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Antarctic and Greenland Snow and Ice Cores: Archives of the Climate and Pollution of the Atmosphere of the Earth

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ABSTRACT. Antarctic and Greenland snow and ice cores have added immensely to our understanding of the history of the climate of our planet and the influence of man activities on its atmosphere. After describing rapidly the procedures which are used to collect, date and analyse these cores, we present here briefly some of the most exciting results obtained so far: the 420 000 year Vostok record of isotopic atmospheric temperature and greenhouse gases; the early pollution of the atmosphere of the Northern Hemisphere for Pb and Cu two millennia ago during Greek and Roman times; and the Greenland snow evidence of a recent hemispheric scale pollution of the atmosphere for Pt and Rh linked with the ever-increasing use of automobile catalytic converters.

Key Words: Antarctica, Greenland, ice, snow, climate, pollution

Introduction

During the last four decades, considerable effort has been devoted by various laboratories to decipher the unique atmospheric archives stored in the successive dated snow and ice layers deposited from several hundred thousand years ago to present in the large Antarctic and Greenland ice caps. They have provided a wealth of fascinating information on past and recent changes in the atmospheric environment of our planet.

In this brief review, we shall first rapidly describe the procedures used to obtain the snow and ice samples in the field, the methods developed for dating them, and the techniques used in the laboratory for the analyses. We shall then present some of the most interesting results which have been recently obtained.

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Experimental Aspects

Field sampling

The longest ice core which has been obtained so far is the 5G Vostok ice core, which reached the world depth record of 3623 m in January 1998. It was obtained within a joint Russian-French-American drilling effort at Vostok Station (78°28'S, 106°48'E), a high altitude (3490 m a.s.l.) site in East Antarctica (Petit *et al.* 1997, 1999, Fig. 1). It is the apotheosis of several decades of drilling activities at this very interesting site which allowed to obtain a series of ice cores using thermal or/and electro mechanical drills in fluid-filled holes. It covers more than S00 000 years.

The depth of the bedrock at Vostok is about 4000 m, but ice drilling had to be stopped well above the bedrock because of the presence of a large size subice fresh water lake between the bedrock and the bottom of the ice itself (Kapitza *et al.* 1996).

For Greenland, the longest ice cores obtained so far are the two sister cores which were recently

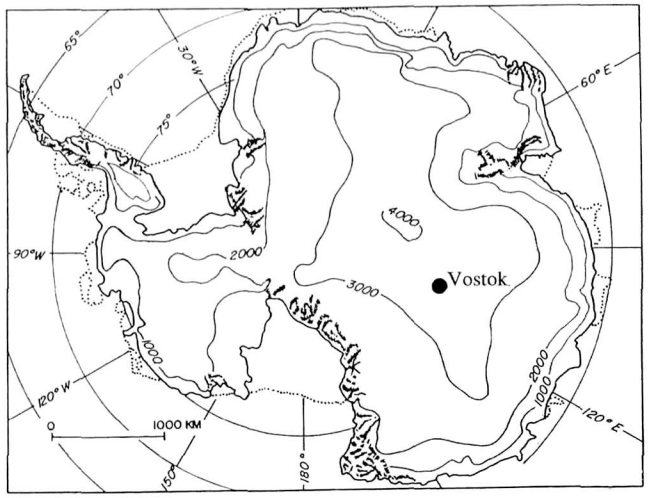

Fig. 1. Sketch map of Antarctica showing the Vostok station where the longest Antarctic ice core was obtained.

drilled down to the bedrock in the Summit (72°34′N, 37°37′W) area (Fig. 2) in central Greenland as part of the European GRIP programme and the United States GISP 2 programme. The GRIP ice core is 3028 m long (Dansgaard *et al.* 1993). The GISP 2 one is 3054 m long (Grootes *et al.* 1993). Both cores cover more than 200 000 years.

Great engineering skill is necessary for such deep drilling operations which remain very risky, as illustrated by the recent failure of several deep drilling efforts both in Antarctica and Greenland.

It is not always necessary to reach such great depths, for instance when investigating the impact of human activities. For such studies on recent periods, samples can usually be obtained either by shallow drilling (see for instance Boutron *et al.* 1991 or Candelone *et al.* 1995) or from the walls of pits, trenches or shafts (see, for instance, Murozumi *et al.* 1969; Borbante *et al.* 1997; Wolff and Suttie 1994).

Ice and snow dating

This is a crucial matter, since Antarctic and Greenland ice or snow samples have no scientific value if no good quality dating is available. Various complementary approaches are generally used, as discussed in some detail for instance in Boutron (1995). One approach relies upon the counting of the successive annual layers through the determination of physical or chemical parameters with pronounced seasonal variations (Hammer 1989).

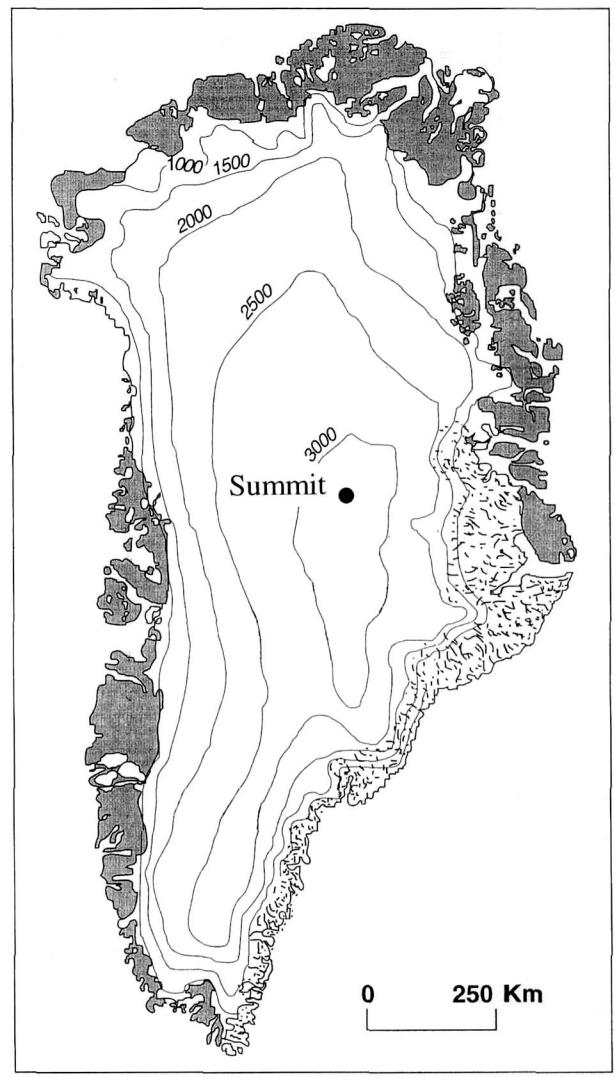

Fig. 2. Sketch map of Greenland showing the Summit site where the longest Greenland ice cores were drilled.

Another approach for recent snow or ice relies upon the identification of reference horizons linked with well documented events such as major volcanic eruptions or atmospheric nuclear tests. Finally, the dating of very old ice is mainly based on ice-flow modeling (Reeh 1989).

The precision of the ages so obtained depends upon various parameters. It is generally excellent for the Holocene : just to give an example, the precision is ±10 years for Summit ice dated on 4018 years ago (depth: 802 m). It becomes much less precise for very old ice, especially when getting close to the bedrock.

Preparation of the snow or ice samples for analysis

The samples obtained as cores are always more or

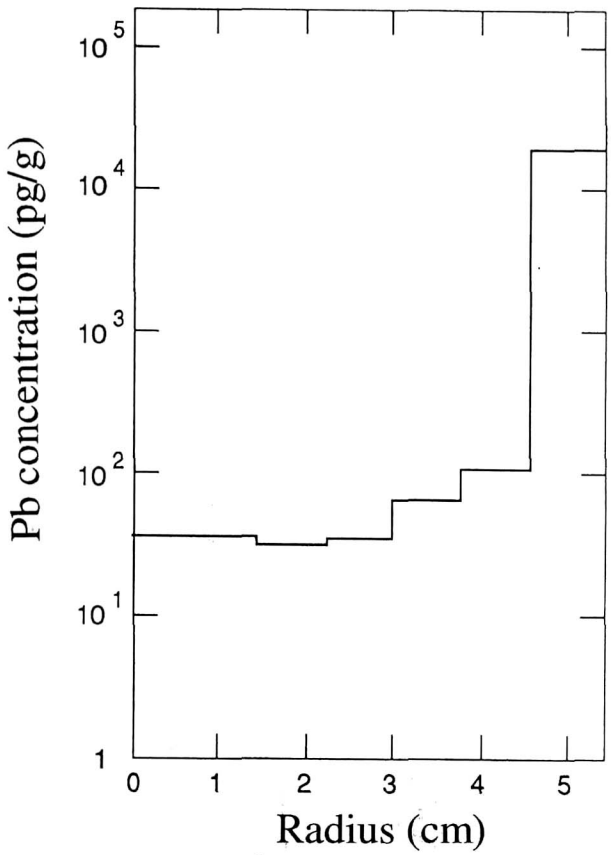

Fig. 3. Changes in Pb concentrations from the outside to the centre of a 498.9-499.2 m ice core section thermally drilled in a fluid filled hole at Vostok, East Antarctica. Adapted from Boutron *et al.* (1987).

less contaminated on their outside during drilling operations. This is especially the case for deep ice cores obtained in fluid-filled holes : the concentrations of elements such as Zn in the outside veneer layers of the core sections can easily be higher by several orders of magnitude than the original concentrations in the ice. Before analysis, it is therefore often mandatory to decontaminate the core sections in order to get the most central uncontaminated part of the core. One technique which has been successfully used involves mechanically chiselling successive veneers of snow or ice in progression from the outside toward the centre of the core section, the core being held in a lathe (Candelone *et al.* 1994).

It is essential to be able to check that the inner part of the core so obtained is free of contamination. This can be done by investigating changes in the concentrations of each investigated element or species from the outside toward the centre of the core (Ng and Patterson 1981). It is only if a clear plateau of concentrations is obtained in the central parts of the core that the concentration measured in these central parts do represent the original snow or ice, Fig. 3.

Such decontamination step is often not required for shallow samples since they can be obtained using clean field procedures. This is especially the case for samples collected from the walls of pits hand dug by operators wearing clean room clothing, using ultraclean bottles or tubes (see, for instance, Barbante *et al.* 1997).

Analysis

A large variety of analytical techniques are used for the analysis of these very valuable samples. They include Stable Isotope Mass Spectrometry for the determination of O and H isotopes (Stievenard *et al.* 1994), Gas Chromatography for the determination of CO_2, CH_4, N_2O and CO (Chappellaz *et al.* 1994), Ion Chromatography (Legrand *et al.* 1993), Graphite Furnace Atomic Absorption Spectrometry (Hong *et al.* 1996a), Thermal Ionization Mass Spectrometry (Chisholm *et al.* 1995), Laser Excited Atomic Fluorescence Spectrometry (Bolshov *et al.* 1997) and Double Focusing Inductively Coupled Plasma Mass Spectrometry (Barbante *et al.* 1997).

Many elements or species are present at extremely low concentrations in Antarctic and Greenland snow and ice. Just to give an example, Rh concentration in Greenland snow dated from the 1970's is as low as~0.03 pg/g (1 pg = 10^{-12} g). Of prime importance for the reliable determination of such minute concentrations is the use of specially designed clean laboratories (Boutron 1990). All containers in direct contact with the samples must be made from carefully selected materials and cleaned using sophisticated cleaning procedures (Boutron 1990). Also, it is essential to be able to quantitatively determine the procedural blanks for each investigated element or species (see, for instance, Chisholm *et al.* 1995).

Some Recent Results

Analyses of polar ice cores have provided a wealth

of fascinating results during the recent decades, especially regarding global climate change and large scale atmospheric pollution. We shall very briefly present here only a few examples of some of the most recent ones.

The 420 000 year Vostok record of the deuterium content of ice and isotopic atmospheric temperature

Oxygen and hydrogen isotopes are amongst the key parameters which have been investigated in Antarctic and Greenland ice cores since the 1960s. They are indeed a unique tool for reconstructing changes in atmospheric temperature during the successive glacial and interglacial periods.

The longest stable isotope time series presently available from polar ice cores is that recently obtained from the analysis of the 3623 m 5G Vostok ice core (Petit *et al.* 1997, 1999). Figure 4 shows the Vostok deuterium profile down to 3310 m, i.e. back to 420 000 years before present. The profile shows large changes in δD values in Antarctic ice during the past 420 000 years, with a succession of warm (interglacial) and cold (glacial) periods. Figure 5 shows changes in atmospheric temperature inferred from the deuterium profile. The overall amplitude of the glacial — interglacial temperature change is ~8°C (temperature above the inversion level).

The Vostok ice core covers four complete glacial-to-interglacial climate cycles. It shows that the climate has been in a continuous state of change during the last 420 000 years, but the observed changes have been remarkably repetitive in sequence. The four transitions from glacial to warm epochs started at ~335 000, 245 000, 135 000 and 18 000 years before present, Figure 5. Time series analysis of the record shows a large~100 000 year contribution to periodicity, along with another at ~40 000 years intervals. It gives further evidence that the astronomical forcing, linked with periodical changes in the Earth orbital parameters (eccentricity, obliquity and precession of axis), is probably the initial cause of late Quaternary glacial-interglacial cycles.

The 420 000 year Vostok record of greenhouse gases

Of special interest is the interplay between greenhouse gases, especially CO_2 and CH_4, and climate. As illustrated in Figure 5, CO_2 concentrations have been naturally fluctuating during the past 420 000 years, with low concentrations down to ~180 ppmv during the coldest stages of the glacial periods and higher concentrations up to ~ 280-300 ppmv during the warm interglacial periods (Petit *et al.* 1999).

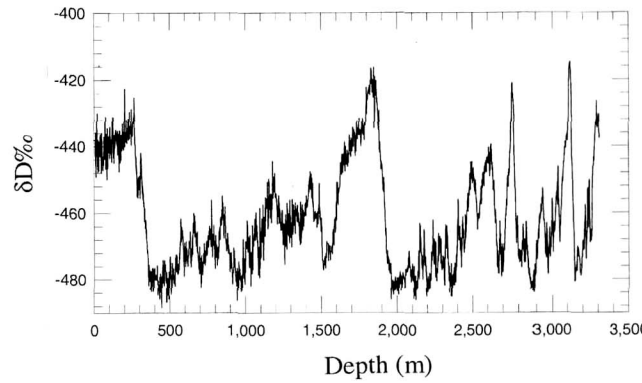

Fig. 4. Vostok, East Antarctica: changes in deuterium content, expressed as δD‰, as a function of depth down to 3310 m. Adapted from Petit *et al.* (1999).

All four climatic transitions from glacial to interglacial periods (around ~ 335 000, 245 000, 135 000 and 18 000 years ago) have been accompanied by an increase in atmospheric CO_2 (see Fig. 5) and CH_4. On the whole, there is an excellent correlation between the CO_2 and CH_4 records and the isotopic temperatures. It suggests that CO_2 and CH_4 could have been important amplifiers of the orbital forcing along with other parameters such as relative humidity, surface albedo (changing ice cover and vegetation) and planetary albedo (changing cloud cover).

The causes and mechanisms of CO_2 and CH_4 increase during the four transitions are still not fully understood (see, for instance, Petit *et al.* 1999; Fischer *et al.* 1999; Broecker and Henderson 1998; Chappellaz *et al.* 1993). For CO_2, the Southern Ocean is likely to be the main agent in regulating atmospheric CO_2 (Broecker and Henderson 1998). Possible mechanisms include changes in CO_2 solubility, phytoplankton productivity and iron fertilization. For CH_4, the observed changes could be linked with variations in the extent and activity of continental sources, mainly wetlands in the tropics and in Northern mean latitudes (Chappellaz *et al.* 1993).

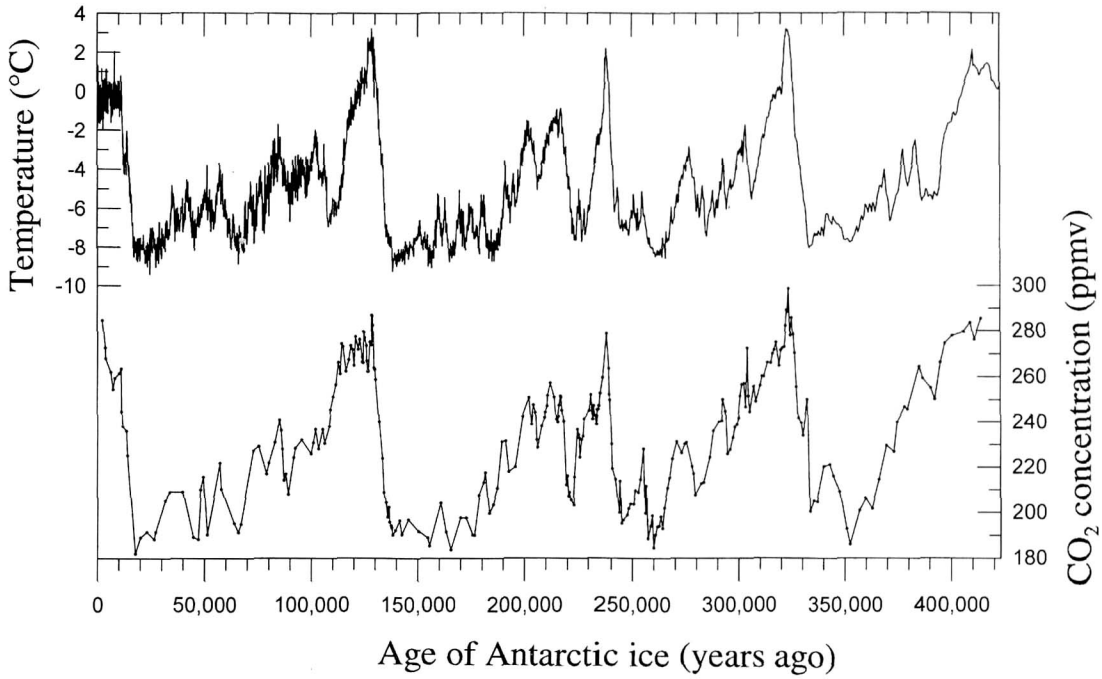

Fig. 5. Vostok, East Antarctica : changes in isotopic temperature of the atmosphere and CO_2 as a function of the age of the ice for the past 420 000 years. Adapted from Petit *et al.* (1999).

Early pollution two millennia ago for Pb and Cu as documented in the GRIP Greenland ice core

The first clear evidence of an early large scale pollution of the atmosphere of the Northern Hemisphere for Pb and Cu have recently been obtained from the analysis of these two metals in various sections of the 3028 GRIP ice core drilled at Summit (see Fig. 2) in central Greenland (Hong *et al.* 1994, 1996b; Rosman *et al.* 1997).

Figure 6 shows changes in Pb concentrations in Greenland ice from 7760 to 470 years ago (Hong *et al.* 1994). The most prominent feature of the data is that Pb concentrations rose well above the natural background values during a ~ 1000 year period from ~500 BC to AD 300. In parallel, the $^{206}Pb/^{207}Pb$ isotopic ratio profile shows a clear dip (Rosman *et al.* 1997). It evidences an early large scale pollution of the atmosphere of the Northern Hemisphere for Pb two millennia ago, long before the Industrial Revolution. This pollution was linked with anthropogenic Pb emissions to the atmosphere from the large Pb-Ag production by Greeks and Romans. Isotopic systematics point to the mining districts in southwest and southeast Spain as the dominant sources of this lead, giving quantitative evidence of the importance of these mining districts to the Carthaginian and Roman civilizations (Rosman *et al.* 1997).

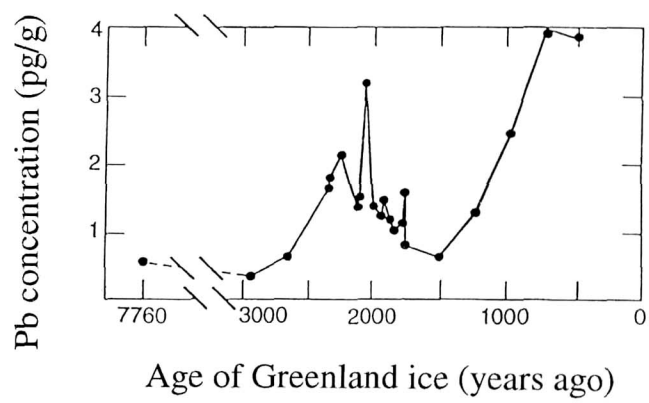

Fig. 6. Changes in Pb concentrations in Greenland ice from 3000 to 500 years ago. Also shown is a data point for ice 7760 years old. Adapted from Hong *et al.* (1994).

The GRIP ice core also allowed to evidence an early large scale Cu pollution of the Northern Hemisphere, beginning ~2500 years ago (Hong *et al.* 1996b). This is illustrated in Fig. 7, which shows changes in Cu fallout flux to central Greenland from eight millennia ago to present. This pollution was attributed to emissions from the crude, highly polluting smelting technologies used for Cu production

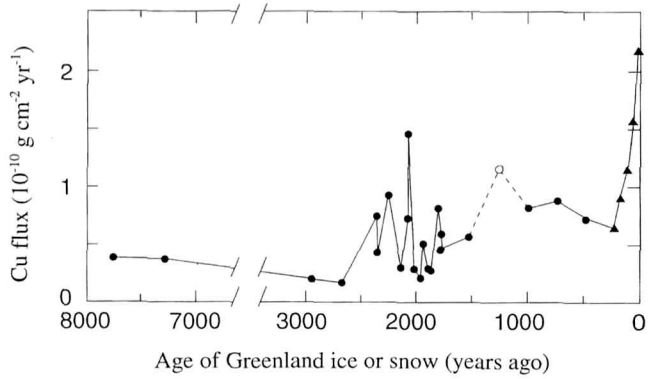

Fig. 7. Changes in the Cu fallout flux to central Greenland from eight millennia ago to present. Adapted from Hong *et al.* (1996 b).

during Roman and Medieval times, especially in Europe and China. It opens up the possibility of future quantitative studies of the history of metal production, which was a crucial factor in social and cultural development, during antiquity.

Greenland snow evidence of an hemispheric scale pollution for Pt and Rh during the last decades

The first data on the changing occurrence of Pt and Rh in Greenland ice and snow have recently been obtained by Barbante *et al.* (1999), Fig. 8.

Seven millennia ago, Pt and Rh concentrations were extremely low in Greenland ice, ~ 0.01 pg/g for Pt and 0.0007 pg/g for Rh. At that time, these two metals totally originated from natural sources such as extraterrestrial dust and volcanoes. In snow dated from 1969 to 1975, i.e. before the introduction of automobile catalytic converters, Pt and Rh concentrations were already respectively ~ 6 and 45 fold the natural level, indicating a large scale pollution of the atmosphere for these two metals at that time. Possible anthropogenic sources included Platinum Group Metals (PGMs) mining and smelting, especially in South Africa and Russia, and the chemical industry (where PGMs are used as catalysers for various purposes).

Much higher concentration values are observed for snow dated from 1994 and 1995. This recent increase is thought to be mainly linked with emissions from automobile catalytic converters, as confirmed by the fact the Pt/Rh ratio in the snow is very similar to the Pt/Rh ratio documented for

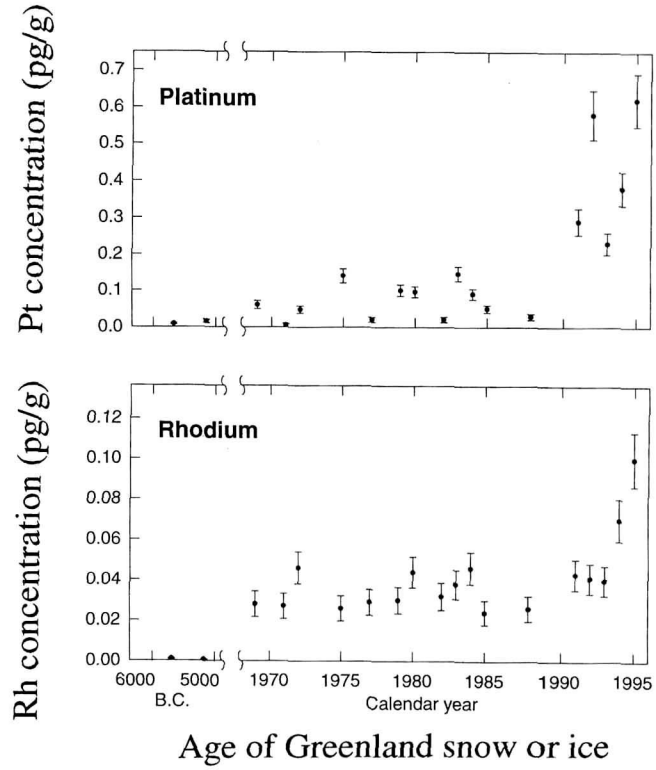

Fig. 8. Changes in Pt and Rh concentrations in Greenland snow from 1969 to 1995. Also shown are concentrations measured in ancient ice dated from five millennia BC. Adapted from Barbante *et al.* (1999).

exhausts from catalytic converters (Helmers and Mergel 1998). The fact that this pollution can be seen at a high altitude location of the remote Arctic indicates that it is certainly spread out all over the Northern Hemisphere. A major issue is then to evaluate possible related health effects and eventually to reconsider the present politically correct strategy of relying upon an ever increasing use of automobile catalytic converters to limit urban air pollution.

Conclusions

During the past few decades, Antarctic and Greenland snow and ice cores have added immensely to our knowledge of the history of the climate of our planet and man-induced pollution. The deciphering of these unique frozen atmospheric archives is however far from being achieved, and various exciting results will probably be obtained in the future.

Moreover, additional data of great importance will certainly be obtained from cold snow and ice cores from non polar areas. Such cores have indeed considerable potential to provide very interesting insights into past changes in climate and atmospheric pollution in mid latitude and tropical areas. This was recently illustrated for instance by the work of Thompson *et al.* (1998) on a Bolivian ice core or by the work of Van de Velde *et al.* (1998) on an Alpine ice core.

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