 40% of the overall model uncertainty. To check the effect of a possible systematic shift between Grenoble and Bern ice core data, we calculated the interpolar difference and the source distribution with data from each laboratory alone. The largest effect but still within the estimated error was found for time-period D, resulting in a changed source distribution between northern and tropical boxes of only 6 Tg/yr. For the other time periods the effect was negligible, confirming the coherency of Grenoble and Bern ice core data.

The source distribution among the three boxes for four typical time intervals are presented in Table 3 and Figure 5. In addition, the estimated source distribution for the glacial epoch is given as well for comparisons. For the estimate an interhemispheric gradient between 0 and 18 ppbv (0 to 5% of the Greenland concentration) was assumed on the basis of preliminary results. The total global source strength obtained for the preindustrial as well as for the glacial epoch are in agreement with an independent estimate of source intensities over the same periods [*Chappellaz et al.*, 1993a].

8. Discussion

On the basis of the Greenland CH_4 measurements alone, we have concluded [*Chappellaz et al.*, 1993b] that the CH_4 increase from the Last Glacial Maximum (LGM) to the period 11.5-9.5 kyr B.P. (A) was caused by a source increase in the tropics, originating from a massive increase in the wetland area. This should create a negligible CH_4 interpolar difference at the start of the Holocene. Our new measurements from Antarctica during period A are indeed significantly lower than the Greenland results. This requires, according to the three-box model, that parallel to the massive emission increase of 53 Tg/yr in the tropics, a comparable increase of 40 Tg/yr took place in middle to high northern latitudes. There are two main candidates for the cause of a boreal increase of the CH_4 sources: degassing of CH_4-hydrate reservoirs from permafrost regions and the continental shelves [*Nisbet*, 1992] and wetland extension on new ice-free areas.

Table 3. Source Distribution Among Three Boxes of our Model for Selected Time Intervals

Time Interval (kyr B.P.)	Sources in Tg/yr North	Tropics	South	Total
LGM	25^{+14}_{-13}	67^{+14}_{-15}	12	104
9.5 - 11.5	66^{+9}_{-8}	120^{+9}_{-9}	15	201
5 - 7	55^{+12}_{-10}	101^{+11}_{-13}	15	171
2.5 - 5	71^{+7}_{-7}	83^{+7}_{-7}	15	169
0.25 - 1	58^{+11}_{-10}	128^{+12}_{-12}	15	201

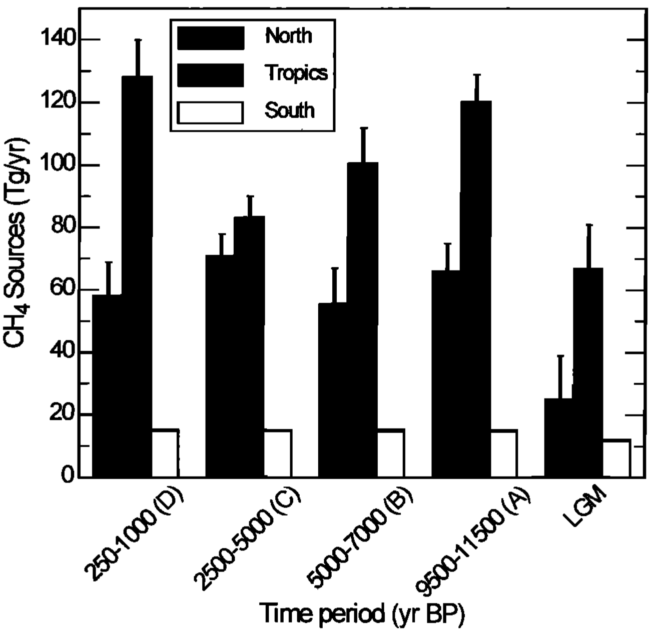

Figure 5. Source distribution among the three boxes of our model, for each of the selected time intervals of the Holocene, and for the Last Glacial Maximum (LGM).

The atmospheric CH_4 change resulting from a dramatic CH_4-hydrate release, linked to the glacial/interglacial warming, has been modeled recently [*Thorpe et al.*, 1996]: the model output suggests that for the detection of such an event in, for example, the GRIP ice core, a sampling interval of a maximum of 50 years is necessary. As shown in Figure 6, we compare the GRIP CH_4 data set over the first 1000 years after the Younger Dryas/preboreal transition with a modeled GRIP record. The latter reflects the signal that would be recorded in the GRIP ice if hydrate decomposition was alone responsible for the CH_4 increase from 480 to 710 ppbv associated with the climatic transition and for maintaining it to the preboreal level. It corresponds to a scenario of regular bursts of 4000 Tg of CH_4, as used in the Thorpe et al's model, recorded at GRIP with a smoothing period of 50 years. In order to produce the observed mean CH_4 level of 710 ppbv at the start of the Holocene, these bursts must appear with a period of 130 years. As shown in Figure 6, the mismatch between the expected and the observed signals is evident. The only way to reconcile the ice-core CH_4 record with a burst scenario would be to decrease the magnitude of each burst and to make them more frequent, in other words, to transform a catastrophic scenario into a regular source (permanent degassing of clathrate reservoirs).

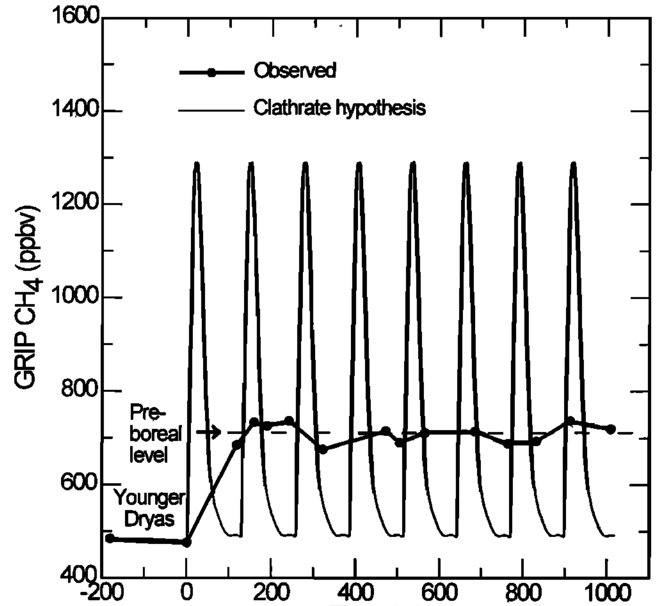

Figure 6. Comparison between a modeled and an observed GRIP CH_4 record over the first 1000 years of the Holocene. The modeled record reflects the signal in the GRIP ice expected if the deglaciation increase of atmospheric CH_4 was solely due to regular bursts of 4000 Tg, each from clathrate outgassing.

According to our model, the clathrate source could not be the only source responsible for the high CH_4 levels of the early Holocene. Leaving the tropical source at its LGM level of 67 Tg/yr, the clathrate source located in the northern box would need to be more than 80 Tg/yr in order to raise the Greenland CH_4 level to 718 ppbv. This would in turn create a Greenland/Antarctic interpolar difference of 78 ppbv, significantly larger than our observations. Consequently, if any, the clathrate source during the early Holocene had to be regular and with a maximum contribution of 40 Tg/yr, i.e., ~20% of the CH_4 budget at that time.

The second candidate for an early Holocene source at high latitudes is the wetland spread following the ice-sheet retreat. A study of available paleodata suggests several potential contributing regions where basal peat dates from the early Holocene: the Canadian Arctic [*Ritchie and Harrison*, 1985; *Zoltai and Vitt*, 1990; *Gorham*, 1991], Alaska [*Peteet and Mann*, 1994], northeastern United States, and maritime Canada [*Peteet et al.*, 1994]. Other regions of the boreal belt, which are important contributors of today's wetland CH_4 sources, could hardly contribute to a high-latitude source: wetlands in the interior of Canada started to expand around 7 kyr B.P. [*Zoltai and Vitt*, 1990]. Scandinavia was mainly dry during the early Holocene [*Harrison et al.*, 1993], and in Russia the peat bog formation took place mainly at the middle of the Holocene [*Gorham*, 1991].

The period 9-11.5 kyr B.P. was the wettest period of the Holocene in the tropics. This is confirmed by data from various regions, including India [*Sukumar et al.*, 1993], Brazil [*Ledru*, 1993], Sahara [*Petit-Maire et al.*, 1991; *Petit-Maire and Guo*, 1996], Tibet and China [*Gasse and Campo*, 1994]. As a consequence, wetland areas increased massively [*Petit-Maire et al.*, 1991; *Street-Perrott*, 1992]. These observations of peat formation in some regions of the boreal belt and of wetland spread in the tropics are thus consistent with our model output.

During the time period B (7-5 kyr B.P.) both the CH_4 mixing ratio and the interpolar difference decrease. Our model requires that the sources in the northern and tropical boxes were reduced. At that time, humidity decreased in the tropics [*Petit-Maire et al.*, 1991; *Petit-Maire and Guo*, 1996] and reached a minimum around 5 kyr B.P. [*Street-Perrott*, 1993]. A possible explanation for the smaller source in the northern box may lie in the natural dynamics of northern wetlands: after the first stage of vertical development the peat growth rate decreased and lateral expansion began, accompanied by an ombrotrophization of the wetland and reduced CH_4 emissions [*Franzén*, 1994].

In period C (5-2.5 kyr B.P.) the CH_4 level changes very little, whereas the largest CH_4 difference is observed between Greenland and Antarctica. Our model suggests, as an explanation, a concomitant decrease of the tropical source and an increase of the boreal source. During that period the tropics experienced an ongoing drying [*Street-Perrott*, 1993]. For instance, today's dry belt in Africa was formed around 3 kyr B.P. [*Petit-Maire*, 1994]. The resulting CH_4 emission decrease may still have been partly compensated by the increase in wetness over South America [*Iriondo and Garcia*, 1993]. In the boreal belt, a significant expansion of wetlands was observed in Russia [*Latypova and Yakheemovich*, 1993; *Gorham*, 1991], Scandinavia [*Franzén*, 1994], and Canada [*Zoltai and Vitt*, 1990]. In general, period C appears as the time with the highest rate of peat formation in high northern latitudes [*Gorham*, 1991].

Finally, the time period D reveals a return of the CH_4 mixing ratios to their highest Holocene level, combined with a reduced interpolar difference. Quantitatively, this requires not only that the boreal source decreases to the expense of the tropical source but also that the tropical source increases enough to strengthen the atmospheric CH_4 burden. As for the time period B, the boreal source decrease may reflect the reduced CH_4 emission even in the case of ongoing wetland growth [*Franzén*, 1994]. For the tropical source our model suggests an increase of 45 Tg/yr, comparable with the increase accompanying the last deglaciation. A possible candidate may be the Amazon Basin that became wetter after 4 kyr B.P. [*Ledru*, 1993]. There are also indications for a recent episode of increased wetness in India [*Sukumar et al.*, 1993]. Finally, one could envisage the possibility that anthropogenic CH_4 sources became significant during time period D, especially in the tropics. A recent quantification of human contribution to the CH_4 budget around 1500 AD suggests that as much as 55 Tg/yr of CH_4, or 26% of the total budget, could be of anthropogenic origin [*Subak*, 1994]. The sources envisaged include domestic animals, irrigated (rice paddies) and wetland agriculture, biomass burning, and wood fuel consumption. More than two thirds of them would have taken place in the tropical region (South and Central America, Africa, and Asia).

Our interpretation of the observed variations in the interpolar CH_4 difference depends on several critical assumptions that cannot be tested at this point: (1) we assume that the exchange time among the three boxes of our model did not change during the Holocene. This may be true for the period 0-7 kyr B.P. but probably not beyond, when the Laurentide ice sheet was still present in the northern hemisphere [*Felzer et al.*, 1996]; (2) we consider homogeneously elevated OH concentrations during the Holocene versus today, whereas some photochemical models suggest a more pronounced effect in the southern hemisphere, due to the fact that NOx concentrations increased in the northern hemisphere with the industrialization [*Thompson*, 1992]; (3) we do not consider the possibility that the seasonality of CH_4 emissions from, for example, wetlands changed over time, a phenomenon that could significantly impact the transport of CH_4 from northern sources to the southern hemisphere, for instance. However, taking into account the fact that our measurement constraints are limited to the north and south pole mixing ratios and their difference and that more complicated assumptions would have been only speculative, we believe that the source scenarios described here have the maximum credibility with respect to the constraints available and to our knowledge of the CH_4 cycle and Holocene conditions.

9. Summary

Our study appears as the first attempt to reveal significant variations in the interpolar difference of atmospheric CH_4 mixing ratio over the Holocene period. In order to achieve this task, we combine three CH_4 records of comparable sampling resolution and good relative dating, using ice cores providing similar trapping conditions for atmospheric gases. With a total of 343 CH_4 analyses covering 75% of the Holocene (a temporal gap in our Antarctic records exists between 7 and 9.5 kyr B.P.), we reveal a mean interpolar difference of 44±7 ppbv. The large number of measurements allows us to quantify the changes of the interpolar difference among four time intervals. The largest change takes place at the turn of the mid-Holocene (~5 kyr B.P.), where the difference moves from the lowest (35±7 ppbv) to the highest (50±3 ppbv) value. We also show that despite a comparable mean CH_4 level, the start and the end of the Holocene experienced a different interpolar difference (44±4 and 35±7 ppbv, respectively).

Using a three-box model, we attempt to translate the measured mixing ratios and gradients into source intensities in the tropics and the northern middle to high latitudes. The main assumptions behind the model lie in an unchanged interhemispheric transport time and in a sink term homogeneously increased by 20% compared with present-day conditions. The model output suggests that the doubling of atmospheric CH_4 between the Last Glacial Maximum and the early Holocene originates from a 53 and 40 Tg/yr increase of the tropical and boreal sources, respectively. The tropical source most likely involved an increased wetland extent accompanying the wettest episode of the Holocene in the tropics. With the present resolution of our records it appears unrealistic to attribute the boreal source to a catastrophic degassing of clathrate reservoirs, as envisaged by *Nisbet* [1992], although a continuous and regular degassing of up to 40 Tg/yr cannot be ruled out. According to the available paleodata the most probable boreal source lies in the Canadian Arctic, Alaska, northeastern United States, and maritime Canada, all of them experiencing favorable conditions for wetland development during the early Holocene.

During the periods 5-7 and 2.5-5 kyr B.P. when the atmospheric CH_4 levels were lower, a decrease, followed by an increase of the interpolar difference, takes place. We interpret this as an ongoing drying of the tropical regions combined with a period of massive peat growth in the boreal regions after 5 kyr B.P. Finally, the recent period 0.25-1 kyr B.P. reveals a small gradient combined with a return to high CH_4 levels. Our model translates these observations into a major increase in the tropical source, which may come from local increase in wetness but also from a significant contribution of humans to the CH_4 budget.

Overall, the combination of the mixing ratio and gradient information allows us to better constrain the parameters responsible for past CH_4 changes. It shows that the tropics had a major contribution to the CH_4 budget over the last 20 kyr, modulated by significant changes in the middle to high northern latitude sources. It also confirms from one global parameter (CH_4) that large variations of the hydrological cycle took place during the Holocene, a period generally considered as climatically stable. An extension of the combined analysis of the CH_4 burden with the interpolar difference to longer time periods, in particular during the fast CH_4 variations characterizing the last glaciation, would be very useful.

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References

Barnola, J.-M., P. Pimienta, D. Raynaud, and Y.S. Korotkevich, CO_2-climate relationship as deduced from the Vostok ice core: A re-examination based on new measurements and on a re-evaluation of the air dating, *Tellus, Ser. B, 43*, 83-90, 1991.

Barnola, J.M., M. Anklin, J. Porcheron, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 evolution during the last millennium as recorded by Antarctic and Greenland ice, *Tellus, Ser. B, 47*, 264-272, 1995.

Blunier, T., J. Chappellaz, J. Schwander, J.M. Barnola, T. Desperts, B. Stauffer, and D. Raynaud, Atmospheric methane, record from a Greenland ice core over the last 1,000 years, *Geophys. Res. Lett., 20*, 2219-2222, 1993.

Blunier, T., J. Chappellaz, J. Schwander, B. Stauffer, and D. Raynaud, Variations in atmospheric methane concentration during the Holocene epoch, *Nature, 374*, 46-49, 1995.

Brook, E.J., T. Sowers, and J. Orchardo, Rapid variations in atmospheric methane concentrations during the past 110,000 years, *Science, 273*, 1087-1091, 1996.

Chappellaz, J., Etude du méthane atmosphérique au cours du dernier cycle climatique à partir de l'analyse de l'air piégé dans la glace antarctique, 214 pp., Ph.D. thesis, Univ. Joseph Fourier, Grenoble, France, 1990.

Chappellaz, J., J.-M. Barnola, D. Raynaud, Y.S. Korotkevich, and C. Lorius, Atmospheric CH_4 record over the last climatic cycle revealed by the Vostok ice core, *Nature*, *345*, 127-131, 1990.

Chappellaz, J. A., I.Y. Fung, and A.M. Thompson, The atmospheric CH_4 increase since the Last Glacial Maximum (1) Source estimates, *Tellus*, *Ser. B*, *45*, 228-241, 1993a.

Chappellaz, J., T. Blunier, D. Raynaud, J.-M. Barnola, J. Schwander, and B. Stauffer, Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr BP, *Nature*, *366*, 443-445, 1993b.

Ciais, P., Forages profonds et sites cotiers en Antarctique: Données isotopiques et climat des 15.000 dernières années, 390 pp., Ph.D. thesis, Univ. of Paris, 1991.

Ciais, P., J. Jouzel, J.R. Petit, V. Lipenkov, and J.W.C. White, Holocene temperature variations inferred from six Antarctic ice cores, *Ann. Glaciol.*, *20*, 427-436, 1994.

Craig, H., C.C. Chou, J.A. Welhan, C.M. Stevens, and A. Engelkemeir, The isotopic composition of methane in polar ice cores, *Science*, *242*, 1535-1539, 1988.

Dansgaard, W., et al., Evidence for general instability of past climate from a 250-kyr ice-core record, *Nature*, *364*, 218-220, 1993.

Dlugokencky, E.J., L.P. Steele, P.M. Lang, and K.A. Masarie, The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, *99*, 17,021-17,043, 1994.

Etheridge, D.M., G.I. Pearman, and P.J. Fraser, Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core, *Tellus*, *Ser. B*, *44*, 282-294, 1992.

Felzer, B., R.J. Oglesby, T. Webb III, and D.E. Hyman, Sensitivity of a general circulation model to changes in northern hemisphere ice sheets, *J. Geophys. Res.*, *101*, 19.077-19,092, 1996.

Franzén, L.G., Are wetlands the key to the ice-age cycle enigma?, *Ambio*, *23*, 300-308, 1994.

Fuchs, A., J. Schwander, and B. Stauffer, A new ice mill allows precise concentration determination of methane and most probably also other trace gases in the bubble air of very small ice samples, *J. Glaciol.*, *39*, 199-203, 1993.

Fung, I., J. John, J. Lerner, E. Matthews, M. Prather, L.P. Steele, and P.J. Fraser, Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, *96*, 13,033-13,065, 1991.

Gasse, F., and E. Van Campo, Abrupt post-glacial climate events in west Asia and north Africa monsoon domains, *Earth Planet. Sci. Lett.*, *126*, 435-456, 1994.

Gorham, E., Northern peatlands: Role in the carbon cycle and probable responses to climatic warming, *Ecol. Appl.*, *1*, 182-195, 1991.

Gow, A.J., Relaxation of ice in deep drill cores from Antarctica, *J. Geophys. Res.*, *76*, 2533-2541, 1971.

Hammer, C.U., H.B. Clausen, and C.C. Langway Jr., Electrical conductivity method (ECM) stratigraphic dating of the Byrd Station ice core, Antarctica, *Ann. Glaciol.*, *20*, 115-120, 1994.

Harrison, S.P., I.C. Prentice, and J. Guiot, Climatic controls on Holocene lake-level changes in Europe, *J. Clim. Dyn.*, *8*, 189-200, 1993.

Iriondo, M.H., and N.O. Garcia, Climatic variations in the Argentine plains during the last 18,000 years, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *101*, 209-220, 1993.

Jacob, D.J., M.J. Prather, S.C. Wofsy, and M.B. McElroy, Atmospheric distribution of ^{85}Kr simulated with a general circulation model, *J. Geophys. Res.*, *92*, 6614-6626, 1987.

Johnsen, S.J., D. Dahl-Jensen, W. Dansgaard, and N. Gundestrup, Greenland palaeotemperatures derived from GRIP bore hole temperature and ice core isotope profiles, *Tellus*, *Ser. B*, *47*, 624-629, 1995.

Khalil, M.A.K., and R.A. Rasmussen, Sources, sinks and seasonal cycles of atmospheric methane, *J. Geophys. Res.*, *88*, 5131-5144, 1983.

Khalil, M.A.K., and R.A. Rasmussen, Climate-induced feedbacks for the global cycles of methane and nitrous oxide, *Tellus*, *Ser. B*, *41*, 554-559, 1989.

Latypova, E.K., and B.L. Yakheemovich, Geochronology of the Pleistocene and Holocene in the Fore-Urals, *Radiocarbon*, *35*, 441-447, 1993.

Ledru, M.-P., Late Quaternary environmental and climatic changes in central Brazil, *Quat. Res.*, *39*, 90-98, 1993.

Lowe, D.C., C.A.M. Brenninkmeijer, G.W. Brailsford, K.R. Lassey, and A.J. Gomez, Concentration and ^{13}C records of atmospheric methane in New Zealand and Antarctica: Evidence for changes in methane sources, *J. Geophys. Res.*, *99*, 16,913-16,925, 1994.

Nakazawa, T., T. Machida, M. Tanaka, Y. Fujii, S. Aoki, and O. Watanabe, Differences of the atmospheric CH_4 concentration between the Arctic and Antarctic regions in pre-industrial/pre-agricultural era, *Geophys. Res. Lett.*, *20*, 943-946, 1993.

Nisbet, E.G., Sources of atmospheric CH_4 in early postglacial time, *J. Geophys. Res.*, *97*, 12,859-12,867, 1992.

Peteet, D.M., and D.H. Mann, Late-glacial vegetational, tephra, and climatic history of southwestern Kodiak Island, Alaska, *Ecoscience*, *1*, 255-267, 1994.

Peteet, D.M., R. Daniels, L.E. Heusser, J.S. Vogel, J.R. Southon, and D.E. Nelson, Wisconsinan late-glacial environmental change in southern New England: A regional synthesis, *J. Quat. Sci.*, *9*, 151-154, 1994.

Petit-Maire, N., Natural variability of the Asian, Indian and African monsoons over the last 130 kyr, in *Global Precipitation and Climate Change, NATO ASI Ser.*, edited by M. Desbois and F. Désalmand, pp. 3-26, Springer-Verlag, New York, 1994.

Petit-Maire, N., and Z. Guo, Mise en évidence de variations climatiques holocènes rapides, en phase dans les déserts actuels de Chine et du Nord de l'Afrique, *C. R. Acad. Sci. Paris*, *322*, 847-851, 1996.

Petit-Maire, N., M. Fontugne, and C. Rouland, Atmospheric methane ratio and environmental changes in the Sahara and Sahel during the last 130 kyrs, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *86*, 197-204, 1991.

Rasmussen, R.A., and M.A.K. Khalil, Atmospheric methane in the recent and ancient atmospheres: Concentrations, trends, and interhemispheric gradient, *J. Geophys. Res.*, *89*, 11,599-11,605, 1984.

Raynaud, D., and J. Chappellaz, The record of atmospheric methane, in *Atmospheric methane: Sources, Sinks, and Role in Global Change, NATO ASI Ser. 113*, edited by M.A.K. Khalil, pp. 39-61, Springer-Verlag, New York, 1993.

Raynaud, D., J. Chappellaz, J.M. Barnola, Y.S. Korotkevich, and C. Lorius, Climatic and CH_4-cycle implications of glacial-interglacial CH_4 change in the Vostok ice core, *Nature*, *333*, 655-657, 1988.

Ritchie, J.C., and S.P. Harrison, Vegetation, lake levels, and climate in western Canada during the Holocene, in *Pollen Records of Late Quaternary North American Sediments*, edited by V. Bryant and R. Holloway, pp. 141-166, Am. Assoc. Stratigr. Palynol. Found., Dallas, Tex., 1985.

Robin, G. de Q., The δ value-temperature relationship, in *The Climatic Record in Polar Ice Sheets*, edited by G. de Q. Robin, pp. 180-184, Cambridge Univ. Press, New York, 1983.

Schwander, J., Gas diffusion in firn, in *Chemical Exchange Between the Atmosphere and Polar Snow, NATO ASI Ser. 143*, edited by E.W. Wolff and R.C. Bales, pp. 527-540, Springer-Verlag, New York, 1996.

Schwander, J., and B. Stauffer, Age difference between polar ice and the air trapped in its bubbles, *Nature*, *311*, 45-47, 1984.

Schwander, J., J.-M. Barnola, C. Andrié, M. Leuenberger, A. Ludin, D. Raynaud, and B. Stauffer, The age of the air in the firn and the ice at Summit, Greenland, *J. Geophys. Res.*, *98*, 2831-2838, 1993.

Sowers, T. A., and M. Bender, Climate records during the last deglaciation, *Science*, *269*, 210-214, 1995.

Sowers, T., et al., An interlaboratory comparison of techniques for extracting and analyzing trapped gases in ice cores, *J. Geophys. Res.*, in press, 1997.

Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, Slowing down of the global accumulation of atmospheric methane during the 1980s, *Nature*, *358*, 313-316, 1992.

Street-Perrott, F.A., Tropical wetland sources, *Nature*, *355*, 23-24, 1992.

Street-Perrott, F.A., Ancient tropical methane, *Nature*, *366*, 411-412, 1993.

Subak, S., Methane from the house of Tudor and the Ming dynasty: Anthropogenic emissions in the sixteenth century, *Chemosphere*, *29*, 843-854, 1994.

Sukumar, R., R. Ramesh, R.K. Pant, and G. Rajagopalan, A $\delta^{13}C$ record of late Quaternary climate change from tropical peats in southern India, *Nature*, *364*, 703-706, 1993.

Thompson, A.M., The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, *256*, 1157-1168, 1992.

Thompson, A.M., J.A. Chappellaz, I.Y. Fung, and T.L. Kucsera, The atmospheric CH_4 increase since the Last Glacial Maximum, 2, Interactions with oxidants, *Tellus*, *Ser. B*, *45*, 242-257, 1993.

Thorpe, R.B., K.S. Law, S. Bekki, J.A. Pyle, and E.G. Nisbet, Is methane-driven deglaciation consistent with the ice core record?, *J. Geophys. Res.*, *101*, 28,627-28,635, 1996.

Uchida, T., T. Hondoh, M. Shinji, P. Duval, and V.Y. Lipenkov, Effects of temperature and pressure on the transformation rate from air bubbles to air-hydrate crystals in ice sheets, *Ann. Glaciol.*, *20*, 143-147, 1994.

Zoltai, S.C., and D.H. Vitt, Holocene climatic change and the distribution of peatlands in western interior Canada, *Quat. Res.*, *33*, 231-240, 1990.

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