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### The ice record of greenhouse gases: a view in the context of future changes

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#### Abstract

Analysis of air trapped in polar ice provides the most direct information on the natural variability of Greenhouse Trace Gases (GTG). It gives the context for the dramatic change in their atmospheric concentrations induced by anthropogenic activities over the last 200 yr, leading to present-day levels which have been unprecedented over the last 400,000 yr. The GTG ice record also provides insight into the processes generally involved in the interplay between these trace gases and the climate and in particular those which are likely to take place in the next centuries in terms of climate changes and climate feedbacks on ecosystems. The paper gives selected examples of the GTG record, taken during different climatic periods in the past, and illustrating what we can learn in terms of processes. © 1999 Elsevier Science Ltd. All rights reserved.

#### 1. Introduction

The experience of the past has widely influenced the course of societies in many fields like economics or social and political sciences. Similarly paleo-climatologists and environmentalists are looking to the past for the key to understanding the future.

As far as greenhouse gases are concerned, anthropogenic activities release different greenhouse trace-gases into the atmosphere which are affecting our climate. We know that their accumulation in the atmosphere most likely leads to an overall increase of temperature, but large uncertainties still remain regarding the climatic sensitivity to greenhouse gases (what is the temperature increase expected for  $2 \times CO_2$ ?), the carbon cycle budget (where is the unidentified  $CO_2$  sink?), and the feedbacks on the ecosystems involved (how will ecosystems react to climate and atmospheric composition changes?).

The predictions for the future are made by using general circulation models when simulating the climate of the  $2 \times CO_2$  world, or carbon cycle models when developing scenarios of future  $CO_2$  emissions. These models are based on our understanding of the processes involved. Because most of the main anthropogenic

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greenhouse trace-gases ( $CO_2$ ,  $CH_4$ ,  $N_2O$ ) were present in the atmosphere and contributing to the radiative budget of the Earth's surface prior to human activities, the evidence for past greenhouse trace-gas changes currently offers a unique tool for investigating what are the active processes occurring under different climatic conditions in the interplay between greenhouse gases and climate.

In this paper we do not intend to give a complete overview of the greenhouse gas record from ice cores. We will focus on some of the recent results obtained on the record to place the current anthropogenic greenhousegas perturbation into the context of natural variability, and to address the insight provided by the ice core record of greenhouse trace-gases into the processes which could be involved in the next centuries as a consequence of the anthropogenic release of greenhouse gases. The potential of the method, consisting of looking at the past for (i) exploring the processes involved in changing the climate and (ii) a better understanding of the interplay between climate changes and biogeochemical cycles, is investigated here under different types of global climate:

- the Holocene conditions which provide the natural background context for the anthropogenic changes;
- the abrupt climatic changes during the last glacial-interglacial transition (Bolling/Alleröd, Younger Dryas) and during the last ice age (Dansgaard-Oeschger events);

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• the glacial-interglacial cycles, which provide the opportunity to investigate the sensitivity of the climate to different forcings.

## 2. The ice record of greenhouse trace-gases: anthropogenic and natural changes

Analysis of the air trapped in ice cores provides the most direct evidences of past changes in atmospheric trace-gases. A synthesis review of the works performed before 1993 on the reliability and the interpretation of the ice record of greenhouse gases can be found in Raynaud et al. (1993). Since then, new sets of measurements, new ice cores (GISP and GRIP cores in Greenland; Law Dome and Taylor Dome cores and the extension of the Vostok core in Antarctica) and firn air sampling in Antarctica have provided fundamental information concerning:

- the variability of CH<sub>4</sub>, CO<sub>2</sub> as well as its isotopic composition and N<sub>2</sub>O over the industrial period and the last 1000 yr (Blunier et al., 1993; Etheridge et al., 1996; Battle et al., 1996; Etheridge et al., 1998; Francey et al., 1999; Machida et al., 1995);
- the Holocene changes in atmospheric methane concentrations (Blunier et al., 1995; Chappellaz et al., 1997) and CO<sub>2</sub> (Barnola et al., 1996; Indermühle et al., 1999);
- changes in greenhouse trace gases during the Younger Dryas and Dansgaard/Oeschger events (Chappellaz et al., 1993; Blunier et al., 1997; Severinghaus et al., 1998; Stauffer et al., 1998);
- the extension of the Antarctic ice record of CO<sub>2</sub> and CH<sub>4</sub> first from 1–2 glacial–interglacial cycles (Jouzel et al., 1993), and most recently to 4 climatic cycles, leading to a unique atmospheric record covering the last 420,000 yr (Petit et al., 1999).

The ice core record enables us to assess the pre-industrial levels of the major greenhouse trace-gases (GTG): 280 ppmv for CO<sub>2</sub>, 700 ppbv for CH<sub>4</sub> and 270–280 ppbv for  $N_2O$ ; it unambiguously indicate that the observed increases of these GTG during the instrumental period are driven by the anthropogenic emissions of the GTG during the industrial era. Measurements of the  $\delta^{13}C$ record of CO<sub>2</sub> over the last 1000 yr provide insight into the variability of the carbon terrestrial and marine sinks prior to industrialization. Inverse methods applied to existing CO<sub>2</sub> and  $\delta^{13}$ C records (Joos et al., 1999 and references therein) suggest that the natural variability in the sinks on time scales of decades to centuries has been one order of magnitude smaller than the sink fluxes driven by the anthropogenic perturbation, and provide constraints and boundary conditions for oceanic and biospheric models used to estimate the uptake of the anthropogenic carbon (Joos et al., 1999). The longer

record indicates that the industrial increases of  $CO_2$  and  $CH_4$  are most likely unique in terms of growth rate and lead to present-day atmospheric concentrations which have been unprecedented over the last 420,000 yr.

### 3. Methane and CO<sub>2</sub> changes during the holocene

Studying the Holocene is of special interest for understanding interactions between climate and biogeochemical cycles under climatic conditions close to those prevailing today. We may thereby provide information related to posssible feedback processes in the projection of future global warming.

High-resolution methane records covering the whole of the Holocene (starting 11,500 years ago, at the end of the Younger Dryas) are now available from Antarctic and Greenland ice cores (Chappellaz et al., 1997). They show, prior to anthropogenic influence, a CH<sub>4</sub> variability of the order of 150 ppbv, together with Greenland concentrations on average 6% higher than the Antarctic ones. This Holocene interpolar gradient is about three times less than today's, the latter being largely influenced by the predominance of anthropogenic sources in the northern hemisphere. But the most striking result lies in the demonstration that we can reconstruct small changes in the interpolar gradient of methane, when choosing ice drilling sites with similar trapping conditions for tracegases. Indeed, the results of Chappellaz et al. (1997) obtained on such sites (GRIP in Greenland and D 47 and Byrd in Antarctica) reveal significant changes in the interpolar difference in methane concentrations over time (Fig. 1a): a minimum gradient  $(33 \pm 7 \text{ ppbv})$  is observed from 7 to 5 kyr BP, whereas the highest gradient (50  $\pm$  3 ppbv) takes place from 5 to 2.5 kyr BP; a relatively high gradient is also observed during the Early Holocene. A 3-box model has been used to translate the measured gradients into quantitative contributions of methane sources in three latitudinal bands. The model output (Fig. 1b) indicates that past natural sources predominantly lay in tropical regions, but the surprise comes from the fact that the contribution of boreal regions appears also significant, especially at the start and during the second half of the Holocene period. The record at the beginning of the Holocene describes what was the situation at the end of a long period of global warming leading from a glacial to an interglacial period. The dramatic increase in atmospheric methane occurring towards the end of the Younger Dryas, combined with the important inter-polar gradient at this time, indicates the importance of the mid-latitude and/or boreal regions, in addition to the tropics, as potential sources of methane when the climate is warming. Recently, a detailed investigation of CH4 changes during the last deglaciation ruled out the possibility of significant and catastrophic CH<sub>4</sub> degasing from hydrate reservoirs (Brook et al., 1999) and



Fig. 1. Holocene ice records of greenhouse trace gases: (a) Records of atmospheric  $CH_4$  in Greenland and Antarctica (Chappellaz et al., 1997). Note the significant variability in the interpolar methane gradient. (b) Results of a 3-box model translating the measured gradients into contributions in  $CH_4$  sources in three latitudinal bands (Chappellaz et al., 1997); (c) and (d) Records of atmospheric  $CO_2$  and its isotopic ( $\delta^{13}C$ ) composition measured along the antarctic Taylor Dome ice core (Indermühle et al., 1999); (e) and (f) Ocean uptake (in GtC/yr) and cumulative biospheric release of carbon (in GtC) responsible for the observed  $CO_2$  changes, as deduced from inverse methods based on a one-dimensional carbon cycle model (Indermühle et al., 1999).

it appears that the spread of wetlands in boreal regions was probably the main contributor of additional  $CH_4$ from these regions. The determination of the interpolar gradient under different climatic conditions and of the isotopic signature of methane in the air trapped in ice should provide a better understanding of the modifications of the latitudinal distribution of the  $CH_4$  wetland sources and their nature as climate changes.

Unlike CH<sub>4</sub>, CO<sub>2</sub> concentrations measured in Greenland and Antarctic ice may differ by much more than the interpolar atmospheric difference and consequently do not allow us to investigate possible changes in the interpolar  $CO_2$  difference. This is because of the much higher content of impurities in Greenland ice, which can lead to in situ CO<sub>2</sub> production via acid-carbonate interactions or oxidation of organic material (Delmas, 1993; Anklin et al., 1997; Haan and Raynaud, 1998). On the other hand, it has been demonstrated that the antarctic record provides the most reliable record of changes in global atmospheric CO<sub>2</sub> (Raynaud et al., 1993), probably within a few ppmv. The Antarctic Taylor Dome  $CO_2$  and  $\delta^{13}C$ records (Indermühle et al., 1999) have recently revealed that the global carbon cycle has not been in steady state during the Holocene. The records show an 8 ppmv decrease in the  $CO_2$  mixing ratio and a 0.3% increase in  $\delta^{13}$ C between 10.5 and 8.2 kyr BP, and then over the following 7 kyr a fairly linear 25 ppmv CO<sub>2</sub> increase accompanied by a ~ 0.2%  $\delta^{13}$ C decrease (Fig. 1c and d). Inverse methods based on a one-dimensional carbon cycle model and applied to the Taylor Dome record (Indermühle et al., 1999) suggest that changes in terrestrial biomass and sea surface temperature are mainly responsible for the observed  $CO_2$  changes (Fig. 1f and e). In particular, the CO<sub>2</sub> increase from 7 to 1 kyr BP could correspond to a cumulative continental biospheric release of about 195 GtC, in connection with a change from warmer and wetter mid-Holocene climate to colder and drier conditions.

The Holocene climate at high northern latitudes is characterized by a much more subtle variability at the century and millenial scale compared to the glacial climate. The  $CH_4$  and  $CO_2$  variations observed during the Holocene confirm that during this period, as revealed by continental proxies, the latitudinal distribution of continental ecosystems and the hydrological cycle experienced significant changes. The study of the Holocene should provide information necessary to test the sensitivity of atmospheric trace gases to latitudinal changes in different climatic forcings (like insolation or aerosols). It should be noted that anthropogenic land use may have already had a relatively small impact on the trace-gas record prior to the industrial era.

### 4. Greenhouse gases and abrupt climatic changes during the last glacial-interglacial transition and the last ice age.

Abrupt climatic changes took place during the past over a few decades and on a hemispheric scale, with wide amplitudes in the North Atlantic region (of the order of 10°C over Greenland). The relatively recent discovery of these past changes was a real surprise and is of importance for exploring the variability of our future climate. We will here assess the relationships between variations in  $CO_2$  and  $CH_4$  and changes in the isotopic composition of the ice (proxy for paleo-temperature). We first stress the importance of using the methane signal in both the Greenland and Antarctic records to synchronize the northern and southern hemisphere climatic records at high latitudes and to provide fundamental information about the North–South climatic teleconnection.

## *4.1. CH*<sup>4</sup> *synchronization: north–south climatic teleconnection*

Increased resolution of the Antarctic and Greenland  $CH_4$  records leads to an accurate synchronization of the bipolar ice core records and major progress has been achieved in correlating changes in the ice isotope records between Antarctica and Greenland (Blunier et al., 1997,1998; Steig et al., 1998).

The glacial-interglacial warming in the northern hemisphere is interrupted, near its end, by the Younger Dryas (YD), an abrupt cold event during which Greenland isotopic values reached almost glacial levels. In contrast, the Antarctic record shows no abrupt isotopic event during the deglaciation, but a period of reversal of the warming trend likely corresponding to a slight cooling and called the Antarctic Cold Reversal (ACR). The methane synchronization applied between the antarctic Byrd and Vostok records and the Greenland GRIP record provides an improved insight into the phase relationship between the YD and the ACR (Blunier et al., 1997). It indicates that the ACR preceded the YD by at least 1800 yr and was synchronous with the warm period of the Boelling - Alleroed in Greenland, whereas Antarctica was warming during the YD (Fig. 2). This new piece of evidence confirms that the northern and southern climates at high latitudes were in anti-phase during the YD event. On the other hand, by using the same method of synchronization, Steig et al. (1998) found that the isotopic signal at the coastal Antarctic Taylor Dome site changed in parallel with the YD rather than with the ACR recorded in the central part of Antarctica. This dilemma is not fully understood. It is possible that Taylor Dome records a regional feature of the antarctic sea surface temperature possibly related to the YD.

Other abrupt climatic events, known as the Dansgaard–Oeschger events, have been documented in the Greenland ice core record during the last glacial period (Dansgaard et al., 1984). They are warmings of several degrees which took place in a few decades and returned more slowly to glacial conditions. Abrupt methane increase parallel to these climatic warmings (Chappellaz et al., 1993), highlighting a likely synchronism of the climatic changes between high northern latitudes and the tropics. The strongest of these fast and large temperature changes observed in Greenland have analogues in the Antarctic temperature record and again, using the methane synchronization, rapid climate changes in Antarctic



Fig. 2. The YD record: timing of the Antarctic Cold Reversal and the atmospheric  $CO_2$  increase with respect to the YD event (Blunier et al., 1997), as deduced from the  $CH_4$  synchronization, the isotopics records of the GRIP, Byrd and Vostok ice cores, together with the  $CO_2$  record from Byrd.

and Greenland are found to have been asynchronous (Blunier et al., 1998; Fig. 3).

Thus,  $CH_4$  synchronization appears to provide a very powerful tool for investigating the phasing between climatic events at high latitudes in Northern and Southern hemispheres. The discovery of the North–South antiphase nature of the abrupt climatic changes during the past is highly relevant to the central issue of understanding how the Northern and Southern hemispheres are coupled in terms of climate dynamics.

# 4.2. Atmospheric $CO_2$ and $CH_4$ and the rapid climatic events

In this section we discuss the relationships between the variations in  $CH_4$ ,  $CO_2$  and changes in temperature during the rapid events.

It has been speculated that atmospheric methane, for instance through catastrophic gas hydrate release (Nisbet, 1992), could have been one of the possible causal mechanisms for rapid climatic changes. The fact, that the age of the air trapped in ice is younger than the age of the surrounding ice and that the difference in age between ice and gas is not perfectly constrained, has largely prevented an assessment of the relative timing between methane and temperature during the rapid climatic events identified in the ice core record. Severinghaus et al. (1998) proposed recently an innovative way to solve the problem by identifying in the gas phase a proxy for temperature changes, thus avoiding the problem of difference in age between air and ice. The temperature-proxy used is based on the fractionation of gas isotopes in the firn layers following a rapid temperature change at the surface. Severinghaus et al. applied the method to the



Fig. 3. Greenhouse gases and abrupt climatic changes during the second part of the last ice age (adapted from Blunier et al., 1999). The GRIP, Byrd, Vostok ice isotopic records (3 top records) are synchronized using the corresponding methane records (3 bottom records). The Byrd  $CO_2$  record is also plotted and the positions of the Heinrich events (H2 to H5) are indicated by triangles. The two dashed lines correspond to the positions of H4 and H5.

abrupt climate warming at the end of the Younger Dryas. The results indicate that the methane increase began 0-30 yr after the warming in central Greenland, that this increase was slower than the temperature warming and that the bulk of the methane increase came after the warming in Greenland. The authors conclude: "a causal role for methane in the warming, already doubtful owing to the small greenhouse effect of methane, is clearly ruled out by these phase data". On the other hand, the results stress how sensitive the natural sources of methane are to an abrupt warming of the Northern Hemisphere.

As for  $CO_2$ , the Antarctic ice core record provides the best evidence for global changes in atmospheric concentrations. All the available records show the same overall increase of about 80 ppmv during the glacial-interglacial transition. The results obtained on the Antarctic Byrd core document with the best resolution the period covering the YD (Blunier et al., 1997). The picture we have now (Fig. 2) is that the glacial-interglacial  $CO_2$  increase may have slowdown or even stopped at the time of the ACR; on the other hand the  $CO_2$  increase was not interrupted during the YD (the record exhibits an increase from 245 to 265 ppmv during this period, Blunier et al., 1997). This is a surprising result in view of the likelihood that the YD cooling in the North Atlantic region was linked to a strong reduction in North Atlantic deep water formation, which tends to decrease the atmospheric CO<sub>2</sub> concentration because of the increasing solubility of this trace-gas in the colder waters and better utilization of nutrients in the waters staying longer at the surface. Recently, the reaction of the atmospheric CO2 concentration to a reduced thermohaline circulation was modelled with a zonally averaged circulation-biogeochemical ocean model (Marchal et al., 1999). A freshwater input triggers a reduction of the thermohaline circulation and associated northward heat flux in order to obtain North Atlantic sea surface temperatures which parallel the Greenland temperature record from ice cores. The model simulates CO<sub>2</sub> concentration changes which are consistent with those measured on the ice core. It also reproduces a slight warming in the southern hemisphere in agreement with the Byrd and Vostok climatic warming during the YD period. It thus appears that a modification of the North Atlantic deep water formation can modify the climate in the opposite sense in the North and in the South and that, at least in the case of a reduction of the thermohaline circulation, the increasing North Atlantic

sink of atmospheric  $CO_2$  can be over-compensated by synchronously warming sea surface temperatures elsewhere (for instance in the Southern Ocean).

We now consider Dansgaard/Oeschger events, many of which are found in association with what have become known as Heinrich layers, reflecting periods of extensive ice-rafted debris recorded in marine sediments from the North Atlantic as a result of large iceberg discharges. After the precise synchronization of the Greenland GRIP and Antarctic Byrd and Vostok ice core records, it appears that two clear warming events found in the antarctic records precede two of the major and long-lasting D/O events (Blunier et al., 1998): the D/O events number 8 & 12, which are themselves associated with Heinrich events H4 and H5. In fact the warm peaks of the Antarctic records correspond to the cold phases in the North, just preceding the two D/O events. Recently, the Byrd ice-record covering the last glacial period back to about 50 kyr BP was re-analyzed. The record was synchronized to the well dated Greenland GRIP core and indirectly to a proxy for North Atlantic (sea surface temperature) SST. The study indicates that atmospheric  $CO_2$  may have changed parallel to Heinrich events, at least in the case of the H4 and H5 events (Stauffer et al., 1998). The CO<sub>2</sub> increases corresponding to H4 and H5 appear to be in



Fig. 4. Greenhouse Trace Gases changes over the last four climatic cycles (Vostok ice core, Petit et al., 1999). The  $CO_2$  and  $CH_4$  records are plotted together with the Vostok ice isotopic record ( $\delta D$ ). The present-day antarctic  $CO_2$  (365 ppmv) and  $CH_4$  (1600 ppbv) are also indicated.

phase with warm events shown in the records of central Antarctica and with glacial episodes in Greenland (Blunier et al., in press; Fig. 3). This suggest that similar processes were governing the climate-carbon cycle system not only during the YD but also during the long-lasting Dansgaard/Oeschger events.

## 5. Climate sensitivity of greenhouse trace gases and the glacial-interglacial cycles

The record of the Vostok ice core now covers about the last 400,000 yr (Petit et al., 1999; Fig. 4). The highest CO<sub>2</sub> and CH<sub>4</sub> mixing ratios are found during the interglacials and the lowest during the glacial maxima. The overall remarkable correlation of CO<sub>2</sub> and CH<sub>4</sub> with Antarctic temperature suggests that the GTG (essentially  $CO_2$ ) are important as amplifiers of the initial orbital forcing. It also reflects the dynamics of the oceanic and the continental biospheric carbon reservoirs in relation to climatic changes. The processes occurring at the scale of the multi-millenial glacial-interglacial changes are generally not directly relevant to the recent and future century-scale variability of the climate and the Carbon cycle. On the other hand, the overall correlation between greenhouse trace-gases and climate over glacial-interglacial cycles, as demonstrated by the ice core results, highlights the potential of past records to investigate the sensitivity of climate to greenhouse gases under different climatic conditions and provide tests for climate models intended to simulate future responses to increasing concentrations of greenhouse gases. The initial forcing due to the direct effect of increasing GTG ( $CO_2$  +  $CH_4 + N_2O$ ) during the glacial-interglacial transitions is estimated to produce a global warming of about 0.95°C (Petit et al., 1999). This initial forcing has been amplified by rapid feedbacks due to associated water vapour and albedo modifications (sea ice, clouds...), as is also the case with the increasing load of anthropogenic GTG. Results from different climate simulations make it reasonable to assume that GTG and their associated rapid feedbacks have contributed significantly (possibly about half, that is  $2-3^{\circ}C$ ) to the globally averaged glacial-interglacial temperature change (Berger et al., 1998; Weaver et al., 1998).

It is interesting to note that the increases of GTG corresponding to the four glacial-interglacial transitions start several thousand years before any intense deglaciation (Petit et al., 1999). This observation leads to a sequence of climate forcings as follows: changing the orbital parameters initiated the glacialinterglacial climatic changes, then the greenhouse gases amplified the weak orbital signal, accompanied several thousand years later by the effect of decreasing albedo during the retreat of the Northern hemisphere ice sheets.

#### 6. Conclusion

We are well aware that the past will not provide a precise analogue of the future, but it provides lessons to be learned from real experiments undergone by the earth-climate system and the paleo-record also shows how the system reacts under different climatic conditions.

The GTG ice record provides the context for the dramatic change in their atmospheric concentrations induced by the growing anthropogenic perturbation over the last 200 yr, leading to present-day levels which have been unprecedented over the last 400,000 yr.

The CO<sub>2</sub> and  $\delta^{13}$ C ice records provide important boundary conditions and constraints for the C models (oceanic and biospheric) used to estimate the uptake of the anthropogenic C by the terrestrial and oceanic sinks. The Holocene results point out the potential of past CO<sub>2</sub> and  $\delta^{13}$ C records, when used in inverse modelling, to provide further constraints on the global carbon budget under different climatic conditions and to provide tests for climate models intended to simulate future responses to increasing concentrations in greenhouse gases.

The  $CH_4$  synchronization of Antarctic and Greenland ice cores appears to be a very powerful tool for investigating the phasing between climatic events at high latitudes in Northern and Southern hemispheres. The discovery of the North–South anti-phase nature of the abrupt climatic changes during the past is highly relevant to the central issue of understanding how the Northern and Southern hemispheres are coupled in terms of climate dynamics.

The evidences from periods of marked cooling occurring in the North on decadal or century time scales provides information on the sequence of events associated with rapid climatic changes and on the atmospheric CO2 sensitivity to a modification of the thermohaline circulation.

The overall correlation between greenhouse tracegases and climate over glacial-interglacial cycles, as demonstrated by the ice core results, highlights the potential of past records to investigate the sensitivity of climate to greenhouse gases under different climatic conditions and to provide tests for climate models intended to simulate future responses to increasing concentrations in greenhouse gases.

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