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Invited Paper**STABLE ISOTOPES AND GASEOUS
AND PARTICULATE IMPURITIES
IN POLAR ICE CORES*****Applications in climatology
and environmental research***C. BOUTRON*⁺, J. JOUZEL^{++*}

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Abstract**STABLE ISOTOPES AND GASEOUS AND PARTICULATE IMPURITIES IN POLAR ICE CORES: APPLICATIONS IN CLIMATOLOGY AND ENVIRONMENTAL RESEARCH.**

Unique information has been obtained during the last few decades on past changes in the climate of our planet through the investigation of oxygen and hydrogen stable isotopes in palaeowaters, especially in successive, well preserved, dated snow and ice layers deposited in the large Antarctic and Greenland polar ice caps. Together with isotopic data obtained from deep ocean sediments, they have provided confirmation that changes in the orbital parameters of the Earth have played a key role in the succession of glacial and interglacial periods. Polar snow and ice cores have also allowed investigation of past and recent changes in the composition of our atmosphere. During the last climatic cycle, there was a close correlation between the atmospheric concentrations of CO₂ and CH₄ and climate, with the lowest concentration values during the coldest periods, which indicates that variations in the concentrations of greenhouse gases are likely to have contributed to glacial-interglacial climatic changes by amplifying the relatively weak insolation change associated with orbital 'forcing'. Of particular interest are the snow and ice layers deposited over the past few centuries, especially since the Industrial Revolution. Anthropogenic increases of CO₂ and CH₄ are well documented both in Greenland and Antarctica. For species with short residence times such

as sulphate, nitrate and heavy metals, the anthropogenic effect is mainly observed in Greenland: for Pb, a two hundredfold increase is observed from several millenia ago to the mid-1960s; it is followed by a decrease of seven and a half times during the past twenty years owing to a reduction in the use of lead alkyl additives in gasoline.

1. INTRODUCTION

A thorough knowledge of the past climatic and environmental history of the Earth is of paramount importance for a better assessment of possible changes induced by man which might affect our climate and environment on a global scale. Such palaeodata can be obtained from various marine and terrestrial datable sediments through approaches based mainly on isotopic studies. Among the most interesting sediments are the successive well preserved snow and ice layers deposited in the central plateau areas of the large Antarctic and Greenland ice caps, whose age can be up to several hundred thousand years.

In this paper, we are concerned mainly with the investigation of the occurrence of oxygen and hydrogen stable isotopes in these polar snow and ice layers with the aim of obtaining detailed information on past changes in the Earth's climate during the last few glacial cycles. We also provide a brief overview of the very interesting results which were obtained on the occurrence of these isotopes in deep sea sediments, which have allowed comprehensive data to be obtained on successive glacial-interglacial cycles during the entire Quaternary era. Finally, we discuss the wide range of information on ancient and recent changes in the composition of the global atmosphere of our planet which was obtained through the investigation of various gaseous and particulate impurities in the polar ice caps.

2. OXYGEN AND HYDROGEN ISOTOPES IN PALAEOWATERS AND THE CLIMATE

2.1. Isotopic fractionation in the atmospheric water cycle

The saturation vapour pressure and molecular diffusivity in the atmosphere of the two stable isotopic forms of water (HDO and H_2^{18}O) are different from those of the main component of water H_2^{16}O . This results in isotopic fractionation at each phase change of water on the successive steps of the atmospheric water cycle [1], which leads to global scale variations in the concentrations of HDO and H_2^{18}O in precipitation.

These global isotopic variations, denoted here in δ units, δD and $\delta^{18}O$ (the relative deviation in per mille from the concentrations in standard mean ocean water (SMOW)), are well documented for present day precipitation. They have the following characteristics:

- (1) For middle and high latitudes, there is a well fitting linear relationship between the temperature, T , and either δD or $\delta^{18}O$;
- (2) This relationship is not observed in tropical and equatorial regions, where isotopic patterns are more significantly influenced by precipitation rates;
- (3) δD and $\delta^{18}O$ are linearly related to each other throughout the world with the following equation: $\delta D = 8 \delta^{18}O + 10$.

Fractionation processes may be modelled using a variety of models. The simplest ones are of dynamic Rayleigh type, in which the treatment is limited to precipitation formed in an isolated air mass [1, 2]. More elaborate ones involve the introduction of isotopic cycles into general circulation models of the atmosphere which take into account better the complexity of the atmospheric processes leading to the formation of precipitation [3, 4]. Figure 1 shows the comparison between the observed $\delta^{18}O$ values for precipitation (annual averages) and those predicted by the United States National Aeronautics and Space Administration/Goddard Institute of Space Studies (NASA/GISS) model. This figure illustrates the capacity of these complex models to reproduce the observed distribution. The existence of a relationship between the temperature and the isotopic content of precipitation, δD or $\delta^{18}O$, constitutes the basis for inferring palaeotemperatures from isotope concentrations in ancient precipitation.

2.2. Available palaeowaters

In low and middle latitudes, the oxygen or hydrogen isotope concentrations in ancient waters can be obtained directly from groundwaters, fluid inclusions in speleothems and Alpine or tropical glaciers (see, for instance, Ref. [5]). They can also be obtained indirectly from precipitated calcite, tree ring cellulose or other organic materials, especially those in lake sediments. In polar areas, a unique undisturbed sequence of palaeowaters is available through the successive dated snow and ice layers deposited on the polar ice caps, especially the two large Antarctic and Greenland ice caps.

To make use of these very valuable isotopic data, palaeoclimatologists assume that at a given location, the slope of the linear temporal relationship between the temperature, T , and either δD or $\delta^{18}O$ for various periods in the past is similar to the well documented present day spatial slope.

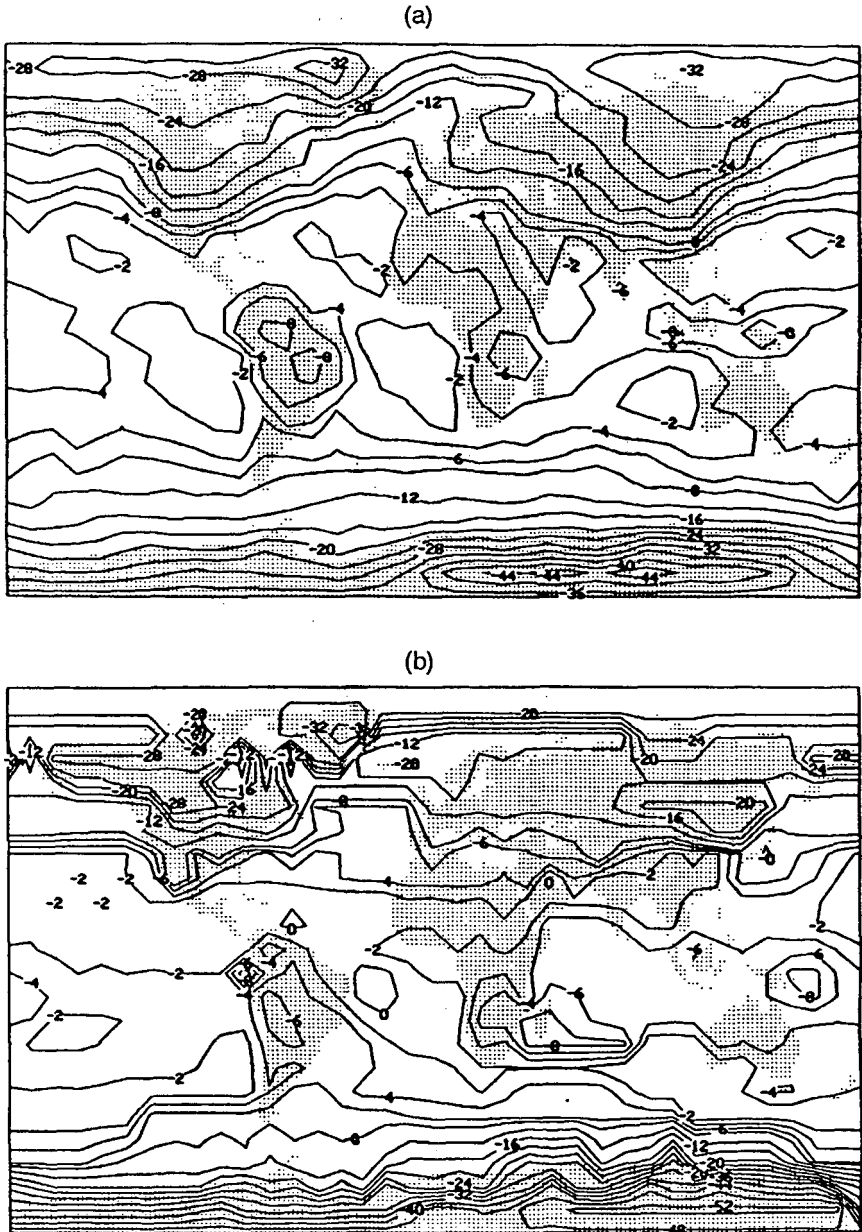


FIG. 1. Mean annual content of $\delta^{18}\text{O}$ (in per mille) in precipitation from (a) a three year simulation performed using the NASA/GISS general circulation model; (b) observations from the IAEA network and from various other sources (adapted from Ref. [4]).

3. OXYGEN AND HYDROGEN ISOTOPES IN ANTARCTIC AND GREENLAND SNOW AND ICE

3.1. Isotope-temperature relationship for Antarctica and Greenland

Although the isotopic composition of polar snows is dependent upon several parameters, a well fitting linear relationship is observed both for Antarctica and Greenland between the mean annual surface temperature and the mean δD or $\delta^{18}O$ values for present day deposited snow [6, 7]. Since there is a strong correlation between this surface temperature and the temperature above the inversion level, where precipitation is formed, a similar relationship also exists when using this last temperature, which is more representative of atmospheric conditions.

As an illustration, Fig. 2 shows the variations in δD in deposited snow as a function of the surface temperature for east Antarctica. It was obtained from the analysis of a comprehensive series of shallow snow cores collected along a 1100 km coast-interior axis in Adelie Land [6]. The slope of the regression line is found to be 9‰ per °C when considering the temperature above the inversion level (it is 6‰ per °C if the surface temperature is considered). It is important to mention that this observed slope is in very good agreement with that derived either from one dimensional atmospheric circulation models or general circulation models [4].

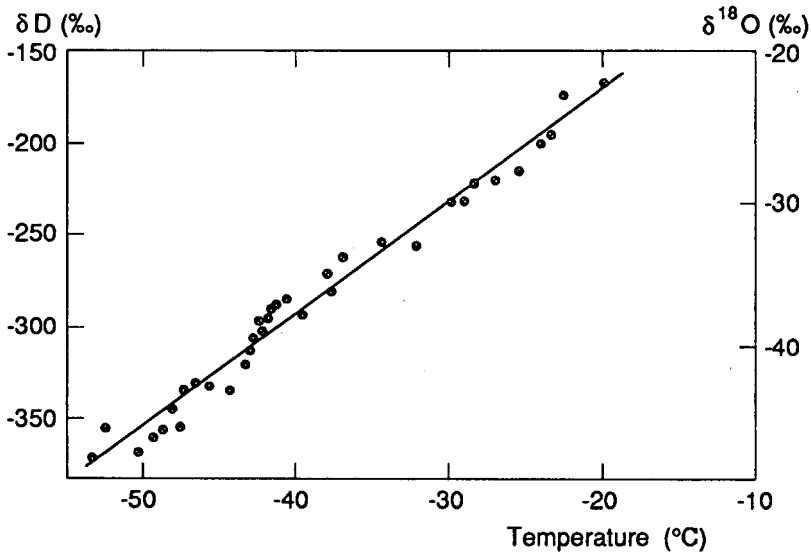


FIG. 2. Variations in the mean annual content of δD in Antarctic surface snow as a function of the local mean annual surface temperature along a 1100 km coast-interior axis in east Antarctica (for surface temperatures lower than 20°C) (from Ref. [6]).

3.2. Sample collection and dating

The difficulties involved in obtaining deep Antarctic and Greenland snow and ice cores covering long enough time periods for climatic studies are formidable. Great engineering skill is necessary for the development and operation of the thermal or electromechanical deep drills which are required (the mean ice thickness in Antarctica is about 2.5 km, but it can be up to 4.5 km in some areas). Moreover, drilling operations are made very difficult and expensive by the remoteness and the very severe climatic conditions (elevations well above 3000 m, very low temperatures, blizzards, etc.). This explains why there are currently very few available deep ice cores reaching back to the last ice age (three for Antarctica and two for Greenland), obtained by only a handful of countries.

The deepest (and oldest) core obtained so far was thermally drilled by the Antarctic expeditions of the former Soviet Union, at Vostok Station (78°28'S, 106°48'E, elevation 3490 m above sea level, mean annual temperature — 55.5°C). It reached a depth of 2546 m (the depth of the bedrock at that location is about 3500 m), which corresponds to a well preserved continuous sequence of 200 000 years of palaeoprecipitation, i.e. more than the full last climatic cycle (but this represents only a small part of the Quaternary era).

The various methods which can be used for the dating of such deep cores have been reviewed in detail by several authors (see, for instance, Ref. [8]). One of these methods relies upon seasonal variations in δD or $\delta^{18}O$. The precision of the dating depends upon a number of factors. For the Holocene (the last 10 000 years), it can be very high. Beyond the Holocene period, absolute dating of the ice is often not possible, and ice core chronologies can only be established either by using glaciological ice dynamic models or by comparison with other palaeorecords, with inherent limitations in accuracy in both cases.

3.3. Isotopic changes during the last climatic cycle

The observed changes in δD as a function of depth in Antarctic ice at Vostok Station during the past 160 000 years [9] are shown in Fig. 3. It is the longest isotopic record obtained so far for both Antarctica and Greenland.

The stages labelled from A to H [10], indicated at the top of the figure, show the successive warm and cold periods. Stage A (the last 10 000 years) corresponds to the present Holocene interglacial. Stages B–F cover the last ice age (from about 13 000 to 116 000 years before present (BP)), with C and E being slightly warmer interstadials, and B being the Last Glacial Maximum (LGM) centred around 18 000 years BP. Stage G (from about 116 000 to 140 000 years BP) characterizes the previous interglacial period (next to last interglacial). Finally, stage H (before 140 000 years BP) is the last part of the next to last ice age.

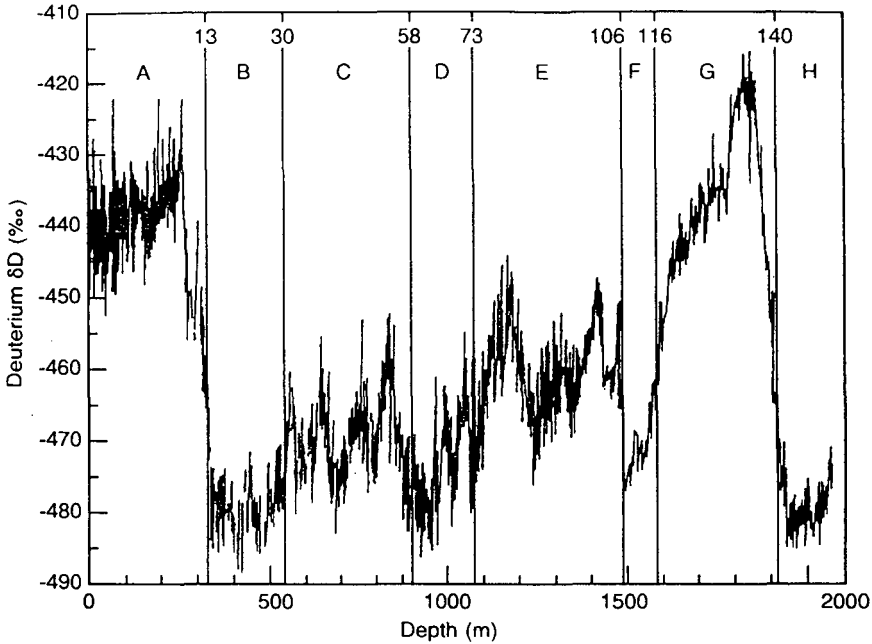


FIG. 3. Changes in δD as a function of depth along the Vostok deep Antarctic ice core (from Ref. [9]). Also shown at the top of the figure are the successive climatic stages referred to in the text, labelled from A to H, and the estimated ages (in thousands of years) corresponding to the limits between these stages.

The chronology was established using a two dimensional ice flow model well adapted to the Vostok area. It has an estimated accuracy of 10 000–15 000 years at the bottom of the core [10]. An important feature of this dating model is that it takes into account the change with time of snow accumulation, assuming that the precipitation rate over the Antarctic Plateau is governed by the amount of available water vapour. This amount is controlled largely by the saturation vapour pressure of water, i.e. by the air mass temperature. This allows estimates of snow accumulation changes along the Vostok record directly from the isotope temperature record, leading to the prediction of a 50% reduction in accumulation at the LGM (stage B in Fig. 3) with respect to modern values. This 50% reduction prediction for the LGM was confirmed by the ^{10}Be profile obtained along the core [11]: concentrations of this cosmogenic isotope whose deposition flux is likely to have remained constant over the last climatic cycle are indeed found to be higher during the LGM by a factor of about two than during the Holocene and the next to last interglacial.

After correction for the isotopic changes which affect sea water between glacial and interglacial periods, the δD profile shown in Fig. 3 can be transformed

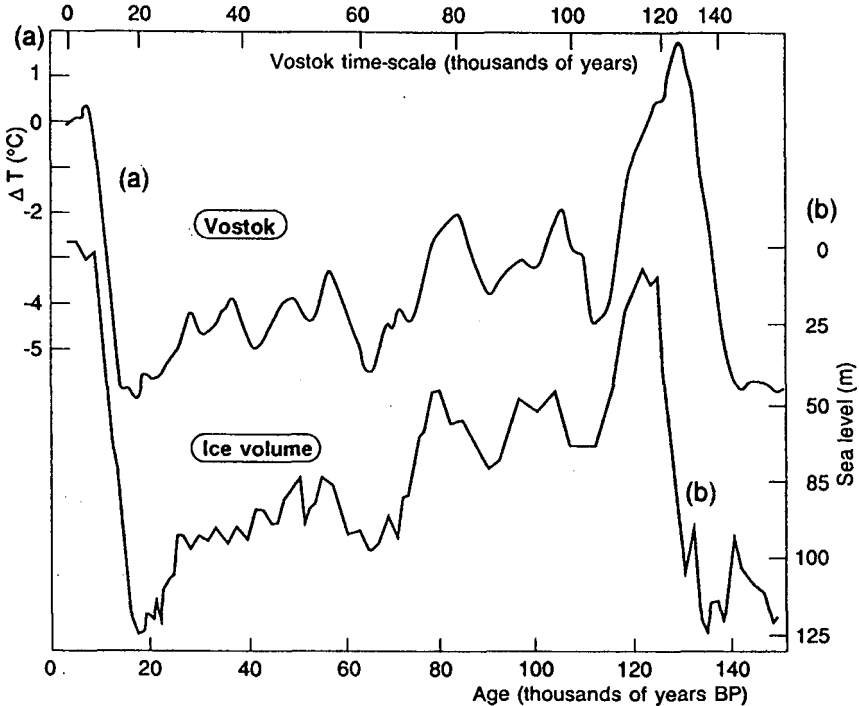


FIG. 4. Time series over the past 160 000 years of (a) atmospheric temperature as deduced from the Vostok δD record (from Ref. [12]), and (b) deep sea sediment $\delta^{18}O$ profile (adapted from Ref. [15]) taken as a proxy of the global ice volume and expressed with respect to sea level changes. The two independent time-scales shown at the top and bottom of the figure are, respectively, the Vostok and marine (BP: before present).

into an atmospheric temperature record using a gradient of 9‰ per $^{\circ}\text{C}$. This record is dominated by the $\sim 100\ 000$ year glacial–interglacial oscillation with an amplitude of about 6°C . The peak of the next to last interglacial period (stage G) is found to be significantly warmer than the present Holocene interglacial period (stage A) by more than 1°C . Three well marked temperature minima are observed during the last ice age (stages B (LGM), D and F); they are separated by two double peak interstadials (stages C and E), during which atmospheric temperatures were up to 3 to 4°C above those observed during the LGM.

This locally determined Vostok temperature record appears to be representative of a large part of Antarctica, as evidenced by the very good agreement [12] between this record and the two other Antarctic temperature records obtained for the Holocene and part of the last ice age from the isotopic analysis of the Byrd [13] and

Dome C [14] ice cores. The main features of this record are probably even of global significance, at least qualitatively, as suggested by the high correlation with the marine $\delta^{18}\text{O}$ record [15] shown in Fig. 4 (lower curve), which represents global ice volume.

Aside from the large $\sim 100\,000$ year signal, the Vostok temperature record displayed in Fig. 4 also clearly shows a $\sim 40\,000$ year signal with four temperature minima roughly in phase with the past total insolation at the Vostok latitude (which is governed by the obliquity cycle of the Earth's orbit with a period of 41 000 years [16–18]). There are also similarities between this Vostok record and the 65°N July insolation changes which play a key role in the Milankovitch theory of the ice ages (these changes are largely influenced by the precession of the equinoxes with periodicities of 19 000 and 23 000 years). The spectral analysis of the Vostok temperature record confirms these visual features: aside from the $\sim 100\,000$ year oscillation, the record is dominated by a strong 40 000 year component and, to a lesser degree, by a $\sim 20\,000$ year signal. These results then fully confirm the importance of the role of astronomical 'forcing' as the initial cause of the Quaternary glacial–interglacial cycles [16–18].

4. ISOTOPIC CLIMATIC RECORDS FROM DEEP SEA SEDIMENTS

The Vostok temperature record described in the previous section, which is the longest ice core record currently available, covers only the last of the multiple glacial–interglacial cycles which occurred during the Quaternary era (the last 1.7 million years) and it will take several years at least before the deepest ice cores, covering the last two or three full glacial–interglacial cycles, become available.

The natural variability in the climate of our planet during the whole Quaternary era has, however, been well documented through the investigation of the remains of the calcareous shells of planktonic Foraminifera (tiny protozoans) in deep ocean sediment cores. These studies, which are comprehensively described in several reviews to which the reader is referred (see, for instance, Ref. [19]), provide evidence that the Quaternary era was characterized by a succession of glacial and interglacial periods corresponding to the growth and decay of large ice sheets in the high latitude continental regions of the Northern Hemisphere, and to large variations in the sea level. The ice trapped in these large ice sheets was isotopically depleted with, as a result, a slight increase (slightly more than 1‰ in $\delta^{18}\text{O}$) in the proportion of light isotopes in sea water, which can be reconstructed through the investigation of oxygen or hydrogen isotopes in Foraminifera calcareous shells found in dated deep ocean sediment cores. Although the isotopic composition of these shells is temperature dependent, the records obtained provide a unique time series of the changes in the global continental ice volume and sea level. This is illustrated in Fig. 5 for the past 300 000 years [15].

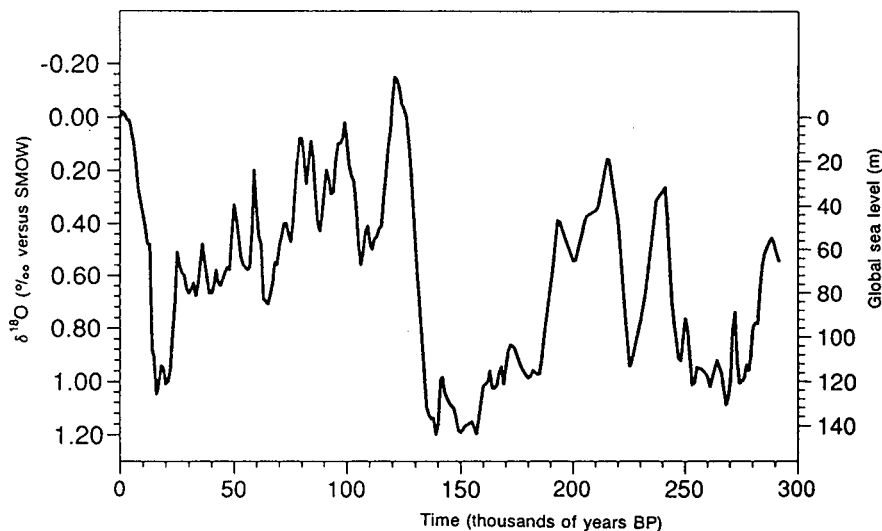


FIG. 5. Changes in $\delta^{18}O$ in a typical deep ocean sediment core (core RC 11-120 from the southwestern subpolar Indian Ocean) over the past 300 000 years (from Ref. [15]). The additional vertical scale given at the right of the figure corresponds to the estimated sea level changes (SMOW: standard mean ocean water).

These deep ocean sediment studies have convincingly demonstrated that there is a conclusive link between this succession of glacial and interglacial periods and variations in the parameters of the Earth's orbit [16]. Periodicities characteristic both of the obliquity ($\sim 41\,000$ years) and of the precession of the equinoxes (23 000 and 19 000 years), the most important orbital parameters as they strongly affect the distribution of available energy between latitude and seasons [17], are clearly observed in these records. However, the most striking feature shown in Fig. 5 is the existence of a strong $\sim 100\,000$ year cycle which is not easy to explain in the context of this orbital theory, despite further developments, including the non-linear response of the ice sheets to orbital forcing [18, 20, 21]. It is also difficult to understand how a relatively weak orbital forcing, when taken on an annual basis ($\sim 0.7\text{ W/m}^2$) can induce a globally averaged annual temperature change of $4\text{--}5^\circ\text{C}$ characteristic of glacial to interglacial shifts and how the main glaciations can be synchronized and be of similar amplitude in both hemispheres.

5. PAST NATURAL CHANGES IN THE COMPOSITION OF THE ATMOSPHERE DURING THE LAST CLIMATIC CYCLE

A unique characteristic of Antarctic and Greenland snow and ice cores is that in addition to the isotopic climatic record, they also provide a wealth of information

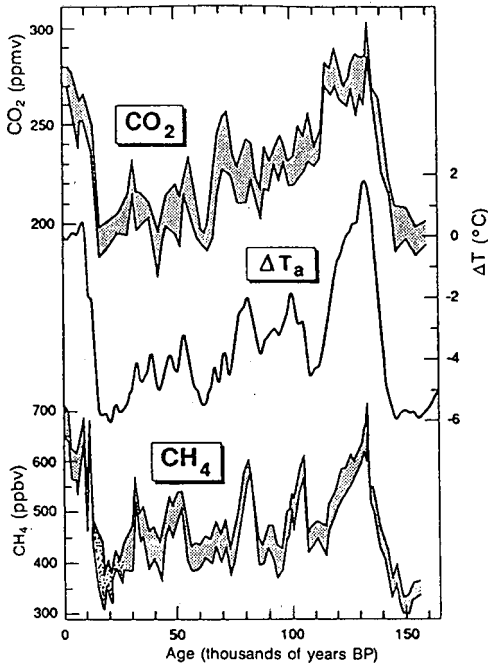


FIG. 6. Changes in the atmospheric concentrations of CO_2 and CH_4 as reconstructed through the analysis of the air bubbles entrapped in the Vostok deep Antarctic ice core (adapted from Refs [22, 23]). The shaded areas correspond to the estimated uncertainties. Also shown are the smoothed atmospheric temperature changes (above the inversion level) (from Ref. [12]) (1 billion = 10^9).

on past changes in the composition of the atmosphere, especially for trace gases and for primary and secondary aerosols of various origins.

5.1. Greenhouse gases

Of particular interest are trace gases, especially greenhouse gases. When deposited snow turns into ice, atmospheric air is entrapped as bubbles. It is possible, by extracting the air enclosed in these bubbles and analysing it for various gases, to obtain a record of the past evolution of these gases in the global atmosphere of our planet. As an illustration, Fig. 6 shows the past variations in the atmospheric concentrations of two key greenhouse gases, CO_2 and CH_4 , during the past 160 000 years, as obtained from the analysis of various sections of the Vostok Antarctic ice core [22, 23]. Both CO_2 and CH_4 concentrations are found to have varied strongly during the last climatic cycle, in close correlation with the climate: concentrations were high during the interglacial periods (around 270–280 ppmv for

CO₂ and 600–700 ppbv for CH₄),¹ and to a lesser extent during the relatively warm interstadials of the last ice age; on the other hand, they were much lower (around 190–200 ppmv for CO₂ and 350–400 ppbv for CH₄) during the coldest stages of the last ice age and of the end of the next to last ice age [22, 23]. The recent discovery of this strong correlation between the atmospheric concentrations of CO₂ and CH₄ and the climate has now led to the idea that CO₂ [20, 24, 25] and CH₄ [23, 26] changes have played a significant role in glacial–interglacial climatic changes by amplifying, together with the growth and decay of the Northern Hemisphere ice sheets, the relatively weak global orbital forcing, and by making a link between the climates of the Northern and Southern Hemispheres. In terms of radiative forcing, such changes in the concentrations of greenhouse gases are important because of the logarithmic increase with concentration. Between glacial and interglacial conditions, this gives an increase in the available energy by about 2 W/m².

These long records have allowed the evaluation, or at least reasonable bracketing, of the climatic role of greenhouse gas radiative forcing in the past [27]. The approach involves performing a multivariate analysis between the Vostok Station temperature record and various climatic inputs. The contribution of greenhouse gases to the Vostok temperature change can be bracketed between a lower estimate of 40% and a higher estimate of 65%. Within the limits of this analysis, 50 ± 10% is a reasonable estimate for the overall contribution of greenhouse gases to the Vostok Station temperature change over the last climatic cycle.

5.2. Crustal and marine aerosols

Figure 7 shows past changes in the atmospheric concentrations of aluminium and sodium during the last climatic cycle, as shown by the analysis of these two elements in various sections of the Vostok Antarctic ice core [28, 29]. Aluminium is a good tracer of windblown rock and soil dust (crustal aerosols), while Na is a good tracer of wind blown sea salt spray (marine aerosols). Aluminium concentrations are documented to have varied by up to two orders of magnitude during the past 160 000 years, with in particular three major peaks during the cold climatic stages B (LGM), D and H (Fig. 7). These peaks are explained by an increase in the strength of the sources of crustal aerosols during these cold periods (increase in the surfaces of arid areas, higher wind speed over continents) and in the efficiency of atmospheric transport from mid-latitude sources to polar areas [28–30]. In addition to these peaks, the Al profile shown in Fig. 7 suggests that there has been a continuous increase in background concentrations from stages F to B. This last increase is attributed to the progressive emergence of large parts of the continental shelves, especially in South America, due to sea level lowering. For Na, the amplitude of

¹ 1 billion = 10⁹.

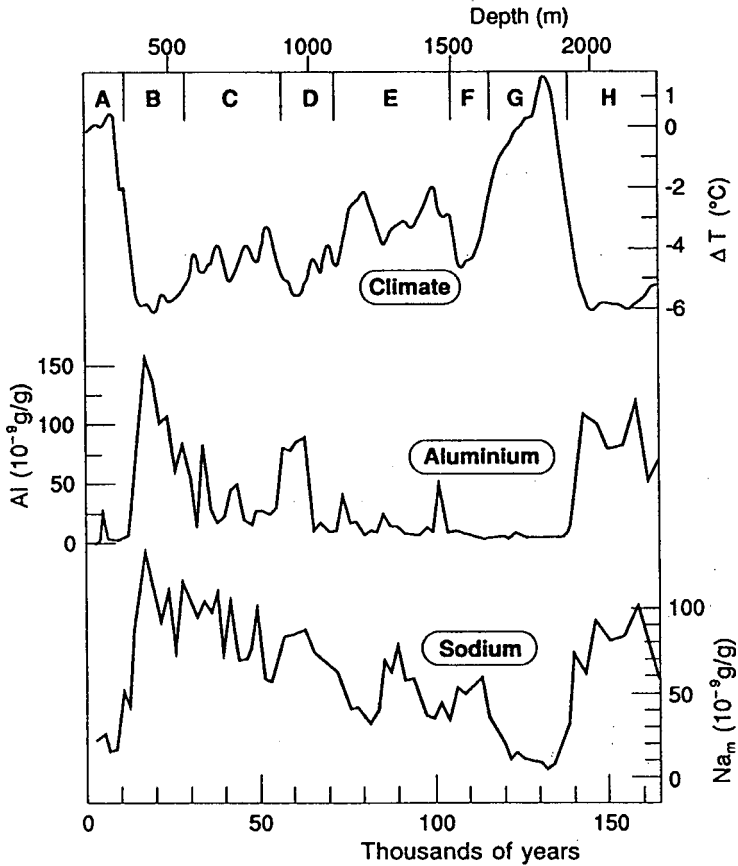


FIG. 7. Changes in Al and Na concentrations in Antarctic ice during the last 160 000 years as seen in the Vostok ice core (Na concentrations have been corrected for the crustal contribution) (from Refs [28, 29]). Also shown at the top of the figure is the atmospheric temperature curve from Ref. [12] (m: marine).

variations is less pronounced than for Al (Fig. 7). The observed variations, however, clearly indicate that during cold periods, the atmospheric concentrations of ocean derived aerosols were significantly higher than during warmer periods. This is explained by an increase in the emission fluxes from the oceans because of higher wind speed and by stronger transport from source areas to Antarctica.

5.3. Heavy metals

Very large changes in the concentrations of various other elements during the last climatic cycle are also recorded in Antarctic and Greenland ice. This is

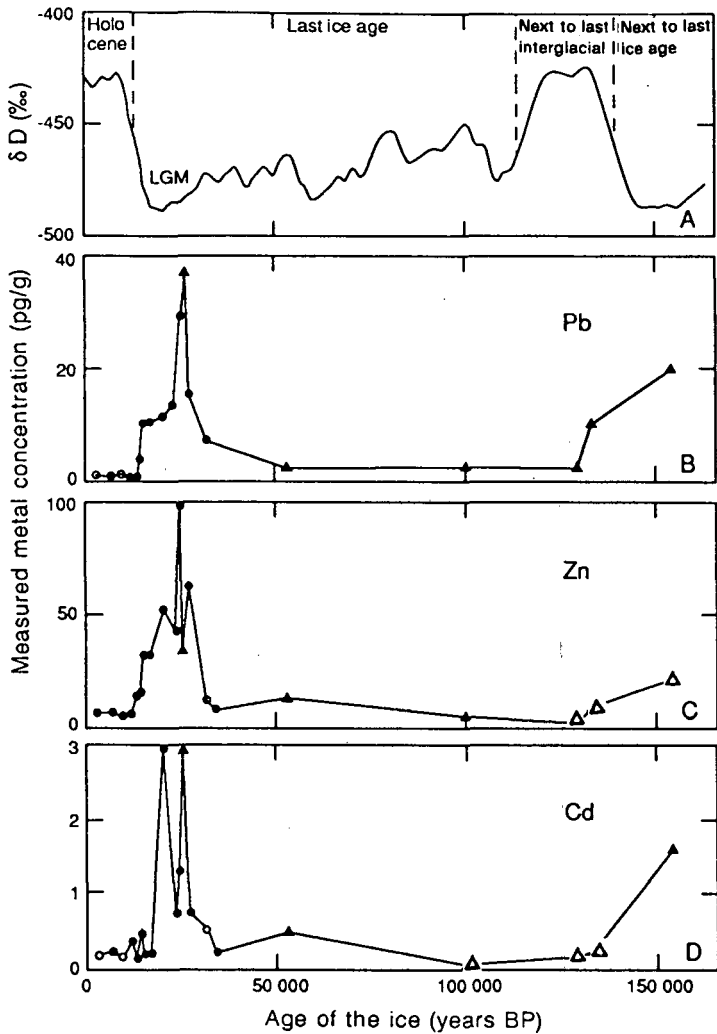


FIG. 8. Changes in Pb, Zn and Cd concentrations in Antarctic ice during the last climatic cycle as documented from the analysis of various sections of the Dome C (○, ●) and Vostok (▲) deep Antarctic ice cores (from Refs [31–34]). Also shown at the top of the figure is the δD curve from Ref. [9].

especially the case for heavy metals such as lead, cadmium and zinc. As illustrated in Fig. 8, the concentrations of these metals were much higher in Antarctic ice during the coldest climatic stages than during interglacial periods [31–34]. These variations in heavy metal concentrations during the last climatic cycle were due mainly to changes in soil and rock dust fluxes: this crustal contribution is found to account for virtually one hundred per cent of the observed Pb, Zn and Cd during the LGM and

the end of the next to last ice age [31–34]. The other natural contributions (volcanic emissions, wild forest fires, continental and oceanic biogenic activities) were significant only during warmer periods, when the crustal contribution was much lower. These results have allowed clear determination for the first time of what were the natural pre-man atmospheric cycles of these metals, thereby providing a firm reference basis against which to evaluate modern time trends linked with human activities.

6. RECENT CHANGES INDUCED BY MAN IN THE COMPOSITION OF THE ATMOSPHERE

Of particular interest are the snow and ice layers deposited in Antarctica and Greenland during the past few centuries, especially since the Industrial Revolution. These layers, which can generally be dated with great precision, permit the collection of a well documented record of the increase in large scale atmospheric pollution in both hemispheres.

6.1. Trace gases

For trace gases which are mixed homogeneously in the atmosphere, the growing impact of human activities is clearly documented both in Greenland and in Antarctica. For CO₂, ice core data have confirmed that there has been a marked increase in atmospheric concentrations from pre-industrial concentrations of about 280 ppmv in the 18th century to about 320 ppmv in the early 1960s [35] (when reliable direct atmospheric measurements became available). This increase is attributed mainly to the combustion of increasing quantities of fossil fuels.

For CH₄ also, ice core measurements have provided the only available data on trends in atmospheric concentrations of this greenhouse gas. They indicate that the concentrations were about 700 ppbv 200 years ago [36, 37], while present day atmospheric values are over 1600 ppbv.

6.2. Sulphur and nitrogen compounds

These are species with rather short atmospheric residence times which are mainly emitted into the atmosphere by human activities in the mid-latitudes of the Northern Hemisphere. This explains why mean sulphate and nitrate concentrations in Antarctic ice and snow are found not to have significantly increased during the past few centuries. In Greenland, on the other hand, there is a marked increase (about three to fourfold for sulphate and twofold for nitrates) [38, 39], which agrees well with the well documented increase in emissions from the use of fossil fuels and from various industrial processes.

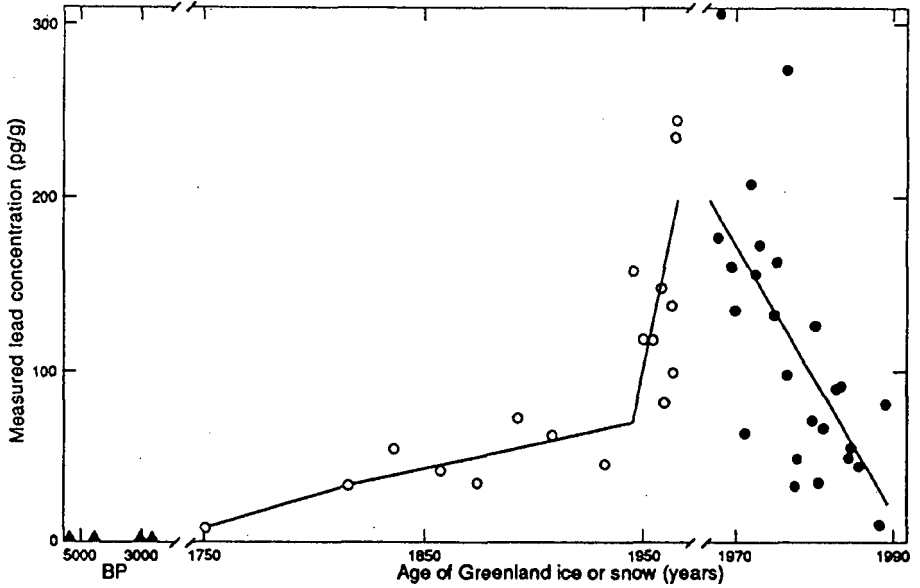


FIG. 9. Changes in Pb concentrations in Greenland ice and snow from several thousand years ago to the present (○: Ref. [40]; ●: Ref. [41]; ▲: Ref. [42]).

6.3. Heavy metals

Most available data are for lead, a highly toxic metal which has been introduced extensively into the environment since the 1930s by human activities, especially by the use of Pb-alkyl additives in gasoline. As shown in Fig. 9 [40-42], Pb concentrations in Greenland ice and snow increased by more than two orders of magnitude from several thousand years ago to the mid-1960s [40] (during the same time period, a clear increase by about one order of magnitude was also observed in Antarctica, which is evidence that this large scale pollution of the atmosphere by Pb has reached even the most remote areas of our planet). However, from the late 1960s to the present, a significant decrease by about 7.5 times has been observed (Fig. 9) Ref. [41]) — clearly the consequence of the rapid fall in the use of Pb-alkyl additives in gasoline during the past two decades, especially in North America, Japan and Europe (i.e. the increasing use of unleaded gasoline and decreasing concentrations of Pb-alkyl additives in leaded gasoline). Over these past twenty years, a significant, although less pronounced, decrease has also been observed in Greenland for Cd and Zn [41], which is attributed to the increasing efforts made in various countries in the Northern Hemisphere to reduce industrial emissions of Cd and Zn (and of other metals and pollutants).

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