

GLACIAL-INTERGLACIAL EVOLUTION OF GREENHOUSE GASES AS INFERRED FROM ICE CORE ANALYSIS: A REVIEW OF RECENT RESULTS

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Ice core analysis provides the most direct evidence of changes in some major greenhouse gases (CO₂, CH₄ and N₂O) over the climatic cycle covering approximately the last 150,000 years. A remarkable overall correlation is observed between the CO₂ or CH₄ record and the climatic changes in the high latitudes of the Southern Hemisphere, with lowest greenhouse gas concentrations found under full glacial conditions. In terms of phase relationship, CO₂ and CH₄ are roughly in phase with the climatic signal during the deglaciation periods; when entering the glaciation, CH₄ appears to decrease in phase with the Antarctic cooling but CO₂ lags strikingly behind. The CH₄ record exhibits a marked signal which is most likely associated with the abrupt cooling of the Younger Dryas. Existing differences between CO₂ and CH₄ records in comparison with climate reflect differences in sources which are mainly oceanic in the case of CO₂ and continental in the case of CH₄. For N₂O only few data are available suggesting that the N₂O concentrations may also have been lower during the Last Glacial Maximum than during the Holocene. Greenhouse gases are likely to have played an important climatic role in amplifying, together with continental ice, the initial orbital forcing of the glacial-interglacial climatic changes.

METHOD

The record is obtained by analyzing the air enclosed in Antarctic or Greenland ice cores. The enclosure process takes place during the densification of snow into ice occurring in the upper layers (generally between 50 and 100 m below the surface) of the ice sheets. It can be compared to a huge sintering experiment in which pores initially connected with the free atmosphere become isolated and thus sample a portion of the atmosphere. It is believed that the air extracted from suitable ice cores has generally a composition which accurately reflects the atmospheric composition at the enclosure time within a few percents. This is supported by the good match observed between the ice core record for CO₂ (Neftel *et al.*, 1985; Friedli *et al.*, 1986) and CH₄ (Etheridge *et al.*, 1988; Pearman and Fraser, 1988) for the most recent period and the corresponding atmospheric records, measured directly in the atmosphere since 1958 for CO₂ (Keeling *et al.*, 1989) and 1978 for CH₄ (Blake and Rowland, 1988).

Furthermore, the glacial-interglacial rises of about 80 ppmv for CO₂ and 300 ppbv for CH₄ have been observed on all suitable ice cores available for this time period. Since these few ice cores originate from different places on both Antarctic and Greenland ice sheets with different climatic and ice flow regimes and with the same glacial-interglacial transition occurring at different depths, we believe that the glacial-interglacial CO₂ and CH₄ signals found in ice are also a direct record of atmospheric change, not significantly affected by the processes involved during air trapping.

CO₂ RESULTS

In the early 1980s work by groups at Bern and Grenoble on the ice core record (Neftel *et al.*, 1982; Delmas *et al.*, 1980) provided the scientific community concerned with the global carbon cycle with challenging evidence showing that atmospheric CO₂ concentrations increased from about 200 to about 280 ppmv during the last glacial-interglacial warming. The CO₂ ice core record was later extended to the last 150,000 years covering the full glacial-interglacial cycle (Barnola *et al.*, 1987), and showing a remarkable overall correlation between changes in ice isotopic composition, a proxy for climate in the high latitudes of the Southern Hemisphere (Jouzel *et al.*, 1987; Pichon *et al.*, submitted for publication), and changes in CO₂. This record was obtained on the Vostok ice core taken by Soviet scientists in the central part of East Antarctica. Differences were nevertheless observed between the Vostok climate and CO₂ records. For instance, CO₂ lags strikingly behind the climatic record in the transition from the last interglacial to the following cold stage (around 120 ka BP in the Vostok chronology), although both parameters vary almost simultaneously during the two deglacial transitions. Barnola *et al.* (1991) carried out a re-examination of the CO₂-climate relationship based on more precise dating of the air and new CO₂ measurements with higher resolution during some key periods in the Vostok core. As the air bubbles entrapped in ice do not become isolated at the surface of the ice sheet, but only near the firn-ice transition (that is at about 90 m below the surface at Vostok), the air extracted from the ice is younger (by

several thousand years at Vostok) than the surrounding ice. It is therefore necessary to get the best estimate of the age difference between the ice itself and the enclosed air when looking at the phase relationship linking the climatic ice record (deduced from the ice isotopic composition) and the record of air composition. Changes in this age difference, which depend on climatic parameters (temperature, accumulation rate), have been estimated using different models simulating the firn density profile at Vostok as a function of temperature and accumulation rate changes. This was not done for the first published record of CO₂ at Vostok (Barnola *et al.*, 1987). The results indicate that the age difference is about 2000–2500 years during the full interglacial periods and up to 6000 years during the glacial maxima. If this improvement in evaluating the age difference does not change significantly the air dating for the interglacials, it makes the age of the air relative to the age of the ice younger, up to about 1500 years, during the glacial periods. The correction is therefore important when investigating the CO₂-temperature phase relationship during the major climatic transitions.

In order to increase the time resolution of the record a special effort has been made for the onset of the penultimate glacial–interglacial warming by sampling at intervals of about 800 years, which is close to the best resolution we can hope for in this part of the Vostok record. Taking into account both improvements (in air dating and time resolution) we conclude that for the penultimate glacial–interglacial transition (Fig. 1) the CO₂ increase is in phase or slightly lags (by less than 1000 years) the Vostok temperature. Because of the poor quality of the ice (presence of cracks) in the upper part of the Vostok core we cannot obtain enough CO₂ measurements to study the corresponding phase relationship at the time of the warming from the Last Glacial Maximum to the Holocene. Fortunately, a set of CO₂ measurements conducted on the Byrd West Antarctica ice core covers this last period with a high temporal resolution (Neftel *et al.*, 1988). The results indicate that CO₂ lags the temperature by less than 1200 years. Evidence from ice cores therefore shows that during the two last deglaciations the warming experienced by the high southern latitudes slightly preceded or was in phase with the CO₂ increase. In contrast, the Vostok record indicates that, during the transition from interglacial to glacial periods (Fig. 1), the CO₂ decrease lags the Antarctic temperature by several thousands of years (Barnola *et al.*, 1987, 1991). The interactions between CO₂ and the climate of high latitudes in the Southern Hemisphere could thus depend on the type of climatic transition.

CH₄ RESULTS

A large glacial–interglacial change in CH₄ concentrations was first demonstrated by measurements performed on air extracted from Greenland (Stauffer *et al.*, 1988) and Antarctic (Raynaud *et al.*, 1988) ice,

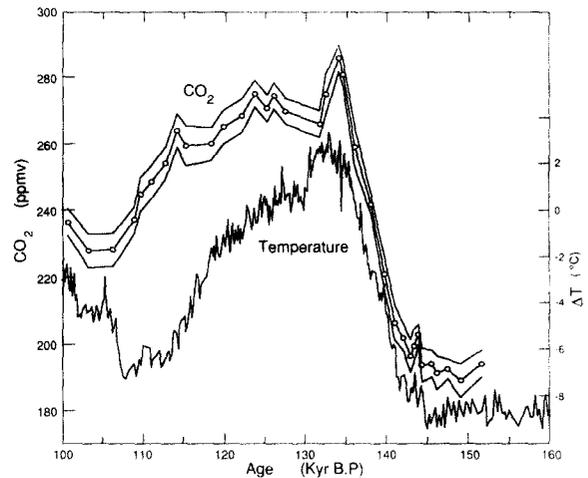


FIG. 1. From Barnola *et al.*, 1991. CO₂ and surface temperature variations recorded in the Vostok ice core between 100 and 160 ka BP. The temperature curve is deduced from measurements of ice isotopic composition (Jouzel *et al.*, 1987). The envelope of the CO₂ curve corresponds to the measurement uncertainties. For details concerning the chronology used see Barnola *et al.*, 1991.

showing that, during the last and the penultimate glacial–interglacial transitions, atmospheric concentrations in CH₄ rose from about 0.35–0.65 ppmv. Further CH₄ measurements in the Vostok ice core (Chappellaz *et al.*, 1990) gave the first description of CH₄ changes for the full climatic cycle (Fig. 2). The record shows strong variations of past atmospheric CH₄ concentrations in the 0.35–0.65 ppmv range, well below the present mean atmospheric concentration (> 1.7 ppmv). As in the case of CO₂, the largest variations are observed to be roughly in phase with the two major glacial–interglacial Antarctic warming phases with a good overall correlation ($r^2 = 0.78$) between the Vostok climate and CH₄ records. Increasing and decreasing CH₄ trends correspond to antarctic warming and cooling periods. Nevertheless, as clearly shown on Fig. 2, there are well marked differences between the CH₄ and CO₂ profiles:

- The decrease of CH₄ centered around 120 ka BP on Fig. 2 is in phase with the interglacial–glacial cooling shown by the ice isotopic record.
- The CH₄ fluctuations found during the glacial period between 110 and 20 ka BP (Fig. 2), are well defined as 4 peaks, with highest values only slightly less than the concentrations observed for the Holocene and the previous interglacial. This part of the record shows a much greater similarity than for CO₂ with the temporal variation of Antarctic temperature.
- The CH₄ record shows an unambiguous and large oscillation at the end of the last glacial–interglacial transition (marked with an arrow in Fig. 2), whose amplitude is ~ 60% of the full glacial–interglacial CH₄ variation. This oscillation may be associated with the abrupt, large but short cooling experienced in the Northern hemisphere between ~ 11–10 ka BP, known as the Younger Dryas event.

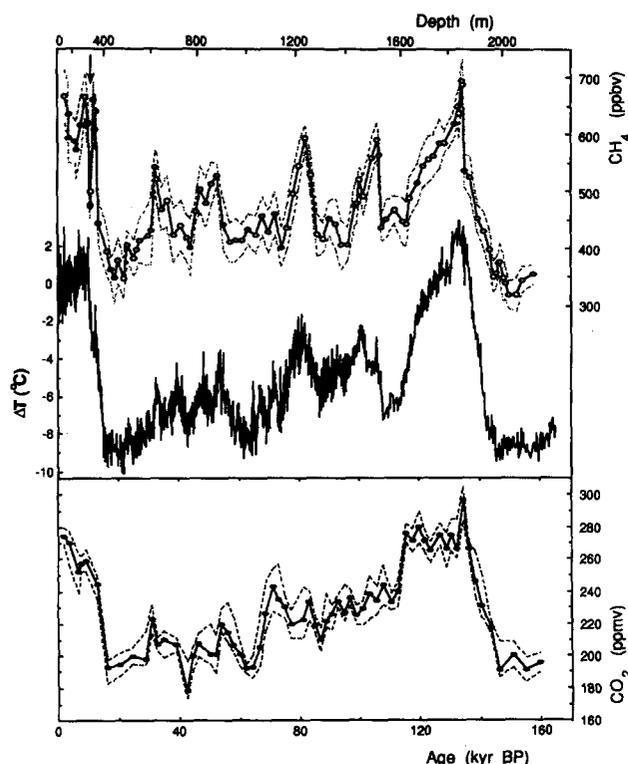


FIG. 2. From Chappellaz *et al.*, 1990. Top: CH_4 and surface temperature variations recorded in the Vostok ice core over the last climatic cycle. The envelope of the CH_4 curve corresponds to the measurement uncertainties. The arrow indicates the CH_4 oscillation attributed to the Younger Dryas. Bottom: The CO_2 record is plotted for comparison. For details concerning the chronology used see Chappellaz *et al.*, 1990.

N_2O RESULTS

N_2O is much less abundant in the atmosphere than CO_2 or CH_4 (N_2O concentration in 1990 is 310 ppbv compared to 353 ppmv for CO_2 and 1.72 ppmv for CH_4), but its radiative forcing per unit molecule change is greater (206 times greater than CO_2 in the present day atmosphere). Furthermore, there are significant overlaps between some of the infrared bands of CH_4 and N_2O which must be taken into account in calculating the CH_4 radiative forcing. Past N_2O variations are less well documented than those of CO_2 and CH_4 . Data from ice core measurements concern mainly the last 3000 years (Khalil and Rasmussen, 1988; Etheridge *et al.*, 1988).

With the long term aim to extend the N_2O record back in time, Zardini *et al.* (1989) initiated a program for measuring N_2O in the air trapped in ice cores. A first set of measurements has been used to check the practicability of measurements with the existing experimental unit, but also provides preliminary measurements of glacial and interglacial levels of atmospheric N_2O . Four horizons have been measured in the Dome C ice core (East Antarctica). The age of the extracted air ranges between approximately 3800 (Holocene) and 13,600 BP (part of the transition between the Last Ice Age and the Holocene). The measurements on Holocene samples indicate an average value of 269 ppbv.

This value is comparable to the 'pre-industrial' value (270 ± 9 ppbv) obtained on younger ice samples using the same analytical unit, but lower than the 285 ppbv average value reported by Etheridge *et al.* (1988) and Khalil and Rasmussen (1988) for the 'pre-industrial' level. The difference in 'pre-industrial' values may be attributable to the different analytical methods and especially to the different calibration gases used. During the transition, the N_2O concentrations decrease (the deepest level dated around 13,600 years shows a mean value of 244 ± 20 ppbv), suggesting that the N_2O concentrations could have been lower during the Last Glacial Maximum than during the Holocene.

CO_2 AND CH_4 CYCLES

CO_2

Previous efforts to explain quantitatively the 80 ppmv CO_2 rise between glacial and interglacial conditions have failed. The mechanisms envisaged mainly involve oceanic modifications including changes in the biological, chemical and physical parameters of the oceanic carbon cycle (see for instance Broecker and Peng, 1986 and references therein). A recent attempt to account quantitatively for the 80 ppmv shift in atmospheric CO_2 has been made by running a series of sensitivity studies with the Hamburg Ocean Carbon Cycle Model, leading to the conclusions (Heinze *et al.*, 1991):

Simple changes in the biological and chemical parameters of the marine carbon cycle can in principle explain the strong pCO_2 reduction during the last glaciation, but the model results are not consistent with other data from marine sediment cores.

A change in the strength of the current velocities (ventilation change), or a change in the structure of the global ocean circulation can both induce an atmospheric pCO_2 reduction, but both experiments fail to reproduce all other observed carbon cycle tracer changes simultaneously.

Improvements of Oceanic Carbon Cycle Models and acquisition of new paleo-climate oceanic tracers are needed. On the other hand, glacial-interglacial changes of carbon storage in vegetation and soils could also have controlled the atmospheric CO_2 shift (Prentice and Fung, 1990; Adams *et al.*, 1990). Thus, Adams *et al.* favour an uptake of carbon in vegetation and soils (including peatlands) of $\sim 1.3 \times 10^{12}$ tons between LGM and Holocene, which would take up CO_2 as the climate warmed. But the equilibrium concentrations of CO_2 at the end of the glacial-interglacial shift were, in any case, ultimately controlled by the ocean.

The record indicates that atmospheric CO_2 is roughly in phase, or lags by less than about 1000 years, the last two glacial-interglacial warming phases in Antarctica, which appear to be in phase, in particular for the penultimate deglaciation (transition between Stages 6 and 5 of the marine chronology), with the warming of

the Southern Ocean (Pichon *et al.*, submitted for publication). On the other hand there is evidence, both from the ice core record (Sowers *et al.*, 1991) and the marine record (Shackleton and Pisias, 1985; Curry and Crowley, 1987), that CO₂ began to increase before the shrinkage of ice volume at the onset of the penultimate deglaciation. The mechanisms suggested for explaining the glacial–interglacial variation of atmospheric CO₂ involve mainly oceanic modifications, but there are, up to now, no satisfactory quantitative explanations for the observed CO₂ increase. Whatever the mechanisms are, they should be able to explain a scenario where CO₂ and Southern temperature changes precede ice volume change.

Although the CO₂ decrease lags the large cooling in Antarctica at the end of the interglacial by several thousand years, it is more difficult to use this observation to constrain the mechanisms of origin of the CO₂ change for this period, since there are also other uncertainties in the phase relationship between the various climatic factors (Antarctic temperature, Southern and Northern ocean temperatures, ice volume . . .).

CH₄

The climatic changes experienced during the glacial–interglacial cycle should have affected both CH₄ sources and sinks. We have interpreted the Vostok CH₄ record as mainly due to changes in wetland areas and in CH₄ fluxes emanating from wetlands (D. Raynaud *et al.*, 1988; J. Chappellaz *et al.*, 1990). We assume that the flux of methane evolved from bacterial processes in freshwater wetland areas was the dominant source prevailing before anthropogenic perturbation, and that the possible changes in the operation of the sink for atmospheric CH₄ (the destruction by OH oxidation in the troposphere) had less influence on CH₄ variations. Although a quantitative evaluation of the changes in CH₄ sources and sinks requires a large modelling effort and the acquisition of new paleo-data, climatically induced changes operating on wetland areas at low latitudes and northern high latitudes appear to be critical when explaining the atmospheric CH₄ record over the last climatic cycle (Raynaud *et al.*, 1988; Chappellaz *et al.*, 1990). In any case, the CH₄ record should reflect climatic changes occurring at latitudes clearly different from the Antarctic geographical situation, and consequently the remarkable similarity between the Vostok temperature and CH₄ records support the concept of the global significance of the Antarctic climatic record.

Finally, the differences, outlined in the section concerning the CH₄ results, between the CO₂ and CH₄ records are most likely to reflect the predominant sources, which are suspected to be mainly oceanic in the case of CO₂ and continental in the case of CH₄.

CLIMATIC IMPACT

The paleo-changes observed in atmospheric CO₂ or CH₄ appear to have been initially driven by the climatic

changes. It is important to evaluate the contribution of the greenhouse gas changes to the variability of past climate. These changes can affect Earth's temperature in three ways: the direct radiative effect, chemical feedbacks (in the case of CH₄) and climatic feedbacks.

The direct radiative effect arises from the trapping of infrared energy by the radiatively active gases. The glacial–interglacial increases of CO₂ and CH₄ result in global surface equilibrium warmings of about 0.5°C for CO₂ and 0.08°C for CH₄.

The CH₄ chemical feedbacks are due to possible CH₄-induced modifications through atmospheric chemistry of tropospheric ozone and stratospheric water vapour, two other radiatively active gases. We estimate that, in the case of the glacial–interglacial CH₄ increase, the chemical feedback would contribute by an additional warming of about 0.07°C (Chappellaz *et al.*, 1990). There are uncertainties in this evaluation but it does emphasize a potentially important amplification of the direct radiative effect of CH₄ as a result of its chemical activity.

So the addition of the direct radiative effects of CO₂ and CH₄ to the effect of the CH₄ chemical feedback leads to a mean global warming of about 0.65°C in the case of the glacial–interglacial transitions. In fact, because of the various fast climatic feedbacks related to tropospheric water vapour, sea ice and clouds, the climate warming due to the increase of greenhouse gases could have been different. For instance, the climate warming linked with the CO₂ and CH₄ glacial–interglacial increases (assuming we can add the effect of the two gases) would be, with boundary conditions corresponding to the current climate, about one to four times the value of 0.65°C as shown from 2 × CO₂ General Circulation Model experiments. This range illustrates the major uncertainty in evaluating climatic feedbacks associated with the greenhouse effect.

We have recently attempted to assess how paleoclimatic data can be used to determine the rôle of greenhouse gases in past global climate change. These changes include not only the fast feedback processes mentioned above, but also longer-term processes such as those linked with slow changes in several boundary conditions. Our approach (Genthon *et al.*, 1987; Lorius *et al.*, 1990) has consisted of evaluating the relative rôle of the different contributions by analyzing the behaviour of climatic forcings and response over the last climatic cycle. As a mathematical tool, we use a linear multivariate analysis in which the climatic output (the Vostok temperature record) is decomposed into one part which can be accounted for by various climatic forcings, and a residual part which is minimized in a least-square sense. We have performed this analysis for 5 climatic forcings, the ice volume taken as a proxy of the Northern Hemisphere forcing, a Southern Hemisphere component represented by the local annual insolation, the greenhouse contribution (CO₂ and CH₄), the aerosol loading and the number of cloud condensation nuclei (with the Vostok dust and non sea-salt sulphate records taken as proxy of these two last

forcings). We conclude that $50 \pm 10\%$ of the Vostok temperature change over the last climatic cycle is accounted for by the overall contribution of greenhouse gases. Most of the other half of the glacial-interglacial change may be accounted for by Northern Hemisphere forcing.

It is interesting to compare these results with temperature changes deduced from GCM simulations for the last deglaciation. Broccoli and Manabe (1987) and Rind *et al.* (1989) showed that, as inferred from the Vostok results, a significant part (i.e. $\sim 40\text{--}50\%$) of the glacial-interglacial global scale warming may indeed be attributed to the greenhouse effect (i.e. direct radiative forcing and associated fast feedbacks). Thus, both the results of our Vostok analysis and GCM results support the conclusion that greenhouse gases along with the Northern Hemisphere ice sheets have significantly contributed to glacial-interglacial changes by amplifying orbital forcing.

Our analysis allows us to evaluate the rôle of fast feedback processes. It suggests that $\sim 2^\circ$ of the $4\text{--}5^\circ\text{C}$ of the globally averaged glacial-interglacial warming may be attributed to the effect of greenhouse gases associated with fast feedback processes (Lorius *et al.*, 1990). Estimating climate sensitivity then simply consists in dividing this 2°C by the corresponding direct forcing (0.65°C), giving a value of ~ 3 .

A further step deals with future greenhouse warming which is possible because, as exemplified by the $2 \times \text{CO}_2$ experiments, climate sensitivity depends primarily on fast feedback processes. For such an experiment, the direct radiative forcing is 1.2°C suggesting that a warming of $3\text{--}4^\circ\text{C}$ ($\sim 3 \times 1.2$) may be a realistic figure. Although being in the middle of the range of values inferred from the GCM experiments ($1.9\text{--}5.2^\circ\text{C}$) this corresponds to a relatively high climate sensitivity.

The approach from paleo-data, which can be improved when a complete N_2O record is available, clearly questions basic points such as the factors controlling climate sensitivity under different climatic boundary conditions (Oglesby and Saltzman, 1990), and the validity of adding radiative forcings of CO_2 and other radiatively active gases (Wang *et al.*, 1991).

CONCLUDING REMARKS

It is now well established from the ice core record that both CO_2 and CH_4 atmospheric concentrations increased by factors of 1.4 and 1.9, respectively, in the two most recent glacial-interglacial warmings. Furthermore, phase relationships between atmospheric CO_2 or CH_4 and Antarctic temperature records suggest that gas increase and warming at high southern latitudes occurred roughly simultaneously ($\pm \sim 1000$ years). Nevertheless, estimating the age difference between the ice and the enclosed air is a sensitive parameter when looking at such phase relationships and the assumption that the air is in diffusive equilibrium all along the firn column when evaluating this age difference needs to be tested.

A CH_4 oscillation, characterized by a drop of about 170 ppbv, has been found near the end of the rise associated with the Last Glacial to Holocene transition and may be associated with the abrupt cooling of the Younger Dryas experienced mainly by the Northern Hemisphere. If our analysis of the climatic forcing of CH_4 during the past is correct, this would have led to a mean equilibrium cooling at the Earth's surface of a few tenths of a degree. The available data for the Younger Dryas do not support the existence of such a marked drop in atmospheric CO_2 concentration, although further measurements are needed to document fully this part of the CO_2 record (Jouzel *et al.*, *in press*).

Only few data are available for N_2O for the Holocene and part of the Holocene-Last Glacial transition. A further record is required in this and other trace gases, such as CO, whose changes lead to modifications in other radiatively active gases (CH_4 , tropospheric O_3). New progress in ice core drilling should offer in the near future the possibility to investigate also the full penultimate climatic cycle.

The glacial-interglacial variations in CO_2 and CH_4 have been triggered by mechanisms related to climatic changes. These mechanisms mainly involve the oceanic reservoir for CO_2 , continental sources and the atmospheric sink for CH_4 . A quantitative account of the variations in these trace gases requires the acquisition of new paleo-data and more work on modelling the changes in the ocean carbon cycle, continental sources and atmospheric chemistry in response to climate.

Changes in radiatively active gases have played a significant rôle in amplifying, together with the growth and decay of the Northern Hemisphere ice sheets, the initial orbital forcing of the climatic changes at the scale of the glacial-interglacial cycle. The factors controlling climate sensitivity to greenhouse gases are not yet well understood, but constitute a key issue when investigating past and future climate.

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