

# Ice-core record of atmospheric methane over the past 160,000 years

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Methane measurements along the Vostok ice core reveal substantial changes over the past 160,000 years which are associated with climate fluctuations. These results point to changes in sources of methane and also show that methane has probably contributed, like carbon dioxide, to glacial-interglacial temperature changes.

MEASUREMENT of the composition of the air in bubbles trapped in polar ice is the most direct way to reconstruct the past atmosphere and the only one available for methane (CH<sub>4</sub>). The ice record previously revealed that the CH<sub>4</sub> concentration was only ~700 p.p.b.v. (parts per 10<sup>9</sup> by volume) two to three centuries ago, that is, less than half its present level of ~1,700 p.p.b.v.<sup>1-4</sup>. More recently, two sets of results showed that atmospheric CH<sub>4</sub> doubled when going from full glacial conditions (350 p.p.b.v.) to interglacial periods (650 p.p.b.v.)<sup>5,6</sup>.

Our study extends the record of past atmospheric CH<sub>4</sub> over the full climate cycle back to ~160 kyr BP. It is based on a set of measurements performed on the 2,083-m-long ice core (3G core) of Vostok (East Antarctica, 78°28 S 106°48 E). Four more samples have been taken at depths of 177.4, 544.7, 554.2 and 642.1 m along a new long ice core (4G) drilled ~75 m from 3G. The 3G core has already given information about the past atmosphere, in particular temperature<sup>7,8</sup>, carbon dioxide (CO<sub>2</sub>) content<sup>9</sup>, aerosol concentration and chemistry<sup>10-12</sup>. The CH<sub>4</sub> profile shows strong variations of past atmospheric CH<sub>4</sub> concentrations in the 350-650 p.p.b.v. range, well below the present atmospheric concentration. These variations are well correlated with climate change deduced from the isotopic composition of the Vostok ice core. Spectral analysis of the record indicates periodicities close to those of orbital variations. We interpret these CH<sub>4</sub> changes to be the result of fluctuations in wetland areas induced by climate changes. We suggest that the participation of CH<sub>4</sub> and associated chemical feedbacks to warming during deglaciations represents about 30% of that due to CO<sub>2</sub>.

## Vostok CH<sub>4</sub> results

The air occluded in the ice bubbles was extracted by melting and refreezing the samples under vacuum. Concentrations of CH<sub>4</sub> were measured using a gas chromatograph equipped with a flame-ionization detector and calibrated with an air standard (CH<sub>4</sub> concentration of 1,200 ± 100 p.p.b.v.). A complete description of the experimental procedure is given elsewhere<sup>6</sup>. Blank values obtained by analysing standard gas with artificial bubble-free ice showed that the analytical system introduces a CH<sub>4</sub> contamination of 37 ± 25 p.p.b.v. in the initial CH<sub>4</sub> content. After correction of the results, our estimated overall accuracy, including uncertainties in contamination and calibration but not the accuracy of the standard gas, is ~40 p.p.b.v. (2σ). In the upper part of the Vostok core (the first 800 m), fractures and thermal cracks may slightly increase CH<sub>4</sub> concentration but this contamination would be <40 p.p.b.v. according to measurements performed on both fractured and unfractured samples taken at the same depth. Comparison with other ice records, as shown below, also indicates that this potential source of error is small.

We analysed 156 samples representing 98 depth levels between 149 and 2,064 m, corresponding to a sampling step of ~25 m. We include the CH<sub>4</sub> results already published for the Vostok ice core<sup>6</sup> at seven depth levels. Owing to the air-enclosure process in the ice, the extracted air is younger than the surrounding ice. Also, the composition of the air enclosed in an ice sample represents an average value over several hundred years because all the pores at the depth of enclosure do not pinch off at the same time<sup>9</sup>. Here we calculate the age of the air using the previously described ice chronology<sup>7</sup> and the age difference between the enclosed air and the surrounding ice<sup>9</sup>. The Vostok ice chronology is under debate, particularly for the period before 110 kyr BP where it departs clearly from the marine chronology<sup>8,13</sup>. This has to be taken into account when discussing the comparison with other records and furthermore could influence the results of any spectral analysis (see below). Our sampling represents a temporal resolution ranging from 300 yr (close to the average time interval covered by a Vostok air sample<sup>9</sup>) to 3,500 yr. The CH<sub>4</sub> record is plotted against sample depth and estimated age of air in Fig. 1, together with the isotope temperature record derived from the Vostok core<sup>8</sup>.

The CH<sub>4</sub> profile, covering the last climate cycle back to ~160 kyr BP (the Holocene, last glaciation, the previous interglacial and the end of the penultimate glaciation), indicates strong variations in the CH<sub>4</sub> content of the past atmosphere. Two main glacial-interglacial transitions appear: one between 2,020 and 1,870 m (150-133 kyr BP) and the other between 450 and 300 m (18-9 kyr BP). In both cases, the CH<sub>4</sub> concentration goes from the lowest values of the Vostok record, ~350 p.p.b.v., to the highest values, ~650 p.p.b.v. In the depth interval between these two transitions (1,870-450 m), four strong peaks centred on depths of 1,520, 1,240, 880 and 620 m (respectively 106, 82, 52 and 32 kyr BP) stand out above a mean level of 400-450 p.p.b.v. and reach values of ~550-600 p.p.b.v. The latter values are only slightly less than the concentrations observed during the last interglacial period (~130 kyr BP) and the Holocene (0-9 kyr BP). The present-day mean CH<sub>4</sub> level of ~1,700 p.p.b.v. is ~2.5 times higher than the maximum value measured in the Vostok ice core.

A striking feature of the CH<sub>4</sub> variations is the large oscillation observed at the end of the last glacial-interglacial transition (marked with an arrow in Fig. 1): after a fast increase from 450 to 650 p.p.b.v. between ~380 and 360 m (13-12 kyr BP), CH<sub>4</sub> concentration decreases by ~170 p.p.b.v. between ~360 and 335 m (12-11 kyr BP), and then reaches again the high value of ~650 p.p.b.v. This feature is confirmed by measurements at several depth levels (seven samples for the 'low' value at 11 kyr BP, six samples for the peak at 12 kyr BP).

The transitions between 'low' and 'high' CH<sub>4</sub> values take place over several thousand years. The rates of the fastest changes observed (at the end of the two main transitions and at the onset of the 1,520-m peak) are ~0.2-0.3 p.p.b.v. yr<sup>-1</sup>. This rate and the extreme values are low estimates because of the sampling step and of the smoothing of variations linked to the air trapping process in the ice. Nevertheless, these values are comparable to a possible rate of change of ~0.3 p.p.b.v. yr<sup>-1</sup> during the Little Ice Age between AD 1450 and 1750<sup>14</sup>. On the other hand, the approximately exponential CH<sub>4</sub> increase (700-1,700 p.p.b.v.)

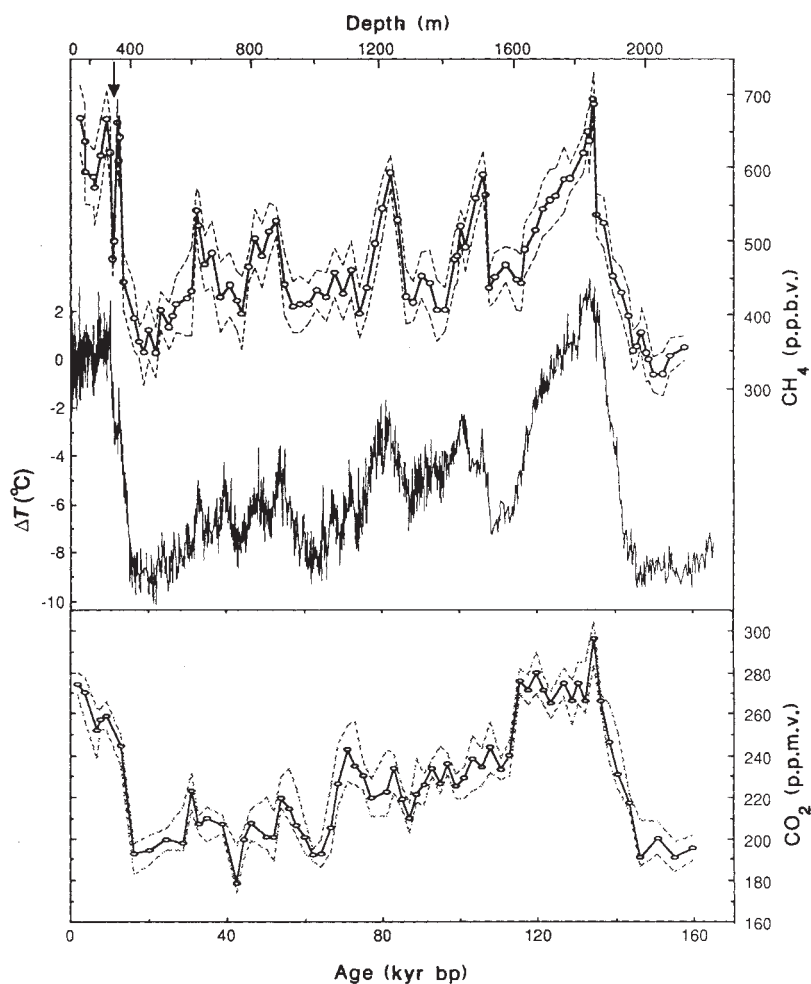


FIG. 1 Vostok ice-core records. Upper curve:  $\text{CH}_4$  record. Circles indicate mean values. The envelope shown has been plotted taking into account the various uncertainty ( $2\sigma$ ) sources. The arrow corresponds to the Younger Dryas  $\text{CH}_4$  oscillation. Middle curve: isotope surface temperature record as a difference from the modern temperature value ( $-55.5^\circ\text{C}$ , ref. 8). For comparison, the lowest curve shows the Vostok  $\text{CO}_2$  record<sup>9</sup>. The timescale applies to all three records. The depth scale applies only to the  $\text{CH}_4$  and  $\text{CO}_2$  curves, because of the difference in age between air bubbles and surrounding ice.

over the past 300 years obtained from ice-core analyses and systematic atmospheric measurements during the past 25 years shows a rate of increase from  $1.5 \text{ p.p.b.v. yr}^{-1}$  between AD 1700 and 1900 to  $17 \text{ p.p.b.v. yr}^{-1}$  today<sup>15</sup>. Thus, not only is the present-day  $\text{CH}_4$  concentration the largest reached in the past 160 kyr, but it also seems that the present rate of increase was not experienced before anthropogenic perturbation.

**Comparison with other ice records.** Stauffer *et al.*<sup>5</sup> have published a record of atmospheric  $\text{CH}_4$  including the last deglaciation, obtained from the ice cores of Dye 3 (Greenland) and Byrd (Antarctica). There is good agreement between the general features of these records and those from Vostok, namely, Stauffer *et al.* found a mean  $\text{CH}_4$  concentration of 650 p.p.b.v. for the Holocene period (0–9 kyr BP) and values of  $\sim 350$  p.p.b.v. during the Last Glacial Maximum ( $\sim 18$  kyr BP). This similarity is corroborated by the Vostok oscillation in  $\text{CH}_4$  between 12 and 9 kyr BP which has also been indicated by a single level in the Dye 3 record<sup>5</sup>. Taking into account the differences between the experimental methods used, we have added confidence in the  $\text{CH}_4$  measurements from ice cores. It also indicates that any potential error linked to fractures in the upper part of the Vostok core is probably small. An extended comparison covering the period before the Last Glacial Maximum is limited by dating problems and a loose sampling step for the Dye 3 and Byrd records.

A few years ago, the idea that the atmospheric  $\text{CH}_4$  concentration remained constant through changes in climate was suggested from the results of Craig and Chou on the Dye 3 ice core<sup>1</sup>. This was supported by a single point in the last glacial period showing a  $\text{CH}_4$  concentration of 650 p.p.b.v. Our results indicate that in fact this point could correspond to one of the peaks occurring between 20 and 110 kyr BP. Indeed, both the Greenland and Antarctic ice cores indicate that large  $\text{CH}_4$  con-

centration changes occurred during climate fluctuations and that glacial and interglacial periods are associated with low and high  $\text{CH}_4$  values respectively.

**Comparison with the  $\text{CO}_2$  record.** The Vostok ice core has already provided a profile of atmospheric  $\text{CO}_2$  concentration over the entire last climate cycle<sup>9</sup>. The use of the same ice core allows us to compare the  $\text{CH}_4$  and  $\text{CO}_2$  curves without dating uncertainties.

Although the highest and lowest values in both records are found during the warmest and coldest conditions respectively, during the last glaciation, the two profiles are different. The  $\text{CH}_4$  profile exhibits four peaks from a quasi-continuous baseline whereas the  $\text{CO}_2$  curve shows a general decreasing trend with a marked break at  $\sim 70$  kyr BP. This difference between the two signals most likely reflects the predominant sources, which are different for  $\text{CO}_2$  and  $\text{CH}_4$ . The  $\text{CO}_2$  variations are suspected to be essentially driven by oceanic changes<sup>9</sup> whereas the  $\text{CH}_4$  cycle, as we discuss below, is mainly controlled by sources from the continental areas.

**Spectral analysis.** To investigate the potential link between astronomical forcing and methane, we performed a spectral analysis of the  $\text{CH}_4$  profile using the multi-taper method (MTM) pioneered by Thomson<sup>16</sup> which provides a high-frequency resolution and a statistical  $F$ -test for the validity of amplitude and location of each peak<sup>17</sup>. This method is known to be far more reliable than the maximum-entropy method previously applied to Vostok isotope temperature and  $\text{CO}_2$  profiles<sup>17</sup>. The  $\text{CH}_4$  record was linearly interpolated to obtain 500 equally spaced points before carrying out spectral analysis.

The MTM spectrum exhibits four significant peaks at the 90% confidence level (Fig. 2). The periods are 122.0, 41.7, 24.8 and 19.0 kyr. When applying MTM to random curves taken in the  $2\sigma$  envelope (see Fig. 1), the results indicate that  $\text{CH}_4$  spectrum

values are not affected by experimental uncertainties on CH<sub>4</sub> measurements. We also checked the effect on the spectral analysis of changes in ice chronology, using a dust event (event 5 in ref. 13) as a time marker to adjust linearly the Vostok ages older than 110 kyr BP to the marine chronology<sup>18</sup>. With this new chronology, the resulting spectrum also shows four significant peaks at 109.9, 38.3, 23.7 and 18.9 kyr with mostly unchanged amplitudes. The four significant CH<sub>4</sub> periodicities seem to be in rather good agreement with orbital frequencies—eccentricity at ~100 kyr, the obliquity component at 41 kyr and the two periodicities of the precession of equinoxes at 23 and 19 kyr respectively. Thus the spectral analysis supports a fundamental relation between orbital climate forcing and CH<sub>4</sub> concentration. At low frequencies, however, the 100-kyr component, which generally dominates palaeoclimate spectra<sup>19</sup>, was not predominant in the CH<sub>4</sub> spectrum whatever chronology we used. This feature may help to constrain the CH<sub>4</sub>-cycle interpretation as discussed below.

**Comparison with temperature profiles.** The continuous record of deuterium content ( $\delta D = [(^2H/^1H)_{\text{sample}} / (^2H/^1H)_{\text{standard}}] - 1$ ) along the Vostok ice core is a remarkable indicator of past temperature conditions in central Antarctica<sup>8</sup>. Briefly, high (low)  $\delta D$  corresponds to 'warm' ('cold') temperature. Comparison of this record of relatively large geographical significance<sup>8</sup> with the CH<sub>4</sub> profile should help in understanding CH<sub>4</sub> cycle/climate interactions. The problem of comparative dating is simplified because both curves are based on the Vostok ice core. The uncertainty that persists because of the evaluation of air-ice difference in age is ~2,000 years between the two records.

As shown in Fig. 1, there is remarkable similarity between the CH<sub>4</sub> and climate temporal variations, with increasing (decreasing) CH<sub>4</sub> trends when the  $\delta D$  profile indicates warming (cooling). This is also true for the CH<sub>4</sub> oscillation observed between 9 and 12 kyr BP which is probably associated with a cold oscillation corresponding to a cooling of ~2 °C at Vostok<sup>8</sup>. The changes of the two parameters are almost simultaneous, going from 'cold' to 'warm' period and *vice versa*. This explains the good correlation ( $r^2 = 0.78$ ) between the two signals which indicates a fundamental link between temperature and CH<sub>4</sub> cycle. Spectral analysis confirms the similarity in the temporal trends of the two records with approximately the same spectra for periodicities corresponding to obliquity and precession (see ref. 17 for  $\delta D$  MTM spectrum). Also cross-spectral analysis (Blackman-Tukey method) between CH<sub>4</sub> data and 'isotope' temperature measurements reveals a coherence of >0.9 for periods >20 kyr, with no significant lag in the phase relationship.

The second salient feature of this comparison lies in some morphological discrepancies in the period between the two interglacials. The  $\delta D$  curve shows for this period (110–20 kyr BP) three minima of temperature at ~20, 60 and 110 kyr BP, and a weak decrease of its baseline. The CH<sub>4</sub> profile exhibits four well marked maxima roughly every 20–30 kyr standing out above a baseline of 400–450 p.p.b.v. and falls to its minimum (350 p.p.b.v.) only during the Last Glacial Maximum. This methane feature probably explains the relatively weak 100-kyr component noted above in the CH<sub>4</sub> spectrum. By comparison, an important component at ~100 kyr is found in the  $\delta D$  spectrum<sup>17</sup>, indicating the marked glacial-interglacial cycle in the deuterium record.

At this stage of the comparison, we could question how representative, on a global scale, are the temperature amplitude changes recorded in the Vostok core. Indeed, here we are mostly interested in temperature signals that may have affected CH<sub>4</sub> sources, but we are confronted by the sparseness of other continental records covering the same period. Guiot *et al.* recently published a 140-kyr record of temperature based on two pollen records from France<sup>20</sup>. It reveals that the two periods of relatively warm temperature taking place at the beginning of the last glaciation at ~80 and 100 kyr BP led to maximum temperatures close to the interglacial ones, thus showing a similar feature to

the amplitude of CH<sub>4</sub> variations at that time. Second, the large CH<sub>4</sub> decrease (~170 p.p.b.v.) at 12–11 kyr BP which parallels a relatively weak cooling (~2 °C) at Vostok, is almost synchronous with a large cold stage taking place in the Northern Hemisphere (the Younger Dryas) for which palaeoclimatic investigations reveal, in both Europe and Greenland, a temperature change of ~7 °C<sup>21,22</sup>. The amplitude relationship between continental temperature at the CH<sub>4</sub> source areas and CH<sub>4</sub> changes could thus have been much closer than the one indicated by the comparison with the Vostok temperature signal.

### CH<sub>4</sub>-cycle implications

The Vostok CH<sub>4</sub> profile allows us to investigate the different components of the CH<sub>4</sub> cycle that can have forced the atmospheric CH<sub>4</sub> variations recorded over the full climate cycle.

Atmospheric CH<sub>4</sub> is mainly destroyed by OH oxidation in the troposphere, and a change of palaeolevels of tropospheric OH could therefore have induced the CH<sub>4</sub> variations. The concentration of OH depends on several parameters including levels of reactive species, temperature and moisture (see, for example, ref. 23 for a complete discussion). We previously estimated the glacial-interglacial change of the sink by examining the temperature dependence of the CH<sub>4</sub>-OH reaction rate coefficient and the OH production from H<sub>2</sub>O<sup>6</sup>. We concluded that there was an increase of the sink during glacial-interglacial warming that implied a decrease of 20% in the CH<sub>4</sub> concentration. Thus a global source increase by a factor of 2.3 would be required to account for the observed CH<sub>4</sub> increase. This estimate does not take into account possible changes of other reactive species which may have also affected OH levels but we have no way of making reliable estimates for such changes at present.

The most important CH<sub>4</sub> sources are continental and are assumed, excluding anthropogenic influence, to be natural wetlands, termites, methane hydrates and wild animals (see, for example, ref. 24 for a recent estimate). The amount of CH<sub>4</sub>

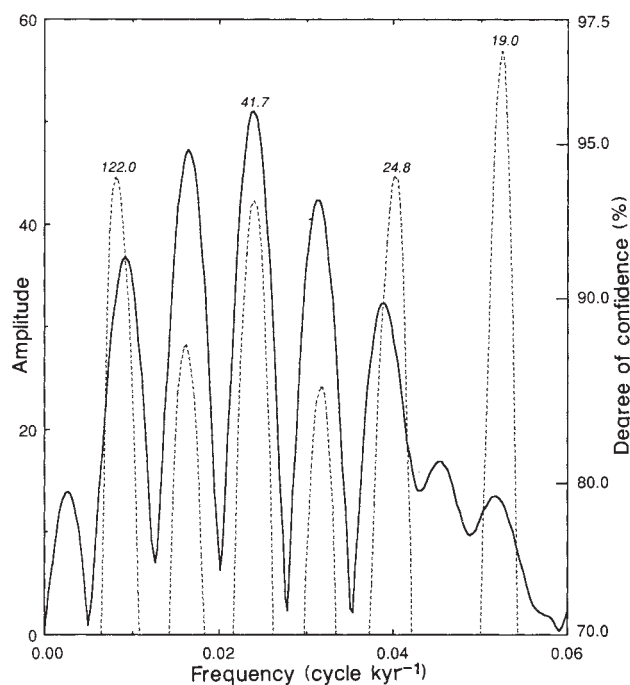


FIG. 2 Spectral analysis of the Vostok CH<sub>4</sub> profile plotted as a function of frequency (kyr<sup>-1</sup>) and obtained by multi-taper method. The continuous line corresponds to amplitude (left scale) and the dashed line to the degree of confidence obtained from *F*-test values (right scale). The annotations give the significant periodicities (kyr).

emitted by the wetlands, the principal natural source, depends on their surface and on the flux from each wetland type. Examination of global databases of the present-day surface distribution<sup>25,26</sup> indicates two principal latitudinal bands, one between 70°N and 50°N and the other between 30°S and 20°N (ref. 25) or 20°S and 10°N (ref. 26). During the glacial-interglacial cycle the high-latitude band could have been controlled by the growth and decay of continental ice sheets inhibiting or liberating some CH<sub>4</sub> sources. Nevertheless the change in continental ice volume estimated from the SPECMAP δ<sup>18</sup>O record<sup>18</sup>, which is dominated by a strong 100-kyr cycle<sup>19</sup>, suggests that this mechanism was probably weak in controlling past atmospheric CH<sub>4</sub> over the full climate cycle. In fact, because of the slow growth of ice sheets, the high-latitude ecosystems may have moved to middle latitudes. Delcourt and Delcourt<sup>27</sup> show, for example, that tundra and boreal forests were widely developed south of the Laurentide ice sheet during the Last Glacial Maximum. On the other hand, during deglaciations, the decay of ice sheets created large areas of open water which may have enhanced the source areas and thus contributed to the approximate doubling of CH<sub>4</sub> at that time.

The low-latitude band may have changed with time because of changes in the hydrological cycle associated with monsoon circulations. Simulations with climate models and palaeodata indicate weaker/stronger monsoon intensity at 18 kyr BP (Last Glacial Maximum)/9–10 kyr BP (for a review see ref. 28). Over the full climate cycle, marine pollen profiles<sup>29,30</sup> and sapropels (organic-rich layers) in the East Mediterranean Sea<sup>31,32</sup> indicate four dominant monsoon maxima at ~10 (in two layers for the sapropels), 80, 105 and 120–130 kyr BP. Furthermore, using key time periods to establish a parameterization between orbital parameters, ice-age boundary conditions and monsoon intensity, general circulation models<sup>28</sup> simulate qualitatively the four maxima indicated by the proxy data as also shown in Fig. 3. We therefore propose that the monsoon circulation could have had a principal role in controlling palaeomethane concentration through variations of low-latitude wetland areas.

Concerning the wetland fluxes, field measurements indicate an enhanced flux with increasing temperature. We have used this trend to infer that the glacial-interglacial warming impact on the wetland fluxes could explain a large part of the corresponding CH<sub>4</sub> increase<sup>6</sup>. The temperature/CH<sub>4</sub> flux relationship obtained from seasonal observations is, however, probably difficult to apply on a kiloyear timescale because over such a timescale some adaptation of methanogenic bacteria may have occurred in response to lowering temperatures. Such adaptations have been reported in the case of high-latitude flux measurements<sup>33,34</sup>. The evaluation of the temperature impact on wetland flux and its quantitative application to past conditions therefore require a better understanding of the role of the different parameters involved in controlling CH<sub>4</sub> flux from natural wetlands.

In summary, changes in atmospheric CH<sub>4</sub> measured along the Vostok core over the last climate cycle could be explained by fluctuations in wetland extent, occurring mainly at low latitudes in response to changes of monsoon intensity and, although not well established, by the effect of temperature on CH<sub>4</sub> fluxes evolving from wetlands.

### Climate forcing of methane

As discussed above, atmospheric CH<sub>4</sub> levels during the climate cycle seem to be controlled primarily by climate. We now examine how observed CH<sub>4</sub> changes could influence the climate through three processes: direct radiative effect, chemical feedbacks (defined below) and climate feedbacks. Only sparse palaeoclimate data are available for the full glacial-interglacial cycle. Consequently, we restrict our discussion to the role of CH<sub>4</sub> during the transitions from full glacial to interglacial conditions. We should, however, emphasize the remarkable Vostok δD-CH<sub>4</sub> link, which supports the continuous involvement of methane in climate change over the full climate cycle.

We calculated<sup>6</sup> that the direct radiative effect of CH<sub>4</sub> results in a global surface equilibrium warming of 0.08 °C when CH<sub>4</sub> increased from 350 p.p.b.v. (full glaciation) to 650 p.p.b.v. (interglacial period).

The chemical feedbacks considered are the CH<sub>4</sub>-induced modifications through atmospheric chemistry of tropospheric ozone (O<sub>3</sub>) and stratospheric water vapour (H<sub>2</sub>O), which are two important 'greenhouse' gases. The O<sub>3</sub> feedback depends on the past atmospheric level of NO. The increase in CH<sub>4</sub> leads to a tropospheric O<sub>3</sub> increase in high-NO environments (>10 p.p.t.v., parts per 10<sup>12</sup> by volume)<sup>35</sup> and to an unchanged<sup>24</sup> or decreasing<sup>35</sup> tropospheric O<sub>3</sub> level in the case of low NO contents. In ref. 6 we calculated the effect of a positive O<sub>3</sub> feedback for past conditions and obtained a further surface warming of ~0.05 °C. But the first estimate of NO palaeolevels, based on O<sub>3</sub> measurements made at the end of the last century, indicates that NO concentration was probably low at that time<sup>36</sup>, suggesting the absence of an O<sub>3</sub> feedback. In the case of stratospheric H<sub>2</sub>O feedback, oxidation of one molecule of CH<sub>4</sub> in the stratosphere produces roughly two molecules of H<sub>2</sub>O. Through this process, CH<sub>4</sub> accounts for ~55% of the present H<sub>2</sub>O level (~6 p.p.m.v.) whereas 45% (2.7 p.p.m.v.) is provided by direct transport from the troposphere to the stratosphere<sup>37</sup>. This second source of stratospheric H<sub>2</sub>O is probably controlled by the low temperature of the tropopause operating as a water-vapour trap. We evaluate the stratospheric H<sub>2</sub>O feedback by considering the tropopause temperature to be, as a first approximation, constant with time and the production of stratospheric H<sub>2</sub>O by CH<sub>4</sub> oxidation to be constant with elevation. A glacial CH<sub>4</sub> level of ~350 p.p.b.v. would then imply a stratospheric H<sub>2</sub>O concentration of 3.4 p.p.m.v. and an interglacial CH<sub>4</sub> value of 650 p.p.b.v. would lead to an H<sub>2</sub>O level of 4.0 p.p.m.v. It has been estimated that a doubling of stratospheric H<sub>2</sub>O from 3 to 6 p.p.m. (by mass) results in a warming of 0.6 °C at the Earth's surface<sup>38</sup>.

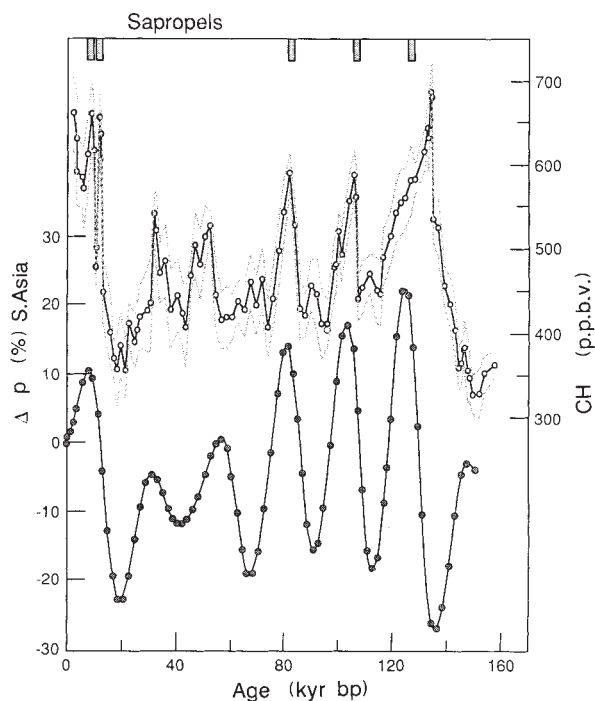


FIG. 3 Upper curve: Vostok CH<sub>4</sub> record plotted against age. Circles correspond to mean values and envelope to the analytical accuracy (2σ). Lower curve: changes of precipitation (in per cent) over southern Asia simulated by general circulation models<sup>28</sup>. 0% corresponds to modern boundary conditions. The vertical bars at the top of the figure indicate the presence of sapropels in the East Mediterranean Sea<sup>31,32</sup>.

Based on this estimate and assuming a linear influence of stratospheric H<sub>2</sub>O concentration on temperature, the change of 0.6 p.p.m.v. of stratospheric H<sub>2</sub>O calculated above as resulting from glacial–interglacial CH<sub>4</sub> increase would thus imply a warming of 0.07 °C. So the combination of the direct radiative effect of CH<sub>4</sub> and of the stratospheric H<sub>2</sub>O feedback would lead to a warming of almost 0.15 °C (and larger if O<sub>3</sub> feedback is positive), that is, ~30% of the direct CO<sub>2</sub> effect for the same transition (~0.5 °C). We may note that in terms of only direct radiative effect (no chemical feedbacks), this percentage drops to 16. We are aware that the above estimate of chemical feedbacks depends on several assumptions that introduce some uncertainty but it does emphasize a potentially important amplification of the direct radiative effect of CH<sub>4</sub> as a result of its chemical activity.

The discussion of the effect of the climate feedbacks driven through the direct radiative effect and the associated chemical feedbacks of the CH<sub>4</sub> change on the glacial–interglacial transition is beyond the scope of this paper. Nevertheless, if we use the estimate of the Goddard Institute for Space Studies three-dimensional global climate model which yields a feedback factor of 3.5 owing to changes in atmospheric water vapour, clouds and snow/ice cover<sup>39</sup>, the glacial–interglacial CH<sub>4</sub> climate forcing including these feedbacks would amount to ~0.5 °C. These climate feedbacks would also apply to CO<sub>2</sub> direct forcing and would lead to a CO<sub>2</sub>-induced surface warming of 1.75 °C. The mean global surface warming corresponding to the last deglaciation can be estimated to be 4.5 ± 1 °C (ref. 40). The combined climate forcing of CO<sub>2</sub> and CH<sub>4</sub> (~2.3 °C) can therefore explain ~50% (~10% for CH<sub>4</sub> alone) of the glacial–interglacial warming, confirming our previous conclusion<sup>6</sup>.

### Younger Dryas CH<sub>4</sub> oscillation

Palaeoclimate data reveal a large cooling, the Younger Dryas, ~11–10 kyr BP in the Northern Hemisphere, particularly in Europe and Greenland. This cooling follows the warming of Bölling–Alleröd interstades (13–12 kyr BP)<sup>21,22</sup>. In the Southern Hemisphere, Antarctic ice cores show a cooling of weak amplitude during the last deglaciation<sup>8,41,42</sup> but its relationship with the northern event is not firmly established. In fact, the CH<sub>4</sub> oscillation (≈170 p.p.b.v.) recorded at Vostok around the period

of concern, which represents ~60% of the full glacial–interglacial variation (300 p.p.b.v.), is the first large-amplitude signal recorded in the Southern Hemisphere that is of global significance.

The cooling of North Atlantic sea surface temperature is suspected to have triggered the Younger Dryas<sup>21,22</sup>. The CH<sub>4</sub> oscillation at Vostok could be linked to the ocean cooling through two processes: (1) an abrupt atmospheric cooling of several degrees (~7 °C) at high latitudes<sup>21,22</sup> which may have forced the freezing of bogs in these regions; (2) a decrease in precipitation rates at low latitudes<sup>32</sup> which may have influenced the wetland areas at these latitudes.

If the assumptions made above about the feedbacks associated with CH<sub>4</sub> change also apply to the Younger Dryas, the CH<sub>4</sub> decrease at 12–11 kyr BP would have led to a mean cooling of the Earth's surface of ~0.3 °C (including chemical and climate feedbacks).

Further CH<sub>4</sub> analyses of this period both on Greenland and Antarctic ice cores should provide useful information for linking observations in the Northern and Southern Hemispheres and for understanding the coupling between such abrupt climate and atmospheric CH<sub>4</sub> changes.

### Conclusions

The record of atmospheric CH<sub>4</sub> over the last climate cycle obtained from the Vostok ice cores reveals fluctuations of natural CH<sub>4</sub> level in the 350–650 p.p.b.v. range. The natural behaviour of CH<sub>4</sub> could be mainly the result of the climate impact on the CH<sub>4</sub> cycle and the role of the low latitudes may be important. The impact of CH<sub>4</sub> (including chemical feedback) on climate is estimated to be ~0.15 °C for glacial–interglacial transitions, that is, ~30% of the CO<sub>2</sub> radiative effect occurring at the same time. Apart from the long-term trend, the Vostok CH<sub>4</sub> profile indicates that methane could also react to abrupt climate change as suggested by the large-amplitude CH<sub>4</sub> oscillation occurring in the last deglaciation which is probably associated with the Younger Dryas climate event.

The fundamental link between CH<sub>4</sub> and climate variations indicated by the Vostok record suggests that the natural CH<sub>4</sub> cycle may provide a positive feedback in any future global warming. □

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