The ice record of greenhouse gases.

by D. Raynaud Jouzel, J.M. Barnola, J. Chappellaz, R.J. Delmas and C. Lorius

Gases trapped in polar ice provide our most direct record of the changes in greenhouse gas levels during the past 150,000 years. The best documented trace-gas records are for [CO.sub.2] and [CH.sub.4]. The measurements corresponding to the industrial period document the recent changes in growth rate. The variability observed over the last 1000 years constrains the possible feedbacks of a climate change on the trace gases under similar conditions as exist today. Changes in the levels of greenhouse gases during the glacial-interglacial cycle overall paralleled, at least at high southern latitudes, changes in temperature; this relation suggests that greenhouse gases play an important role as an amplifier of the initial orbital forcing of Earth's climate and also helps to assess the feedbacks on the biogeochemical cycles in a climate system in which the components are changing at different rates.

Man has caused large increases in atmospheric concentrations of [CO.sub.2], [CH.sub.4], and [N.sub.2]O since 1800, and of chlorofluorocarbons (CFCs) since 1950. We urgently need to understand how sensitive Earth's climate is to the radiatively active gases (also called greenhouse gases). We also need to understand how changing climate affect the biogeochemical cycles of these gases.

After an initial temperature change induced by a modification in greenhouse gases, several important feedbacks determine the climate sensitivity. They include (i) changes in the atmospheric content of water vapor (which is another greenhouse gas), (ii) changes in the surface albedo resulting from modifications in snow and ice cover and to a lesser extent in vegetation, and (iii) changes in cloud distribution and content. Most of these parameters are included in the general circulation models. The results of most simulations of a doubling of atmospheric [CO.sub.2] levels predict a global warming between

2. and 5 [degrees] C[1]. The wide range of these predictions reflects mainly the uncertainties linked with cloud feedback[2].

In addition, there are a number of potential feedbacks on the [CO.sub.2], [CH.sub.4], and [N.sub.2]O cycles when the climate is changing [see[3] for a review]. Thus, exchanges of atmospheric [CO.sub.2] with terrestrial ecosystems and the ocean are largely controlled by temperature and oceanic circulation. Likewise, [CH.sub.4] emissions from wetlands are particularly sensitive to temperature and soil moisture. These feedbacks are generally difficult to quantify.

There is another type of feedback that complicates the understanding of the greenhouse gas-climate system. It results from the complex atmospheric chemistry involved, and we term it "chemical feedback." One illustration is the oxidation of [CH.sub.4] by OH radicals producing stratospheric water vapor and tropospheric [O.sub.3], two other radiatively active gases. Also, gases that have a small effect on the radiative budget may still play an important role. For example, changing atmospheric concentrations of CO modify the oxidizing capacity of the atmosphere and consequently the level of atmospheric [CH.sub.4].

One way to examine the effects of these various feedbacks is to look at past records of climatic changes and atmospheric gases. Of the available atmospheric records, the most direct is obtained from ice cores. It integrates the complexity of all the system involved (terrestrial ecosystems, ocean, chemistry of the atmosphere, and climate), and reveals the net global response of the atmosphere to a given climate change. In this article, we review the reliability of the ice core record of critical greenhouse trace gases and describe and discuss its major features during different time periods.

The currently available ice record of-greenhouse gases comes from shallow and deep cores (Table 1) drilled both in Greenland and Antarctica (Fig. 1). This record is documented in detail for the recent period (the last 200 years) and extends with less resolution back to the end of the penultimate glacial period [160 ka (thousands of years ago)]; it thus covers a full glacialinterglacial cycle. The record covers climatic conditions generally equivalent to or colder than those today, with interesting exceptions like the previous Interglacial at

120 to 130 ka. [TABULAR DATA OMITTED]

Reliability of the Record

Because of the remoteness of the polar ice sheets from anthropogenic and biological influences, the composition of the polar atmosphere generally reflects the background levels of the different constituents. In the upper 50 to 100 m (depending on the site) of the Antarctica and Greenland ice sheets, the polar atmosphere can occupy and mix in the open pores of the firn, the stage where the snow deposited at the surface transforms into bubbly ice. The air becomes ultimately trapped in the pores as they close off and form air bubbles. Most of the pores close off in the lowest part of the firn layer[4, 5]. The end of the closure process corresponds to the firn-ice boundary. The question is to know to what extent the composition of the air extracted from the ice represents accurately the atmospheric composition at the time of the trapping.

As illustrated in Fig. 2, several processes could cause the gas record measured on ice samples to be different from the original atmospheric composition. Potential mechanisms include: (i) the physisorption and chemisorption of gases on the surface of snow and ice crystals, (ii) the separation by gravity and the molecular diffusion of the gases in the firn column, (iii) the alteration of the gas composition by formation of air hydrates at great depths in the ice sheet or by the presence of drilling-induced fractures or thermal cracks in the ice samples, and (iv) the alteration by chemical interaction between the gases and the ice on long time scales. Even though fundamental work is still needed to evaluate quantitatively the effects of these chemical and physical processes, the impacts can generally be tested or calculated.

With regard to the first mechanism, analysis of ice that has sampled recent air indicates (Fig. 3) that the [CO.sub.2] and [CH.sub.4] records obtained from antarctic ice core measurements connect well with the corresponding atmospheric records[6, 7]. This would not be the case if the physisorption and chemisorption of gases on the surface of snow and ice crystals significantly modified the greenhouse gas concentrations before air is trapped in the ice.

In absence of mixing by convection, the heavier gas molecules are preferentially enriched toward the base of the firn by gravity. In addition, it takes some time for any changes in atmospheric concentrations, such as the anthropogenic perturbation today, to be transmitted to the deepest layers of the firn where the air becomes permanently isolated from the atmosphere. It was recently shown that the composition of the air column sampled at different depth levels in the open porosity of the firn, before its enclosure as air bubbles in ice, essentially reflects diffusive and gravitational equilibrium with the atmosphere at the surface of the ice sheet[5]. As a consequence the air, just before being trapped at the base of the firn column, has a composition that departs slightly from the atmosphere at the surface of the ice sheet. These effects are generally small (for instance, of the order of 1% of the initial atmospheric concentration for the gravitational effect) compared to the variations observed and can be calculated with confidence.

Air hydrates and fractures. The uncertainties concerning the reliability of the record increase with the age of the ice and the depth of recovery of the core, and it has been suggested that the long-term [C0.sub.2] record is an artifact caused by the structural changes of the ice with depth and by postcoring processes[8]. The progressive caging of the air molecules inside the ice molecular structure (air hydrate formation) under the increasing load pressure with depth, or the occurence of fractures or cracks produced as a consequence of the drilling, may cause the composition of the extracted gas to differ from that of the air initially enclosed in the ice. The formation depth of the air hydrates can be directly observed in the core[9] or calculated from the equilibrium diagram [10]. Glaciologists have identified a brittle zone, which generally extends between 250 and 1400 m below the surface, from which the recovered ice commonly contains a high density of cracks or fractures.

The record itself provides evidence that the changes observed are not caused by the presence of air hydrates or fractures. For example, increases in [CO.sub.2] and [CH.sub.4] concentrations in the Vostok core are similar for the last two glacial-interglacial transitions, even though only the most recent transition is located in the brittle zone. Such evidence argues that the atmospheric trace-gas signal is not strongly affected by the presence of the brittle zone (an increasing scatter of the trace-gas concentrations can be observed in ice samples contaminated by drilling fluid intrusions; such scattered data must be interpreted with caution). Also, the last glacial-interglacial transition has been investigated along the two Antarctic ice cores from Byrd and Vostok stations. The transition is in the region of air-hydrate formation at Byrd but not at Vostok, yet the [CO.sub.2] and [CH.sub.4] records from the two cores are similar. We are consequently confident that the large [CO.sub.2] and [CH.sub.4] increases, recorded during the glacial to interglacial transitions and showing similar amplitudes from one core to another, are not an artifact linked with the airhydrate occurence in ice.

More generally, the good agreement obtained for the glacial-interglacial changes of [C0.sub.2][11-14] and [CH.sub.4] levels[15-17] recorded in different types of ice (with and without air hydrates or fractures or cracks, as well as different temperatures, snow accumulation rates, ice structures, and so on) on the same core (Vostok) or among different cores support the notion that, overall, the long-term trace-gas record from ice cores accurately reflects atmospheric changes. That the records can be reproduced with a new set of measurements performed several years after the initial measurements [see[13, 18] for instance] is another reason for confidence in the atmospheric signal of the ice record of trace gases.

Chemical interactions between the gases and the ice. When air hydrates form, the air in the ice is in contact, either at the walls of the bubbles or within the ice matrix, with the various chemical impurities scavenged at cloud level by snow flakes or deposited to the snow surface by dry deposition. Over long periods of time, two types of chemical interactions may be envisaged. First, [CO.sub.2] (which is an acid anhydride) could react with alkaline chemical species[19]; as a result, the [CO.sub.2] content could be decreased. However, gases, except He, are not able to diffuse easily in the ice, and no evidence has been found that salts can migrate. Thus, this process appears unlikely to occur to any great extent in polar ice. Second, it has been recently proposed[20] that ice containing both acids and carbonates can generate[CO.sub.2] over time[21]. There are some indications that this reaction is possible in ice that formed during times when [H.sub.2][SO.sub.4] was present in the polar aerosol and carbonate dust was abundant. This situation might have occurred in Greenland during specific periods of the last climatic transition; such a possibility has also been suggested for rapid changes of [CO.sub.2] levels observed in Greenland ice during the latter part of the ice age[22, 23] but this notion is not yet proven either. On the other hand, the lack of carbonate dust in Antarctic ice for all studied periods [attested by the constant acidic nature of Antarctic ice [24]] has prevented any significant formation of excess [CO.sub.2]. Chemical reactions with the ice lattice are thus possible, but their impact on the true [CO.sub.2] values is, in any event, restricted to Greenland ice for limited time periods. In particular, the low [CO.sub.2] concentrations revealed by analysis of ice age ice both in Antarctica and Greenland are not questionable. Finally, there is no suggestion of any chemical interaction involving [CH.sub.4].

Dating and Climate Reconstruction

Establishing reliable chronologies for ice cores is a primary requirement for their interpretation as environmental records. Various approaches can be used that fall in four broad categories[25], namely dating by seasonal variations, by correlating reference horizons, by ice flow modeling, and by radioactive isotopes (still in its infancy for ice cores). Seasonal variations supplemented by well-dated reference horizons (volcanic eruptions) provide year-by-year dating for the recent period. For deep ice cores, dating is based on layer counting and on ice flow modeling or more generally on a combination of those two methods. The use of seasonal variations is then based on multiple parameter techniques[26] as is well illustrated from Greenland cores Dye 3 in South Greenland[27] and more recently the GRIP[28] and GISP II[29] cores drilled at the summit site in Central Greenland. The same type of approach was applied for the Byrd core[30] in West Antarctica (dating used in Fig. 4). On the East Antarctic Plateau, the accumulation rate is too low (less than 5 cm of water equivalent) for clear isotopic or other, annual signals to form. The strategy adopted for Vostok therefore was to use a glaciological model [31]. This model accounts both for past accumulation changes[31-33] and for thinning of the ice layer with depth. The uncertainty on the accumulation rate largely contributes to the overall dating uncertainty, which is estimated to be 10,000 to

15,000 years at 150 ka[31].

The age of the air enclosed in ice is of central interest here. It is younger than the age of the ice itself (which corresponds to the time of the snow deposition at the surface), in that the air is trapped well below the surface (typically between 50 and 100 m below surface, depending on the site). Furthermore, ice samples analyzed for trace-gas compositions typically contain several thousands of air bubbles that closed off at different times. This means that the age of the air cannot be represented by a single figure but by a mean value and an age distribution. Dating the air with respect to the ice implies knowing where the pore closure occurs in the firn and how well mixed the air is in the firn. This requires measurements of porosity and air composition in the firn[5]. The mean age difference between snow deposition and air enclosure varies under present-day conditions from about 35 years at DE08[7], where the snow transforms quickly to ice, to 2500 years at Vostok[18], where the firn formation is slow because of the low accumulation rate of snow and extremely cold temperatures. The corresponding widths of age distribution are about 14 and 300 years. The uncertainties in these numbers are difficult to assess. They are larger for older ice, mainly because of the uncertainty on the past accumulation rates. Ongoing firn measurements in different sites will improve our evaluation of the uncertainty in the age of the air.

Past temperature changes are derived from the isotopic contents of the ice ([delta]D or [[delta].sup.18]O) by use of the linear relation between the isotopic content of a precipitation and the local temperature observed for middle and high latitudes[35]. It is preferred, at least for the central East Antarctic Plateau where a strong inversion exists, to refer to the temperature change above the inversion layer, where the precipitation is formed and which appears to be more relevant than the surface temperature for characterizing the global temperature. It is this approach that was followed for deriving the Vostok temperature record (Fig. 5). The derived temperature record shows a remarkable correlation with the ocean record of ice volume change back to 110 ka (Fig. 5). Such an agreement does not hold for the earlier period. Here, the temperature increase leading to the Last Interglacial Period evidently occurred 10,000 years earlier than the change in the ice volume ocean record. Various ways of correlating the Vostok and the deep-sea records from temperature profiles[36] and from [[delta].sup.18]O in air bubbles[37] show that part of the difference is real and part is attributed to chronological problems either of the ice or of the ocean records (or of both).

The Recent Period and Last 1000 Years

The evolution of important trace gases in terms of radiative balance or atmospheric chemistry has been precisely documented by direct atmospheric measurements only for the most recent period (for instance for [CO.sub.2] since 1958 and for [CH.sub.4] since 1978). The three greenhouse gases of interest here, [CO.sub.2], [CH.sub.4], and [N.sub.2]O, are increasing today primarily because of anthropogenic influence. The current mean atmospheric concentrations are 355 ppmv for [CO.sub.2], 1700 ppbv for [CH.sub.4], and 310 ppbv for [N.sub.2]O. As pointed out above, the ice records of recent [CO.sub.2] and [CH.sub.4] levels compare well with the atmospheric records. They also show that the atmospheric levels just before the time of the major anthropogenic [CO.sub.2] and [CH.sub.4]

```
emissions were  280 ppmv for [CO.sub.2] and
 700 ppbv for [CH.sub.4]. [N.sub.2]O measurements
```

for this period are more scattered, largely because of larger experimental errors. They do suggest that levels increased over the last 200 to 300 years from initial concentrations of between 260 and 285 ppbv (38, 39).

The combined ice core and atmospheric records of [CO.sub.2] levels covering the last 140 to 200 years has been used together with standard models for the [CO.sub.2] uptake by the ocean and emission data of fossil fuel carbon to calculate the changes in the net [CO.sub.2] flux between terrestrial ecosystems and the atmosphere [for a review see [40]]. The results indicate that the total net [CO.sub.2] release from terrestrial ecosystems to the atmosphere was 25 to 50 gigatons (Gt) of C from A.D. 1850 to the present (in comparison 6 Gt of C are currently being released each year by burning fossil fuels). The net flux changed with time, and there is an indication of a net uptake of C by the terrestrial biomass between about 1950 and 1980. This approach may be substantially improved in the future by obtaining ice core records with better time resolution. The [CH.sub.4] record between 1841 and 1978 has been recently measured on the DE08 ice core (East Antarctica), which has the most suitable time resolution of any existing ice core for gas analysis of the industrial period. The detailed record[7] indicates that the [CH.sub.4] growth rate has generally increased since preindustrial times, except from A.D. 1920 to 1945, during which the growth rate remained constant.

The last thousand years have not yet been documented in detail, but this period is of special interest in that it may reveal greenhouse gas variations related to minor global climatic deviations from the presentday climate - for instance, the Little Ice Age or the Medieval Warming - and set upper limits on the feedbacks of these gases into the climate system. There are a few published measurements suggesting that [CO.sub.2] levels may have changed by order of 10 ppmv, possibly linked with these climatic fluctuations[41]. On the other hand, [CH.sub.4] and [N.sub.2]O levels may have varied by up to 50 and 20 ppbv, respectively, before A.D. 1800[38, 39, 42].

The Glacial-Interglacial Cycle

The ice record of greenhouse gases.

The [CO.sub.2] record. The search for possible changes in [CO.sub.2] concentrations between glacial and interglacial air bubbles was largely unsuccessful during the seventies because of inappropriate methods for extracting the air. The idea of crushing the ice under vacuum for collecting the air trapped in the ice led to the first reliable results, showing that [CO.sub.2] concentrations (190 to 200 ppmv) during the Last Glacial Maximum (LGM), around 18 ka, were lower than Holocene concentrations (270 to 280 ppmv) by 25 to 30%[11, 12]. The discovery of this large increase of [CO.sub.2] levels parallel with the warming from the LGM has now been documented from several ice cores taken both in Antarctica and Greenland and has focused attention upon the role of greenhouse gases in the worldwide warming associated with the deglaciation. Since then, a [CO.sub.2] record with generally high temporal resolution has been obtained for the interval from 50 to 5 ka from the west Antarctic Byrd core (Fig. 4) [14], and the record has been extended to the full glacial-interglacial cycle over the last 150,000 years by analyzing the east Antarctic Vostok core (Fig. 5)1[3, 18]. The Vostok record highlights the prevailing character of the increase in [CO.sub.2] levels associated with deglaciations. It shows that the warming corresponding to the earlier glacial-interglacial transition (at 140 ka) was also accompanied by an increase in [CO.sub.2] levels that is similar to the shift between the LGM and the Holocene (Fig. 5). The record shows, in a general way, a remarkable correlation between changes in Antarctic temperature and changes in [CO.sub.2] levels. Besides the large glacial-interglacial signal, a dominant 20,000 year periodicity in [CO.sub.2] concentrations, close to the orbital precession frequency, is shown by spectral analysis[13]. These features strongly suggest that a coupling exists between atmospheric [CO.sub.2] levels and climate over the last 150,000 years.

A striking feature of the Vostok [CO.sub.2] record is the asymmetry between the major warming and cooling transitions of the glacial-interglacial cycle. The Byrd and Vostok records indicate that the increase in [CO.sub.2] levels is in phase with or may slightly lag (by less than about 1000 years) the beginning of Antarctic warming corresponding to the deglaciations[14, 34], but in contrast, the decrease in [CO.sub.2] levels (documented by the Vostok core) lags by several thousand years the onset of the glacial Antarctic cooling (starting around 130 ka on Fig. 5).

Most of the effort in understanding the cause of the variations in [CO.sub.2] levels has concentrated on the last glacial-interglacial increase (from 200 to 280 ppmv). This increase corresponds to an addition of 170 Gt of C in the atmospheric reservoir, which results from the adjustment of the atmosphere-ocean system toward a new [CO.sub.2] equilibrium. It is likely that the continental biosphere extracted several hundred Gt of C from the atmosphere-ocean system as a consequence of the glacial-interglacial climatic change[43].

The net result is that the ocean must have released [CO.sub.2] in an amount corresponding to several hundred of gigatons of C between the last part of the glaciation and the beginning of the Holocene. Following the glacial period, oceanic warming caused [CO.sub.2] to be degassed to the atmosphere, but the melting of the continental ice lowered the salinity of the ocean and consequently also the partial pressure of [CO.sub.2] in the ocean. The net effect of these two processes could account for an atmospheric increase of only up to about 18 ppmv[44]. Other mechanisms that may have influenced the[CO.sub.2] changes from glacial to interglacial episodes include oceanic combination of changes in biological productivity, ocean alkalinity, and oceanic circulation, and changes in sea ice cover, and deposition of Ca[CO.sub.3] in coral reefs [44-46].

The isotopic content of C in past atmospheric [CO.sub.2] ([delta].sup.13]C) may help to discriminate among these various processes; for example, it would be altered by changes in biological productivity, because organic matter is isotopically depleted in [C.sup.13], whereas changes in alkalinity would, in themselves have no such effect. The data available so far[47] either from ice cores (Fig. 4) or from other sources are not yet conclusive for explaining the glacial-interglacial increase in[CO.sub.2] levels.

Finally, the discovery[22, 23] in Greenland ice of abrupt changes in [CO.sub.2] concentrations around 30 to 40 ka (that is, during the ice age period) opens the question of the occurence of rapid (within less than 100 years) shifts of atmospheric [CO.sub.2] concentrations by 50 ppmv parallel with abrupt climatic events. So far the measurements performed with high time resolution along the Antarctic Byrd core to search for these abrupt changes have been unsuccessful, and it is therefore unclear if they are real or represent artifacts in the Greenland ice records.

The Younger Dryas (YD) is another abrupt climatic event of particular interest: it was a clear interruption in the warming occurring during the second half of the last deglaciation and led to a major cooling in the North Atlantic Ocean, Europe, and Greenland. [CO.sub.2] measurements have been performed on several ice cores to search for a YD signal in [CO.sub.2] [see[48] for a review]. No convincing signal has been detected, but the increase in [CO.sub.2] levels, linked with the deglaciation, seems to have stalled around the time of the YD.

The [CH.sub.4] and [N.sub.2]O records. Although today the atmospheric concentrations of [CH.sub.4] and [N.sub.2]O are much smaller than for [CO.sub.2], their direct contribution to the radiative forcing per molecule change is about 20 times more important for [CH.sub.4] than for [CO.sub.2] and 200 times for [N.sub.2][3]. Unlike [CO.sub.2], these trace gases play an active role in the chemistry of the atmosphere. The atmospheric evolution of these trace gases may also have been strongly controlled by different biotic feedbacks of a changing climate during the past. These reasons have made it attractive to obtain, after [CO.sub.2], equivalent records for [CH.sub.4] and [N.sub.2]O.

The glacial-interglacial changes in [CH.sub.4] were first measured for both Greenland[15] and Antarctic ice cores[16]. The record has subsequently been extended over all the last climatic cycle by analyzing the Vostok core[7]. As for [CO.sub.2], atmospheric [CH.sub.4] levels dramatically increased during the last two deglaciations. The change, with concentrations nearly doubling (from about 350 to 650 ppbv), was similar from one deglaciation to the next. In a more general way, the record over the full climatic cycle shows strong variations of past atmospheric [CH.sub.4] concentrations from 350 to 650 ppbv, that is, well below the present mean atmospheric concentration of - 1700 ppbv. As for [CO.sub.2], the overall correlation is remarkable between the [CH.sub.4] levels and Antarctic temperature. The variations in [CH.sub.4] levels are closer in phase with the Antarctic temperature: thus, unlike for [C.sub.2], the decrease in [CH.sub.4] levels at the end of the interglacial is roughly in phase with cooling toward glacial conditions. The fundamental link between atmospheric [CH.sub.4] levels and climate variations during the last climatic cycle suggests that climate directly impacts the [CH.sub.4] budget. It is tempting to deduce from the good correlation (Fig. 6) that a global increase in temperature of 1 [degree] causes an increase in atmospheric [CH.sub.4] levels of about 50 ppbvv under natural conditions (that is, without the anthropogenic perturbation) [49]. Finally, the [CH.sub.4 record also shows the presence of orbital frequencies, and much variance is concentrated around the precession cycles[17].

The large oscillation recorded near the end of the last deglaciation at Vostok[17], with an amplitude of about 60% of the full glacial-interglacial variation in [CH.sub.4] levels, is one striking feature of the [CH.sub.4 record. This oscillation is suspected to be associated with the YD event. Because of the atmospheric lifetime of [CH.sub.4] (today about 10 years), an almost contemporary signal should have been experienced worldwide. A similar interruption in the deglacial increase of [CH.sub.44] levels was possibly also recorded in the Greenland Dye 3 core but at only one depth level[15]. The analysis of the two new deep ice cores recently drilled in central Greenland will provide more definitive data that will be of great help in comparing the chronological sequences of the Greenland and Antarctic ice cores.

The large changes of the atmospheric [CH.sub.4 burden on the glacial-interglacial time scale reflect modifications of the sinks or sources of [CH.sub.4, or both. Natural [CH.sub.4] sources include wetlands, wild animals, termites, biomass burning, oceans, and lakes. Another potential source could be the degassing of [CH.sub.4] clathrates buried in areas of permafrost and on the continental shelfs. Sinks are essentially the oxidation by OH in the troposphere, and bacterial consumption in aerated soils. Most recent attempts at quantifying the natural [CH.sub.4] budget for the key time periods of the LGM and the Pre-Industrial Holocene, suggest that changes in the extent of wetlands linked to changes in moisture conditions on the continents played a major role in driving changes in atmospheric [CH.sub.4] concentrations; on the other hand, the oxidizing capacity of the atmosphere would have only slightly decreased from glacial to interglacial conditions and therefore would be responsible for a minor part of the [CH.sub.4] doubling associated with these climatic changes[50]. A scenario involving clathrate decomposition has been also proposed to explain the doubling of CH4 levels during the last deglaciation[51], but further investigations are needed.

Only one set of [N.sub.sub].20 measurements, obtained along the Byrd core, covers the last deglaciation and part of the ice age (39). As for [CO.sub.2] and [CH.sub.4], [N.sub.2]O concentrations (Fig. 4) were lower during the ice age and increased during the deglaciation (approximately from 190 to 265 ppbv). This increase could have resulted from a reduction in the loss of [N.sub.20] by photochemical decomposition in the stratosphere (the major sink) or an increase of the nitrification or denitrification processes in the soils and oceans (the main natural sources), or both. The measurements obtained for the period between 20 and 40 ka suggest that the variations in [N.sub.2]O and [CH.sub.4] levels are parallel. If confirmed after the record is extended to a complete climatic cycle, this result would be consistent with the notion that [N.sub.O] production in soils dominates.

Leads and Lags

Explanations of the changes in trace gas composition observed over the last climatic cycle should account for the interplay, including leads and lags, between climate and biogeochemical cycles. The major evidence for leads and lags between different atmospheric or climatic parameters of global significance, including atmospheric trace gases and continental ice volume, or, at least, large geographical significance (high latitude air temperature or ocean temperature and atmospheric or oceanic circulation) arises from a comparison of the ice core and sea sediment records[52] (Table 2). One infers leads and lags by comparing the times at which different signals corresponding to the same event (for example a glacial-interglacial transition) occur, or by spectral analysis. The main limitations are the time resolution of the records, the dating problems when comparing different records, and the difficulty in separating the signal of interest in a given record from the background noise when determining the time at which the signal starts. In the case of the ice core record, the validity of the results obtained by spectral analysis is limited by the shortness of the record (currently one climatic cycle only).

Table 2. Summary of proxy data used for extracting information about trace gases, temperature, ice volume, and atmospheric and oceanic circulation from either ice or deep-sea cores.

Atmospheric trace gases
([CO.sub.2’] [CH.sub.4’] and so forth)
(i) Ice cores: air enclosed in ice.
(ii) Deep sea sediments: difference ([DELTA][[delta].sup.13]C in C) between planktonic and benthic foraminiferal [[delta].sup.13]C as a proxy for [CO.sub.2] (54) and [[delta].sup.13]C in [C.sub.37] alkedienones (47)

Temperature
(i) Antarctic and Greenland air temperature; isotopic composition ([delta]D or [[delta].sup.18]O) of ice.
(ii) Ocean temperature: various proxies (such as faunal or isotopic) in deep-sea cores.

Ice volume
(i) Ice cores: [[delta].sup.18]O of air bubbles
(ii) Deep-sea sediments: [[delta].sup.18]O of foraminiferas, mostly.

Atmospheric and oceanic circulation
(i) Ice cores: concentration of aerosols (atmospheric circulation).
(ii) Deep-sea sediments: [[delta].sup.13]C and Cd/Ca in forams (oceanic circulation) and aeolian input (atmospheric circulation).

Together, [CO.sub.2] and [CH.sub.4] levels and temperature at high southern latitudes changed approximately in phase during the two last deglaciations, although the results are also consistent with a lag of the trace-gases after temperature of up to about 1000 years. The relation between temperature and [CH.sub.4] levels is consistent with the notion that the extent and activity of wetlands have a dominant control on the atmospheric [CH.sub.4] concentrations. Furthermore, information about the relation between [CO.sub.2] levels and ice volume has been obtained from the Vostok ice record for the penultimate deglaciation, by interpreting the changes in [[delta].sup.18]O value of the air trapped in ice as a proxy for the variations in oceanic [[delta].sup.18]O values and hence continental ice volume [37] (Table 2). The results indicate unambiguously that the [[delta].sup.18]O values of air began to shift after [CO.sub.2] levels started to increase (Fig. 7). After deconvolving the [[delta].sup.18]O air signal into an oceanic [[delta].sup.18]O curve, atmospheric [CO.sub.2] concentrations appear to have increased 4000 to 7000 years before there was any significant input of continental ice melt water into the ocean. The record suggests that [CO.sub.2] levels had risen already by about 35 ppmv before continental ice began to be noticeably reduced. This view is qualitatively supported by the deep sea record and a comparison between changes in [DELTA][[delta].sup.13]C and [[delta.sup.18]O values measured on foraminifera (Table 2); these values are used, respectively, as proxies for atmospheric [CO.sub.2] levels and ice volume. The deep sea record consistently shows that the decrease in ice volume systematically lagged behind increases in Southern Hemisphere SST (sea surface temperature) and [CO.sub.2] levels[53, 54]. Radiative forcing attributed to the greenhouse gases therefore started to change ahead of the ice volume. All this evidence indicates that a change in sea level was probably not the initial cause for the increase in [CO.sub.2] levels during deglaciations and, together with the phase relations between [CO.sub.2] levels and temperature in the Southern Hemisphere, favors a mechanism in which internal forcing in the ocean caused the [CO.sub.2] increases. However, results from the antarctic cores of Dome C and Byrd suggest that the phase relation between [CO.sub.2] and continental ice volume during the last deglaciation may have been different from during the previous one (34, 55). Finally, the lag of several thousand years of [CO.sub.2] levels behind temperatures at high southern latitudes during the onset of the glaciation suggests that the sequence of mechanisms controlling atmospheric [CO.sub.2] concentrations was different from that operating during a deglaciation.

Climatic Implications

The Vostok temperature record strongly shows the obliquity cycle (40,000 years), and the precession cycles (19,000 and 23,000 years)[56] are also evident. These results support independently of the deep sea record[57], the notion that orbital forcing as a principle cause of glacial-inter-glacial climatic changes. Such a relation constitutes the basis of the astronomical theory of the ice ages (Milankovitch theory) in which the changes in Northern Hemisphere summer insolation play a key role in the growth and decay of the Northern Hemisphere ice sheet and thus in the change in global ice volume.

The reasonably good knowledge of the anthropogenic and natural variations in [CO.sub.2] and [CH.sub.4] concentrations (and to a less extent in [N.sub.2]O concentrations) at various time scales adds to our understanding of mechanisms involved in glacial-interglacial climatic changes. The most striking feature of the [CO.sub.2] and [CH.sub.4] records, put together in Fig. 5, is the close correlation between greenhouse gases and climate over the last climatic cycle. This correlation, as well as the phase relation among greenhouse gases and climatic parameters suggest that those greenhouse gases have participated, along with the orbital forcing, in the [glacial-interglacial changes. Furthermore, at least partly, a link between climates in the Northern and Southern hemispheres and the explanation of the enigmatic 100,000 year cycle can be provided by greenhouse gases. Still, the presence of orbital frequencies in both the [CO.sub.2] and [CH.sub.4] records strongly suggests that the preindustrial changes in the concentrations of the two greenhouse gases are orbitally driven.

Lorius et al.[58] estimated that about half of the Vostok temperature change over the last climatic cycle may be accounted for by the contribution of [CO.sub.2] and [CH.sub.4]. In their analysis, other potential forcings, such as changes in aerosol loading, do not appear to have a significant contribution. Most of the other half of the temperature change may be accounted for by the effect of the growth and decay of the Northern Hemisphere ice sheets on global climate.

This relatively high contribution of greenhouse gases is well supported by simulations of the LGM in which the role of greenhouse gases, evaluated separately, accounts for 40 to 50%[59]. The role of the inferred temperature change changes in [CO.sub.2] concentrations in glacial-interglacial changes has also been suggested from the results of other climate model studies[60]. Although new results, mainly from deepsea cores, support the key role of astronomical forcing[61], other data suggest that the link between climate and astronomical forcing may be more complex[62]. In any case, the ice core data indicate that [CO.sub.2] and more generally greenhouse gases influenced, likely in an important way, the late quaternary climate.

The ice core data also allow estimation of global climate sensitivity, a parameter for assessing the magnitude of future greenhouse warming. Changes in water vapor, clouds, and sea ice have rapid effects on global climate. As a result, the GCM-predicted equilibrium temperature change attributed to a doubling of [CO.sub.2] levels (global climate sensitivity, [DELTA][T.sub.2X]) is substantially larger than the 1.2 [degrees] C warming that would be predicted if there were no such feedbacks. It ranges from 1.9 [degrees] to 5.2 [degrees] C [1]. Although the time scales involved in paleoclimates and in future greenhouse warming are different, it is fully recognized that paleoclimate data contain information on global climate sensitivity. This is because greenhouse gases have contributed to the glacial-interglacial temperature changes through their direct radiative forcing associated with those same fast feedbacks. Indeed, paleoclimate data have the advantage that the changes in forcings were maintained for a sufficiently long time for equilibrium to be achieved[63]. Central to this approach is that once we admit that the direct radiative forcing is correctly evaluated, it is not necessary to understand fully the above mentioned complexity of the glacial-interglacial mechanisms and the sequence of possible forcings. Thus, whether the change in the levels of greenhouse gases lead or lag the climate change is not by itself relevant for the study of fast feedbacks and consequently for getting empirical estimates of the global climate sensitivity[58].

Different methods have been used to evaluate the global climate sensitivity from data. A direct approach consists in comparing climate simulations for different boundary conditions with paleoclimate data accounting for changes in greenhouse gases (as derived from ice cores). Modelers have generally used the LGM, which is well documented[64].

Estimates of [DELTA][T.sub.2X] range from 2.5 [degrees] to 5 [degrees] C with the Goddard Institute for Space Studies model[63]. Two different versions of the Geophysical Fluid Dynamics Laboratory model with [DELTA][T.sub.2X] of 2.3 [degrees] and 4 [degrees] C were tested against LGM data; although it is difficult to determine which of the two is more realistic, they both may not be too far from reality[65]. Using energy balance models, Harvey[66] and Hoffert and Covey[67] obtained estimates of 2.2 [degrees] to 3 [degrees] C and of 2.0 [degrees] [+ or -] O.5 [degrees] C, respectively. In an opposite approach, Lorius et al.[58] used their estimated percentage of 50% contribution of greenhouse gases to glacial-interglacial changes to back calculate the climate sensitivity; they concluded that a [DELTA][T.sub.2X] of 3 [degrees] to 4 [degrees] C is most reasonable in view of available paleoclimate data.

The observed global temperature trend over the last century offers another way of estimating [DELTA][T.SUB.2X], again largely thanks to ice cores, which have provided detailed records of greenhouse gas increases (and potentially of other forcings) since the beginning of the preindustrial period (Fig. 3). Here, an equilibrium climate is never reached and the delaying effect of the ocean must be accounted for through a simple ocean model (68). Various studies have consistently provided lower estimates of [DELTA][T.sub.2x] than that derived from glacial-interglacial data [1.5 [degrees] C in[68], even when the counterbalancing effect of the increase of anthropogenic atmospheric sulfate are taken into account. In that case, estimates of 2.2 [degrees] 2.2 [degrees] [+ or -] 0.8 degrees] C[68] and of 3 [degrees] C[69] have been obtained. These estimates may be lowered if changes in solar irradiance are accounted for[70].

New results on the change of [N.sub.2]O levels during the last deglaciation indicate that [N.sub.2]O also contributed significantly to the change in radiative forcing[39]. The [N.sub.2]O contribution is estimated to be about 15% of that of [CO.sub.2], that is roughly as important as for [CH.sub.4]. Thus, accounting for [N.sub.2]O would lower the glacial-interglacial estimates of global climate sensitivity by 15% and help to reduce the discrepancy between estimates based on glacial-interglacial changes and on changes during the last century data.

These empirical estimates, which would not be feasible without ice core data constitute one independent check of climate model predictions. In the near future, this approach will provide perhaps the best way to reduce uncertainties in global climate sensitivity. Both recent past and glacial-interglacial data show that positive feedbacks operate in the climatic system and strongly support the prediction of a significant greenhouse warming for the next century.

Conclusion

It is now firmly established that, after selecting appropriate sampling sites, the ice record of greenhouse gases provides the most direct evidence for past atmospheric change. This conclusion is convincingly demonstrated from the close agreement of [CO.sub.2] and [CH.sub.4] measurements for the recent period with direct atmospheric measurements (which also holds, most likely, for [N.sub.2]O and from the long-term record, which shows that the processes that may occur during the slow sinking of the ice within the ice sheet do not significantly affect the atmospheric signal. One possible problem is for Greenland ice corresponding to climatic transitions and to abrupt changes, at least until the possible influence of production of excess [CO.sub.2] by in situ chemical interaction be fully understood.

For the recent period, the ice record puts into perspective man’s impact on the atmospheric composition; the current high levels of [CH.sub.4], [CO.sub.2], and [N.sub.2]O are unprecedented for the last 200,000 years. It, also, provides information on the rate of greenhouse gas changes since the beginning of the industrial revolution.

The best description of the greenhouse gas variations over the last climatic cycle is currently obtained from the two antarctic cores of Byrd and Vostok. The trace gases exhibit large changes in concentration. These variations appear to be generally associated with global climatic changes. The [CO.sub.2] variations observed are essentially driven by oceanic mechanisms, but also by changes in the continental biosphere. The different [CO.sub.2]-climate phase relations highlight the complexity of the mechanisms involved and probably the greater ability of the ocean to release than to absorb [CO.sub.2]. Atmospheric [CH.sub.4] levels changed parallel and with little delay to climatic changes throughout climatic cycles; this observation is consistent with the idea that the atmospheric [CH.sub.4] concentrations were controlled by the extent of wetlands. Although variations in [N.sub.2]O concentrations seem to parallel the [CH.sub.4] variations, more data are needed for understanding the causes of the [N.sub.2]O changes. Atmospheric chemistry and continental ecosystems can play an important role in determining the atmospheric [N.sub.2]O budget, but changes in nitrification and denitrification processes in the ocean may also be important.

The changes of [CO.sub.2], [CH.sub.4], and [N.sub.2]O levels appear generally as a consistent response of the biogeochemical cycles and atmospheric chemistry to an initial climatic forcing, which is most likely of orbital origin. These changes are thought to play a significant part (about half] in the glacial-interglacial climate changes in amplifying the orbital forcing and act together with the growth and decay of the Northern Hemisphere ice sheets. The ice core data also provide information on climate sensitivity. Both recent past and glacial-interglacial data show that positive feedbacks operate in the climatic system and strongly support the prediction of a significant greenhouse warming for the next century.

Most of the information concerning the ice record of greenhouse gases have been obtained during the last decade. The records have still to be completed and extended to several climatic cycles. The recent efforts made to obtain deep drillings in the central part of Greenland should provide important information concerning the timing of greenhouse gas changes and of the Northern Hemisphere climate record back to more than 200 ka and hopefully will resolve the question of whether abrupt changes occurred in past [CO.sub.2] levels.

REFERENCES AND NOTES

[1.] J. F. B. Mitchell, Rev. Geophys. 27,115 (1989), G. J. Boer, N. A. McFarlane, M. Lazare, J. Climate 5, 1045 (1992). [2.] R. D. Cess et al, Science 245, 513 (1989), R. D. Cess et al., J. Geophys. Res. 95, 10601 (1990). [3.] G. T. Houghton, J. T. Jenkins, J. J. Ephraums, and the Intergovernmental Panel on Climate Change (IPCC), Climate Change, The IPCC Scientific Assessment (Cambridge Univ. Press, Cambridge, 1990). [4.] J. Schwander et al., J. Geophys. Res., in press. [5.] J. Schwander and B. Stauffer, Nature 311, 45 (1984). [6.] A. Neftel, E. Moor, H. Oeschger, B. Stauffer, ibid. 315, 45 (1985); H. Friedli, K. Loetscher, H. Oeschger. LJ. Siegenthaler, B. Stauffer, ibid. 324, 237 (1986). [7.] D. M. Etheridge, G. I. Pearman, P. J. Fraser, Tellus 44B, 282 (1992). [8.] Z. Jaworowski, T. V. Segalstad, N. Ono, Sci. Total Environ. 114, 227 (1992). [9.] H. Shoji and C. C. Langway, J. Physique 48, 551 (1987). [10.] S. L. Miller, Science 165, 489 (1969). [11.] R. J. Delmas, J. M. Ascencio, M. Legrand, Nature 284, 155 (1980). [12.] A. Neftel, H. Oeschger, J. Schwander, B. Stauffer, R. Zumbrunn, ibid. 295, 222 (1982). [13.] J. M. Barnola, D. Raynaud, Y. S. Korotkevich, C. Lorius, ibid. 329, 408 (1987). [14.] A. Neftel, H. Oeschger, T. Staffelbach, B. Stauffer, ibid. 331, 609 (1988). [15.] B. Stauffer, E. Lochbronner, H. Oeschger, J. Schwander, ibid. 332, 812 (1988). [16.] D. Raynaud, J. Chappellaz, J.-M. Barnola, Y. S. Korotkevich, C. Lorius, ibid. 333, 655 (1988). [17.] J. Chappellaz, J-M. Barnola, D. Raynaud, Y. S. Korotkevich, C. Lorius, ibid. 345, 127 (1990). [18.] J. M. Barnola, P. Pimienta, D. Raynaud, Y. S. Korotkevich, Tellus 43B, 83 (1991). [19.] The amount of C02 naturally present in the bubbles is typically 0.7 to 1.0 [mu]KM. In general the only chemical species suspected to react with [CO.sub.2] are carbonates, in particular calcium carbonate, according to: [CO.sub.2] + Ca[CO.sub.3] + [H.sub.2]O [arrow] Ca [(HCO.sub.3).sub.2] The presence of Ca[CO.sub.3] in ice is linked to the transport of continental dust, but in any case, the scavenging of [CO.sub.2] by carbonate would occur only if the reaction was possible in the solid phase, a phenomenon that seems to be unlikely because of the low mobility of gases and salts in ice. [20.] R. Delmas, Tellus, in press. [21.] Sulfuric acid aerosol is ubiquitous in the atmosphere. it is scavenged and deposited on the ice by snowflakes. Carbonate dust (loess) is only present in Greenland ice where particularly high levels are observed during ice ages [C. U. Hammer et al, in Greenland Ice Core: Geophysics, Geochemistry and the Environment, C. C. Langway, Jr., et al, Eds. (American Geophysical Union, Washington, DC, 1985), pp. 90-94]. The possible formation of excess [CO.sub.2] would occur according to: [2H.sup.+] + [CaCO.sub.3] [arrow] [Ca.sup.+ +] + [H.sub.2]O + [CO.sub.2] [22.] B. Stauffer, H. Hofer, H. Oeschger, J. Schwander, U. Siegenthaler, Ann. Glaciol. 5, 760 (1984). [23.] The late glacial rapid variations of [CO.sub.2] levels during late glacial time and the climatic changes re observed in exactly the same layers. This result is difficult to explain because the changes are expected to occur simultaneously and thus should not appear at the same depth, because of the age difference between the air and the ice [T. Staffelbach, B. Stauffer, A. Sigg, H. Oeschger, Tellus 43B, 91 (1991)]. [24.] M. R. Legrand, C. Lorius, N. I. Barkov, V. N. Petrov, Atmos. Environ. 22, 317 (1988). [25.] C. U. Hammer, in The Environmental Record in Glaciers and Ice Sheets, D. Konferenzen, H. Oeschger, C. C. Langway, Eds. (Wiley, New York, 1989), pp. 99-121. B. R. Stauffer, in ibid., pp. 123-139; N. Reeh, in ibid., pp. 141-159. H. Shoji and C. C. Langway, in ibid., pp. 161-175, [26.] Layer counting combines information from stable isotopes (however because of diffusion, differences in the isotopic ratios disappear with time), microparticles, and chemical species like ammonium, calcium, and nitrate that show well marked seasonal variations. The abrupt Younger-Dryas Pre-boreal transition is independently dated at 11,550 [+ or -] 70 at GRIP (28) and 11,660 [+ or -] 250 GISP 11 (29). This consistency gives confidence in the validity of the multiparameter counting approach. [27.] C. U. Hammer, H. B. Clausen, H. Tauber, Radiocarbon 28, 284 (1986). [28.] S. J. Johnsen et al., Nature 359, 311 (1992). [29.] R. Alley et al., Eos 73, 259 (1992). [30.] C. U. Hammer, H. B. Clausen, C. C. Langway, Ann. Glaciol. 7, 214 (1985). [31.] C. Lorius et al., Nature 316, 591 (1985). (32.) The accumulation change (lower during cold than during warm periods) is estimated directly from the temperature record. The validity of this method is now confirmed from the GRIP core where layer thickness estimated from this approach is in excellent agreement with that derived from seasonal variations (D. Dahl-Jensen, S. J. Johnsen, C. U. Hammer, H. B. Clausen, J. Jouzel, in preparation). For Vostok, the accumulation rate estimate is independently supported by the [Be.sup.10] profile (33, 34). [33.] F. Yiou, G. Raisbeck, D. Bourles, C. Lorius, N. 1. Barkov, Nature 316, 616 1985). [34.] J. Jouzel et al., Quat. Res. 31, 135 (1989). (35.) This relationship, which results from the successive isotopic fractionations occurring at each phase change of the water during its atmospheric cycle, is particularly well obeyed for present-day Greenland and Antarctic precipitation. The isotopic contents [delta] and [delta.sup.18] are expressed in per mil with respect to the V.S.M.O.W. standard Vienna Standard Mean Ocean Water). The interpretation of ice core data in terms of models which range from simple Rayleigh models [Dansgaard et al. Tellus 16, 436 (1964). J. Jouzel and L. Merlivat, J. Geophys. Res. 89, 11749 (1984)] to GCM isotopic models [J. Jouzel, R. D. Koster, R. Suozzo, and G. Russell, Eos 73, 105 (1992); S. Joussaume and J. Jouzel, J. Geophys Res. in press; J. Jouzel, S. Joussaume, R. D. Koster, paper presented at the Dahlem Workshop, report ES12, Global Change in the Perspective of the Past, J. A. Eddy and H. Oeschger, Eds. (Wiley & Sons, Chichester, in press)] which support the use of present-day observed surface temperature gradients for interpreting ice core data. This approach accounts for possible seasonal changes [G. de Q. Robin, in The Climatic Record in Polar Ice Sheets (G. de . Robin, Ed. (Cambridge Univ. Press, Cambridge, 1983). pp. 184-189. D, A. Fisher, Cold Regions Sci. Tech. 21, 61 (1992)] or the origin of precipitation [S. J. Johnsen, W. Dansgaard, J. White. Tellus 41B, 452 (1989). D. A. Peel and R. Mulvaney, ibid. 44B, 430 (1992)), that are often cited as limiting factors of the temperature interpretation. The various isotopic records show remarkable similarities, at least for their long-term changes, both for Antarctica (33) and Greenland (27). This indicates that the derived climatic information is clearly regionally robust. [36.] J. J. Pichon, L. D. Labeyrie, G. Bareille, M. Labracherie, J. Duprat, J. Jouzel, Paleoceanography 7, 289 (1992). [37.] T. Sawers, M. Bender, D. Raynaud, Y. S. Korotkevich, J. Orchado, ibid. 6, 679 (1991). [38.] D. Etheridge, G. I. Pearman, F. de Silva, Ann. Glaciol. 10, 28 (1988); M. A. K. Khalil and R. A. Rasmunssen, ibid. 10, 73 (1988); D. Zardini, D. Raynaud, D. Scharffe, W. Seiler, J Atmos. Chem. 8, 189 (1989). [39.] M. Leuenberger and U. Siegenthaler, Nature 360, 449 (1992). in this article, Leuenberger and Siegenthaler derived a total glacial-interglacial greenhouse forcing of 3 W [m.sup.-2], 50% higher than that used by Lorius et al. (56) because of a different formulation of the [CO.sub.2] forcing. [40.] R. A. Houghton, in preparation; see also E. Sundquist, Science 259, 934 (1993). [41.] D. Raynaud and J. M. Barnola, Nature 315, 309 (1985) U. Siegenthaler et at, Ann. Glaciol. 10, 151 (1988). [42.] M. A. K. Khalil and R. A. Rasmunssen, Tellus 41 B, 554 (1989). [43.] I. C. Prentice, M. T. Sykes, M. Lautenschlager, S. P. Harrison, O. Denissenko, P. J. Bartlein, in preparation. [44.] W. S.

Broecker and T.-H. Peng, in preparation. [45.] W. S. Broecker and T.-H. Peng, Radiocarbon 28, 329 (1986). [46.] W. F. Budd, in Carbon Dioxyde and Climate: Australian Research, G. I. Pearman, Ed. (Australian Academy of Sciences, Canberra, 1980), pp. 115-128; F. Faure, C. R. Acad. Sci. Paris 305, 523 (1987). [47.] M. Leuenberger, U. Siegenthaler, C. C. Langway, Nature 357, 488 (1992); B. D. Marino, M. D. McElroy, M. J. Salawitch, W. G. Spaulding, ibid., p. 461; J. P. Jasper and J. M. Hayes, ibid. 347, 462 (1990). [48.] J. Jouzel et al., in The Last Deglaciation: Absolute and Radiocarbon Chronologie, E. Bard and W. S. Broecker, Eds. (NATO ASI Ser. 12 (Springer, Berlin, 1992), pp. 229-266. [49.] According to the Vostok results, the regression between [CH.sub.4] concentration (C) and Vostok surface temperature [T.sub.s] is: C (ppbv) = 23.7 [T.sub.s] ([degrees] C) + 591.5. Based on the temperature estimates for the glacial-interglacial transition, a 1 [degrees] C change in global temperature corresponds to a 2 [degrees] C change in the surface temperature at Vostok. Consequently, the corresponding [CH.sub.4]-temperature gradient is 47.4 pppv/[degrees] C. [50.] J. A. Chappellaz, I. Y. Fung, A. M. Thompson, Tellus 45B, in press; A. M. Thompson, J. A. Chappellaz, I. Y. Fung, T. L. Kuscera, ibid., in press. [51.] E. G. Nisbet, J. Geophys. Res. 97, 12859 (1992). [52.] D. Raynaud and U. Siegenthaler, in Global Changes in the Perspective of the Past, J. A. Eddy and H. Oeschger, Eds. (Wiley, Chichester, in press). [53.] J. Imbrie, A. McIntyre, A. Mix, in Climate and Geosciences, A. Berger et al., Eds. (Kluwer, Norwell, MA, 1989), pp. 121-164. [54.] N. J. Shackleton and N. G. Pisias, in The Carbon Cycle and Atmospheric [CO.sub.2] Natural Variations Archaean to Present, E. T. Sundquist and W. S. Broecker, Eds. (American Geophysical Union, Washington, DC. 1985), pp. 303-317; W. B. Curry and T. J. Crowley, Paleoceanography 2, 489 (1987). [55.] T. Sowers, M. Bender, J. M. Barnola, Eos 73, 260 (1992). [56.] J. Jouzel et al., Nature 329, 403 (1987) P. Yiou et al., J. Geophys. Res. 96, 20365 (1991). [57.] J. D. Hays, J. Imbrie, N. J. Shackleton, Science 194, 1121 (1976). [58.] C. Lorius, J. Jouzel, D. Raynaud, J. Hansen, H. Le Treut, Nature 347, 139 (1990). [59.] A. J. Broccoli and S. Manabe, Climate Dynam. 1, 87 (1987); A. Berger, H. Gallee, C. Tricot, J. Glaciol., in press. [60.] B. Saltzman, Climate Dynam. 5, 67 (1990); M. Ya. Verbitsky and R. J. Oglesby, J. Geophys. Res. 97, 5895 (1992). [61.] J. Imbrie et al., Paleoceanography, in press. Two articles on the structure and origin of major glaciation cycles in two parts (i) linear response to Milankovitch forcing and (ii) the 100,000 year cycle. [62.] I. J. Winograd et al., Science 258, 255 (1992); R. A. Kerr, ibid., p. 220; W. S. Broecker, Nature 359, 779 (1992); K. Lambeck and M. Nakada, ibid. 357, 125 (1992). [63.] J. E. Hansen et al., in Climate Processes and Climate Sensitivity, J. E. Hansen and T.

The ice record of greenhouse gases.

Takahashi, Eds. (American Geophysical Union, Washington, DC, 1984), pp. 130-163. [64.] CLIMAP project members, Geol. Soc. Am. Map Chart Ser. MC 36 (1981). [65.] S. Manabe and A. J. Broccoli, J Atm. Sci. 42, 2643 (1985). [66.] L. D. D. Harvey, J. Geophys. Res. 94, 12783 (1989). [67.] M. I. Hoffert and C. Covey, Nature 360, 573 (1992); These authors derived climate sensitivity both from LGM and mid-Cretaceous data and obtained a [DELTA] [T.sub.2x] of 2 [degrees] [+ or -] 0.5 [degrees] C for the LGM and 2.5 [degrees] [+ or -] 0.2 [degrees] C for the mid-Cretaceous. However, as noted by E. Barron [Nature 360, 533 (1992)] the LGM estimate would yield a sensitivity closer from 3.0 [degrees] C if a value of 5 [degrees] C colder than the present (instead of 3.0 [degrees] C) would have been taken as estimate of the glacial temperature. [68.] T. M. L. Wigley and S. C. B. Raper, Nature 357, 293 (1992). [69.] M. E. Schiesinger, X. Jiang, R. J. Charlson, in Climate Change and Energy Policy, L. Rosen and M. Glaser, Eds. (American Institute of Physics, New York, 1992), pp. 75-108. [70.] P. M. L. Kelly and T. M. L. Wigley, Nature 360, 328 (1992); M. E. Schlesinger and N. Ramankutty, ibid., p. 330. [71.] T. Sawers, M. Bender, D. Raynaud, Y. S. Korotkevich, J. Geophys. Res. 97, 15683 (1992). [72.] S. J. Johnson, W. Dansgaard, H. B. Clausen, C. C. Langway, Nature 235, 429 (1992). [73.]T. Sowers et al., in preparation. [74.] D. G. Martinson, N. G. Pisias, J. D. Hays, J. Imbrie, T. C. Moore, N. J. Shackleton, Quat. Res. 27, 1 (1987). (75.) We thank P. Duval for a review of the existing data on the brittle and clathrate zones, D. Etheridge for providing Fig. 3, and M. Bender, D. Etheridge, R. Francey, and M. Leuenberger for comments and discussions. Part of this review was prepared during a 3-month stay of D.R. at the Division of Atmospheric Research (CSIRO). The research on the ice core record of greenhouse gases is in France, supported by PNEDC (Programme National d’Etudes de la Dynamique du Climat) and by the Commission of the European Communities.