

# Ice core record of CO variations during the last two millennia: atmospheric implications and chemical interactions within the Greenland ice

By D. HAAN\* and D. RAYNAUD<sup>1</sup>, *Laboratoire de Glaciologie et de Géophysique de l'Environnement, 54 rue Molière, BP 96, 38402 Saint Martin d'Hères, France*

(Manuscript received 18 March 1997; in final form 2 February 1998)

## ABSTRACT

In order to study in detail the pre-industrial CO level during the last two millennia and its temporal variations, several ice cores from Greenland and Antarctica were analysed. Our Antarctic CO results remain very close to those observed previously for the last 150 years and suggest that carbon monoxide concentration did not change greatly over Antarctica during the last two millennia. Between 1600 and 1800 AD, CO concentrations obtained in the Greenland ice are also very close to those already reported for the 1800–1850 AD period. In contrast, the oldest part of the Greenland CO profile exhibits high CO levels (100–180 ppbv) characterised by a strong variability. This part of the Greenland record likely does not reflect the true atmospheric CO concentrations. We discuss the possible processes which could have altered the atmospheric CO signal either before or after its trapping in the ice. The oxidation of organic material in the oldest part of the investigated Greenland ice appears as the most likely explanation. Because there are strong similarities between the Greenland CO and CO<sub>2</sub> concentration profiles for the 1000–1600 AD period, mechanisms involved in both cases could be at least partly the same. Therefore, oxidation of organic materials is a serious candidate for in-situ CO<sub>2</sub> production in the Greenland ice. Due to the fact that the Antarctic ice contains much less impurities and show no peculiar variability in CO concentrations, we are more confident about the atmospheric significance of our Antarctic CO concentration profile.

## 1. Introduction

Carbon monoxide (CO) is one of the most important gaseous compounds of the tropospheric chemistry. This compound acts in a significant manner on both budgets of ozone and hydroxyl radicals (OH) and generally speaking on the global oxidative capacity of the atmosphere. CO is generated by various polluting sources and represents

a tracer of the anthropogenic activity. It is removed from the atmosphere almost exclusively by the OH radicals, and therefore constitutes an excellent tool for testing the capacity of the current atmospheric chemistry models to reproduce the evolution of the photochemical sink in the atmosphere. In this context, past atmospheric CO concentration data help to better understand past changes of the oxidative capacity of the atmosphere as well as natural CO sources.

The analysis of the air enclosed in polar ice cores provides important information about past changes of atmospheric trace gases (Raynaud et al., 1993). We recently developed an experi-

\* Current affiliation: Max Planck Institut for Chemistry, Air Chemistry Division, Postfach 3060, 55020 Mainz, Germany.

<sup>1</sup> Corresponding author.

mental procedure for extracting and measuring CO from polar ice cores. With this method and a careful selection of the samples, it is possible to keep the contamination below the detection limit and, for the first time, consistent results in terms of atmospheric CO concentrations were obtained (Haan et al., 1996). Thus, Greenland ice samples (Eurocore) show a significant increase of about 20 ppbv of CO concentrations during the period 1800–1950 AD. This increase is well correlated to anthropogenic CO source changes such as coal and petroleum consumptions. Nevertheless, CO concentrations corresponding to the beginning of the 19th century are higher than those calculated for pre-industrial simulations by the current atmospheric chemistry models. This could reflect active biomass burning events in the boreal regions during this period and/or the existence of anthropogenic CO sources (wood and waste combustions) already prior to the industrial revolution. In contrast, Antarctic ice samples (D47 ice core) covering the period 1860–1920 AD exhibit fairly constant CO levels which indicates that Antarctica remained mainly under the influence of natural CO sources during the first part of the industrial period.

In this paper, we present new results which support the atmospheric significance of the CO concentrations measured in the Antarctic ice and which indicate that the atmospheric signal may be distorted under certain conditions in the Greenland ice. Possible processes which could have altered the atmospheric CO signal either before or after its trapping in the ice are discussed.

## 2. Experimental procedure and sampling

For the present study, each ice sample has been analysed using the experimental procedure previously described in Haan et al. (1996). This method consists of melting and refreezing the ice in order to extract the air. The gas is then analysed by gas chromatography using a mercuric oxide reduction detector. A new set of blank tests, performed with standard gas added to artificial gas-free ice, confirmed that our CO extraction method does not induce any significant CO contamination providing that: (i) the extraction time is kept short (about 20 minutes); (ii) the surface samples are decontaminated in a clean air bench using a sterile sharp knife and vinyl gloves. Besides the extraction

method, there are several other potential sources of contamination that we discuss below.

First, we noticed that, like for methane (Chappellaz et al., 1990), visible micro-fractures in ice samples may systematically lead to higher CO levels than those generally obtained for unfractured ice samples. CO concentrations were also found to be reproducible only when good quality ice core samples, taken at the same depth level, were analysed. The results shown in this paper have been obtained on samples selected after a careful inspection of the ice in order to detect and avoid visible cracks. Another contamination problem arises when using ice cores recovered by drilling in a fluid. The latter is mostly composed of saturated and unsaturated hydrocarbons which are likely to generate CO through oxidation reactions (Haan, 1996). This is not the case for the present study which has only been performed on ice cores (Eurocore, BH3 and BH5) drilled without fluid.

We also performed a set of incubation tests where the air is first extracted from the ice and CO measured according to our usual procedure after which several freezing-refreezing cycles are repeated under different time sequences. The results (Fig. 1) indicate a significant CO production in the presence of the liquid phase whereas this does not appear below the freezing point. A similar behaviour (methane production in the presence of a liquid phase) has already been observed when extracting the gas for CH<sub>4</sub> measurements (Chappellaz, 1990). In the case of CO, the behaviour appears the same for all types of ice studied whether they are natural (Greenland, Antarctica) or artificial (gas-free ice). Furthermore, no significant difference was observed in the CO production rates whether the tests were performed with ice core air or with standard gas. An additional information is provided by the blank tests reported above (see Fig. 1): they indicate, despite of the large CO production observed, that our extraction procedure does not induce any significant contamination for CO measurements in polar ice cores as long as the time span during which the sample is in liquid phase is kept short (about 20 min). CO production mechanisms depicted in Fig. 1 still remain not well understood, mostly because of the very limited knowledge of the chemical composition of each type of ice studied. We may note that CO growth rates observed when the ice is melted again are each time very similar suggesting that

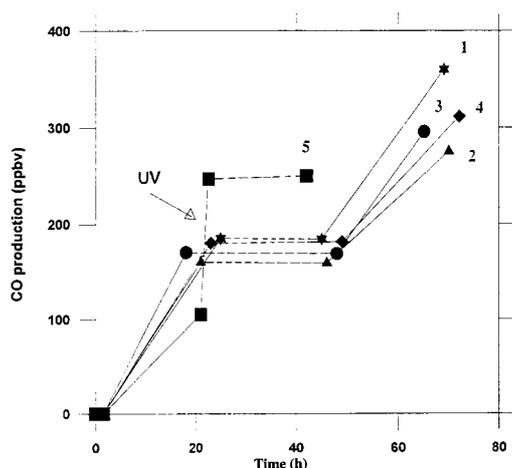


Fig. 1. CO production versus the time during which various types of ice samples were kept under vacuum and either in liquid phase at room temperature (full lines) or in solid phase at  $-20^{\circ}\text{C}$  (dashed lines). Curves 1, 2, 3, 4 respectively correspond to the following samples: Eurocore (104 m); Eurocore (211.35 m); Vostok BH3 (108.6 m) and artificial gas-free ice. Curve 5 corresponds to the same test as curve 2 except that the meltwater was irradiated by UV for 1 hour 30.

the mechanisms can be re-activated. Two types of processes may have been involved in these tests. First, a CO desorption from the inner wall of the glass cell can occur in presence of water vapor. Zumbunn et al. (1982) already observed such type of mechanisms for  $\text{CO}_2$ . If this would be the case for the CO analysis, it would explain why all the different ice samples exhibit the same behaviour and why the CO production is much smaller at low temperatures corresponding to a lower water vapor content. The second one could be a chemical CO production occurring in the liquid phase. The involved mechanisms seem to be at least partly photolytical. For one of the tests described above, the ice sample has been irradiated by UV radiations (360 nm). As shown in Fig. 1, reaction rates, in this case, are more important. CO productions in aqueous systems will be described more in details in Section 4.

In the following, we present an extension of the Antarctic and Greenland CO profiles recently reported in Haan et al. (1996). As the same calibration scale was used for both studies, this new set of CO measurements can also be directly compared with the previous one. 24 new samples

taken from the Eurocore ice core (Greenland) were analysed. The main characteristics of this core (length, gas dating ...) are summarised in Haan et al. (1996). In addition, 9 samples taken from the Vostok BH3 and BH5 ice cores (Antarctica) were studied as well. These two 180 meters long cores were drilled at the Vostok station and the same gas dating procedure as used for the deep Vostok 4G ice core has been adopted (Barnola et al., 1991). As mentioned above, the 3 cores analysed here were drilled without using drilling fluid and each sample was carefully chosen in order to avoid visible microcracking in the ice. Therefore, we consider that our sampling and analytical method did not induce any significant CO contamination for these ice samples.

### 3. Description and significance of the records

Carbon monoxide mixing ratios obtained from the Vostok BH3 and BH5 and the Eurocore ice cores are reported in Table 1 and plotted versus the mean gas age in Fig. 2, together with the previous results presented in Haan et al. (1996). CO levels observed on Antarctic ice exhibit no significant changes during the 300 BC–1400 AD period, showing an average value of  $50 \pm 4$  ppbv ( $2\sigma$ ). These results are very close to those obtained from the Antarctic D47 ice core for the 1860–1920 AD period (Fig. 2).

By contrast, two distinct periods can be observed in the Greenland CO concentration profile (Fig. 2). CO levels exhibit no significant change during the 1600–1800 AD period and remain very close, at about 90 ppbv, to those previously measured for the 1800–1850 AD period (Haan et al., 1996). For the 1000–1600 AD period (below 155 meters), CO levels are characterised by very high and variable values (in the 100–180 ppbv range).

There are several reasons why at least part of the Greenland Eurocore CO record between about 1000 and 1600 AD is not a pure atmospheric record:

First, as shown in Fig. 2, CO concentrations observed for the 1000–1600 AD period are generally much higher than those previously recorded for the industrial period (1800–1950 AD) and even higher than those observed more recently by direct atmospheric measurements performed at high northern latitudes (Corazza and Tesi, 1995; Novelli

Table 1. CO mixing ratios measured from Eurocore, BH3 and BH5 ice cores

Depth (m)	Gas age (year AD)	CO (ppbv)	Depth (m)	Gas age (year AD)	CO (ppbv)
<i>Eurocore</i>					
118.23	1778	89.6	187.03	1471	110.8
122.69	1756	93.6	191.38	1452	119.6
123.23	1754	91.9	211.35	1357	162.0
134.23	1710	90.3	212.43	1353	156.3
144.08	1671	91.6	227.73	1280	111.9
154.03	1625	92.4	232.03	1260	119.4
156.68	1612	128.6	232.08	1260	118.6
163.84	1579	87.9	242.36	1212	100.8
165.48	1571	124.3	259.68	1130	150.2
170.53	1546	119.5	259.73	1130	157.0
177.13	1515	130.2	269.48	1086	146.0
183.73	1486	127.6	269.53	1086	179.0
<i>Vostok</i>					
108.6	1375	52.1	132.0	323	48.7
112.0	1250	54.4	134.0	235	51.0
115.0	1093	49.7	142.0	−89	48.4
117.0	991	53.3	146.0	−237	51.0
128.0	523	48.1			

et al., 1992, 1994). It is unlikely that higher CO concentrations could exist pre-industrially, due to probably weaker and fewer sources in the northern hemisphere. Furthermore, a lower CO gradient between the high northern latitudes and Antarctica is expected for the pre-industrial period as compared with the present period. However, this does not appear in our new results: the difference, between the Greenland and Antarctic CO values corresponding approximately to the same age, ranges up to about 130 ppbv. Under present day conditions, the gradient between high northern latitudes and Antarctica is on average about 100 ppbv (Haan et al., 1996, and references therein).

Second, there are periods of large variability in the oldest part of the Greenland CO profile. Also, in this part, several samples taken at the same depth level were analysed twice and led to differences up to more than 30 ppbv which is higher than the CO increase observed in the Greenland ice for the whole 1800–1950 AD period.

#### 4. Possible processes able to affect the CO concentrations of the air bubbles

In this section, we investigate various processes able to have modified the original atmospheric

concentrations of CO recorded in the oldest part of the Eurocore ice.

As suggested by experiments described in Section 2, a significant CO contamination can occur when working on brittle ice. The Eurocore ice becoming more brittle below about 180 meter depth (J. Schwander, personal communication), ice samples were carefully selected by visual inspection. The consistence of data also obtained along the brittle part of the core in terms of atmospheric methane concentrations (Blunier et al., 1993) suggests that no contamination of air bubbles through cracks have occurred in this part of the core giving confidence for CO measurements as well.

Large amounts of CO were found in snow and supposed to be adsorbed on the surface of the snow crystals (Rasmussen et al., 1982). However, the snow samples were collected from a mid northern latitude site (Mount Hood, Oregon) and are not representative of a polar environment where physical properties of snow are different. Since this study, consistent results in terms of atmospheric CO record have been recently obtained by analysing CO concentrations in the air extracted from Greenland and Antarctic ice cores (Haan et al., 1996). It is likely that adsorbed CO on snow, if in significant amount, has been

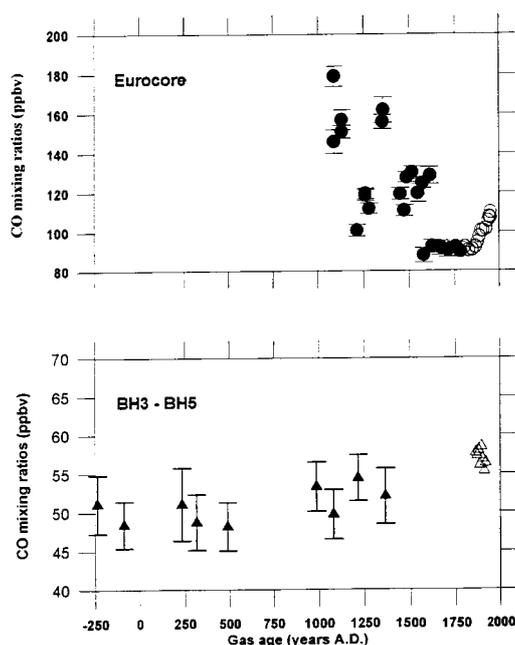


Fig. 2. CO mixing ratios versus the mean gas age. Full triangles correspond to BH3 and BH5 Vostok samples (Antarctica) and full circles to Eurocore ice core samples (Greenland). CO mixing ratios reported in Haan et al. (1996) are mentioned too: open triangles represent results observed in the D47 ice core (Antarctica) for the 1860–1920 AD period; open circles represent those obtained in the youngest part of the Eurocore ice core (1800–1950 AD). Error bars represent the 95% confidence interval.

hereafter lost through processes of sublimation and condensation of the ice grains occurring during the transformation of snow into ice. Furthermore, during this transformation, the specific surface of snow is dramatically reduced.

In melt layers, which are due to seasonal surface melting, large CO production (as suggested in Fig. 1) may occur. Nevertheless, the mean annual temperature at Summit is  $-32^{\circ}\text{C}$  and the occurrence of snow melting at the surface is very rare. Only one melt layer has been observed at 38 m depth in the Eurocore ice (Schwander et al., 1993).

The air becomes enclosed in ice bubbles below the surface of the ice sheet, when the porosity of the firn closes off from the atmosphere. At the Summit site, the complete air enclosure in the ice bubbles occurs at about 80 m depth (Schwander et al., 1993). Down to a depth of about 70 m, the

air is mixed by convective (in the uppermost part of the firn) or diffusive processes inside the open porosity of the firn. Thus any amount of CO, which would be produced through processes like seasonal melting or adsorption on snow grains, and then released to the firn open pores would be mixed within the surrounding air. It is, then, unlikely that CO produced in surface melt layers may significantly disturb the concentrations of CO in the firn. Inside the firn, a gravitational separation of heavier molecules also occurs with depth. The gravitational effect for CO can be neglected: at equilibrium it will tend to deplete by only 0.5 ppbv the CO mixing ratio in the air bubbles compared to the atmospheric one at the surface of the ice sheet.

All the preceding processes are not able to significantly modify the original atmospheric CO concentrations, apart from a smoothing effect of the high frequency atmospheric fluctuations due to the diffusion in the gas phase of the firn. Here, we discuss the possibility that chemical reactions are able to produce CO in ice layers (after bubbles close off). There are several examples showing that chemical reactions are able to slowly proceed within the ice. The reduction of  $\text{H}_2\text{O}_2$  by mineral dust and the subsequent decreasing concentrations with depth observed at Summit is a good example (Nefel et al., 1986; Sigg and Nefel, 1991). CO productions have already been reported from various aqueous systems (Conrad and Seiler, 1982; Redden and Gordon, 1982; Mopper and Stahovec, 1986; Mopper et al., 1991; Valentine and Zepp, 1993; Zuo and Jones, 1995) probably resulting from the photochemical degradation of dissolved organic matter (Zuo and Jones, 1996) or from the oxidation of hydrocarbons or carbonyls by hydroxyl radicals and peroxides (Zika, 1981). This would also be supported by our results from the incubation experiments (see Fig. 1, curve 5). Nevertheless, we cannot conclude that reaction occurring in aqueous phase are also taking place in cold ice.

On the other hand, investigations of organic material trapped in polar precipitations still remain very limited. Recent studies have dealt with short-chain organic species including light carboxylic acids (formate, acetate and oxalate) as well as formaldehyde. By studying present-day aerosols reaching Summit in summer, Clain (1995) found longer chain organic species dominated by

esters and a remarkable absence of long-chain aldehydes. The sudden occurrence of high CO concentrations at about 155 m depth (around the age 1600 AD) may suggest an unusual presence of organic species able to produce carbon monoxide, which were so far either absent or present within the ice in insufficient amount. An alternative explanation could be that the CO production inside the ice is time and/or pressure dependent. The only relevant records of organic species spanning continuously the last millennium in Greenland ice are the ones of formate, acetate and oxalate at Summit. Several studies (Legrand et al., 1992; Legrand and De Angelis, 1995, 1996) pointed out that the levels of these light carboxylic acids together with those of ammonium in the Greenland ice were sporadically enhanced during the past in relation to high-latitude biomass burning events reaching the Greenland ice cap. Recent studies (Legrand and De Angelis, 1996; Savarino, 1996) have shown that the frequency of these perturbations over the last millennium is related with the frequency of boreal forest fires. These events were more frequent in the Summit ice layers located between 26 and 57 m depth (i.e., 1830 to 1930 AD), 111 and 133 m depth (i.e. 1500 to 1600 AD), and 167 and 201 m depth (i.e., 1200 to 1350 AD). It was also shown that the ammonium formate perturbation detected in the Summit snow layers have been accompanied by enhanced concentrations of HCHO and H<sub>2</sub>O<sub>2</sub> (Fuhrer et al., 1993). Thus, the deep part of the Eurocore ice core (below about 165 m depth) is characterized by an higher content of organic acids, and the high CO levels observed in this part of the core could be due, at least partly, to an in-situ production of carbon monoxide from oxidation of organic material produced in biomass burning plumes.

The direct evidence of such an in-situ CO production requires a study of CO and its organic precursors in the same layers. Even if HCHO is the most plausible precursor, such a comparison (CO, HCHO) is not yet possible. In contrast with formate, no continuous HCHO record spanning the last millennium is available at the Summit site (Staffelbach et al., 1991). The HCHO perturbation observed in formate rich layers has diffused in neighbouring layers, likely through post-depositional processes. That complicates, up to now, any attempt to demonstrate the validity of an in-situ CO production by oxidation of organic

species related to biomass burning. We note that the events found at the depths ranging from 26 to 57 m occurred in the firn layers located above the close-off of the air bubbles and consequently cannot affect our CO record which starts below the close-off depth. On the other hand, the high frequency signal of boreal forest fires recorded between 111 and 133 m depth, which is weaker than in the 167–201 m interval, does not correspond to high CO concentrations. This points out to the need for extended studies of the speciation of the organic material contained in ice.

Finally, the presence of a rich HCHO surface snow layer which accompanied a biomass burning input over Greenland, and the subsequent possible photodissociation of this species in snow layers nearby the surface may also occur. However, again, such process taking place in the firn should not alter the concentrations of CO preserved in air bubbles.

Methane can as well be oxidized to CO. However, it seems unlikely that this reaction occurs in air bubbles in Greenland ice. As we mentioned before, the Eurocore CH<sub>4</sub> record exhibits consistent variations in terms of atmospheric signal (Blunier et al., 1993). Furthermore, no clear correlation is observed between the fluctuations of CH<sub>4</sub> and CO concentrations obtained from the deep part of the Eurocore ice core, nevertheless we note that different depth levels were analysed for CO and CH<sub>4</sub>.

Although our Greenland CO record does not clearly correlate with other existing proxy-records obtained in Greenland ice for organic compounds we cannot yet judge whether the oxidation of organic materials in the ice represents or not the main contribution to the high CO levels observed in the deep part of the Eurocore ice core. Indeed, we should keep in mind that only 10% of the total amount of organic compounds dissolved in ice have already been identified and even less if we take into account the gaseous organic compounds (M. Legrand, personal communication). To get additional information, we will compare in the next section the CO and CO<sub>2</sub> records.

## 5. Comparison of the CO and CO<sub>2</sub> Eurocore records

In two recent papers (Barnola et al., 1995; Anklin et al., 1995), the pre-industrial CO<sub>2</sub> levels

and their temporal variations have been compared for Greenland and Antarctic ice. The  $\text{CO}_2$  concentrations are systematically higher in the north than in the south ranging from 20 ppmv at the turn of this millennium to nearly zero around the 18th century. Such an inter-hemispheric  $\text{CO}_2$  gradient appears unrealistic, as a maximum difference of only 5 ppmv between Greenland and Antarctica can be reasonably explained in terms of carbon cycle for the time period investigated (Fig. 3b). Barnola et al. (1995) finally concluded that the oldest part of the  $\text{CO}_2$  Greenland record may have been contaminated whereas the Antarctic profile would represent a real atmospheric signal. Anklin et al. (1995) listed all the organic compounds already quantified in ice cores from both polar regions and showed that organic acids ( $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{C}_3\text{O}_4^-$ ), formaldehyde, carbonates (deduced from  $\text{Ca}^{2+}$  measurements) and black carbon are all present in higher amounts in Greenland ice than in Antarctic ice. The total potential in-situ produced  $\text{CO}_2$  was estimated for Greenland ice to be roughly one order of magnitude higher than for Antarctic ice.

The reaction between carbonates ( $\text{CO}_3^{2-}$ ) and acidity ( $\text{H}^+$ ) was discussed as being potentially one of the main  $\text{CO}_2$  production processes involved.

Although different depth levels of the Eurocore ice core were analysed for CO and  $\text{CO}_2$ , both profiles exhibit similar trends in the deep part of the core (Figs. 3a, b). This would suggest that both signals could have been at least partly contaminated by the same processes. As carbonates cannot be a source of CO, other mechanisms based on the oxidation of organic compounds should also be considered. In fact, this type of chemical reactions can lead to CO and  $\text{CO}_2$  together whether they are complete or not. According to the sporadic changes observed in the Greenland CO and  $\text{CO}_2$  concentrations, chemical enhancements in ice must be temporarily very variable.

From the comparison between the Greenland CO and  $\text{CO}_2$  records it also clearly appears that chemical reactions occurred within the deep part of the Eurocore ice core. The correlation between both records needs to be more investigated to be confirmed by analysing the same Eurocore samples for both gases. More studies on the speciation of the organic matter dissolved in polar ice core are also needed.

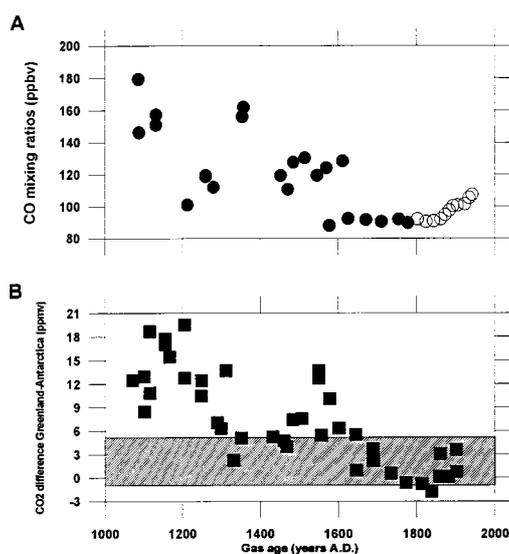


Fig. 3. (a) Greenland CO record already presented in Fig. 2; (b) Differences between  $\text{CO}_2$  results obtained from the Greenland (Eurocore, GRIP) and Antarctic ice cores (South Pole, D47, D57) as reported by Anklin et al. (1995). The hatched area indicates the range of  $\text{CO}_2$  differences which can be explained by the inter-hemispheric gradient.

## 6. Pre-industrial CO level variations over Antarctica

By contrast with the Greenland CO profile, high and scattered CO levels do not appear in our new Antarctic record (Fig. 2). Furthermore, the impurity content of the Antarctic ice is much lower than in Greenland ice, reducing significantly the risk that the CO Antarctic record could have been contaminated. Both facts suggest that this new set of CO measurements is likely to represent a real record of the atmospheric CO evolution covering the last two millennia at high southern latitudes. A further clue of the atmospheric significance of the Antarctic record is the 20 years overlapping of the  $\text{CO}_2$  record from Antarctic ice with the record from direct atmospheric measurements (Etheridge et al., 1996). Indeed, it confirms that the  $\text{CO}_2$  mixing ratio of the ice core air is representative of the atmosphere to within 1.2 ppmv and consequently is not significantly

affected by the low impurity content of the Antarctic ice.

However, since CO production processes can be active in the Greenland ice, small modifications of the CO concentrations within the Antarctic ice cannot be excluded. By assuming a production of CO in Greenland ice corresponding to CO concentrations up to about 100 ppbv (see Section 3) and taking into account impurity concentrations one order of magnitude lower in Antarctic ice than in Greenland ice, then a maximum CO production of 10 ppbv would be expected within the Antarctic ice. We note that such a small CO contamination is close to the accuracy of our CO measurements.

Haan et al. (1996) published the first record of past CO level variations over Antarctica during the 1840–1920 AD period. The results indicate that carbon monoxide concentrations did not change significantly during this period at high southern latitudes. From the comparison between these results and those obtained from recent atmospheric CO measurements, it also appears that this high stability persisted throughout the 20th century despite, for example, of the observed methane increase which may have slightly enhanced the CO concentrations by about 10 ppbv (Haan et al., 1996). Such a small change still remains difficult to discern above the analytical precision. Furthermore, as concluded by Haan et al. (1996), this stability will need more investigations to be substantiated like CO measurements in firn air and atmospheric measurements using the same calibration scale as the ice core measurements.

Our new results obtained from the Vostok BH3 and BH5 ice cores provide an extension of the previous Antarctic record to the last two millennia. Although the CO concentrations obtained are by 5 to 10 ppbv lower than those observed in the D47 ice core (Haan et al., 1996), this difference is not significant. It suggests that CO concentration remained fairly constant during the whole period investigated, and that CO source and sink strengths may have remained fairly stable during this period in Antarctica. Oxidation of methane and nonmethane hydrocarbons (NMHCs) and CO emissions from oceans are considered as the main CO sources at high southern latitudes. Ice core measurements indicate that pre-industrial CH<sub>4</sub> concentrations over Antarctica increased on average by about 600–700 ppbv during the last two millennia (Chappellaz et al., in press). By

using a 2-D model of atmospheric chemistry (Martinerie et al., 1995; Haan et al., 1996), it is found that a methane increase of about 100 ppbv under pre-industrial conditions would not lead to more than a 2 ppbv growth for CO (P. Martinerie, personal communication). This is consistent with our results. Furthermore, as the Holocene is, on a global average, a stable climatic period, we can assume that the other CO sources mentioned above did not change significantly as well. The stability of CO levels revealed by our new Antarctic ice core measurements also suggests that the transport of CO originating from lower latitudes towards Antarctica did not significantly influence the tropospheric CO mixing ratios at high southern latitudes during the last two millennia.

## 7. Conclusions

CO concentrations observed in the deep part of the Greenland Eurocore ice core (below approximately 155 m depth which corresponds to air trapped in the ice around 1600 AD) appears to be too high and too scattered to be interpreted in terms of atmospheric CO variations. The different experimental tests presented in this paper indicate that precautions should be taken to avoid various contamination sources which may occur during the recovery of the ice cores or in the course of the gas extraction. In the case of the Eurocore CO results, all these conditions were generally fulfilled. We thus have to consider a CO production either within the Greenland ice sheet or during the ice storage after the core recovery, in relation with other impurities contained in this ice. Oxidation and photodissociation of organic compounds initially enclosed in the ice are considered. Oxidation processes of organic matter remain the most likely mechanism.

The Greenland CO<sub>2</sub> record (in particular at Eurocore) shows a very similar pattern: anomalous enhancement and scattering of the concentrations starting approximately at the same depth level. Decomposition of carbonates have been advocated as a likely explanation (Delmas, 1993), but oxidation of organic compounds cannot be ruled out. The apparent correlation between the CO<sub>2</sub> and CO anomalies supports the potential influence of the oxidation of organic compounds. However,

involved chemical compounds remain very difficult to identify and more information are needed about the chemical composition of the Greenland ice.

As for CO<sub>2</sub>, the very stable CO concentrations measured in the air trapped after 1600 AD in the Greenland ice are likely to reflect changes in atmospheric composition. The same remark applies for the Antarctic CO data presented here, which indicates that carbon monoxide concentrations of the low troposphere over central Antarctica did not change greatly during the last two millennia. The atmospheric significance of the Antarctic record may well be due to its much lower content in impurities compared to the Greenland ice. Nevertheless, we cannot rule out a background CO production due to this low level of impurities, which we estimate to be less than 10 ppbv.

## 8. Acknowledgements

This work was supported by the French program on Atmospheric Phase of Biogeochemical Cycles (PACB) and Fondation de France. The drilling of the Eurocore was supported by E.E.C. We thank J. R. Petit who provided us the Vostok BH3 and BH5 ice samples and the main characteristics of these ice cores, P. Martinerie for sensitivity runs using the 2-D model of atmospheric chemistry and C. Mullet-Marquis who carried out part of the incubation experiments described in Fig. 1. We are very grateful to J. M. Barnola, C. A. M. Brenninkmeijer, J. Chappellaz, R. Delmas, R. Francey, M. Legrand, P. Martinerie and E. Michel for their useful comments. Particularly, we would like to thank more M. Legrand for providing us his insights and extensive comments on the atmospheric chemistry of the Greenland ice record.

## REFERENCES

- Anklin, M., Barnola, J. M., Schwander, J., Stauffer, B. and Raynaud, D. 1995. Processes affecting the CO<sub>2</sub> concentrations measured in Greenland ice. *Tellus* **47B**, 461–470.
- Barnola, J. M., Pimienta, P., Raynaud, D. and Korotkevich, Y. S. 1991. CO<sub>2</sub>-climate relationship as deduced from the Vostok ice core: a re-examination based on the new measurements and on a re-evaluation of the air dating. *Tellus* **43B**, 83–90.
- Barnola, J. M., Anklin, M., Porcheron, J., Raynaud, D., Schwander, J. and Stauffer, B. 1995. CO<sub>2</sub> evolution during the last millennium as recorded by Antarctic and Greenland ice. *Tellus* **47B**, 264–272.
- Blunier, T., Chappellaz, J., Schwander, J., Barnola, J. M., Desperets, T., Stauffer, B. and Raynaud, D. 1993. Atmospheric methane, record from Greenland ice core over the last 1000 years. *J. Geophys. Res.* **20**, 2219–2222.
- Chappellaz, J. 1990. *Étude du méthane atmosphérique au cours du dernier cycle climatique à partir de l'analyse de l'air piégé dans la glace Antarctique*. PhD Thesis, University J. Fourier Grenoble, France.
- Chappellaz, J., Barnola, J. M., Raynaud, D., Korotkevich, Y. S. and Lorius, C. 1990. Ice core record of atmospheric methane over the past 160,000 years. *Nature* **345**, 127–131.
- Chappellaz, J., Blunier, T., Kints, S., Dallenbach, A., Barnola, J. M., Schwander, J., Raynaud, D. and Stauffer, B. 1997. Changes in the atmospheric CH<sub>4</sub> gradient between Greenland and Antarctica during the Holocene. *J. Geophys. Res.* **102**, 15,987–15,997.
- Clain, M. P. 1995. *Étude de la composante organique de l'aérosol atmosphérique*. PhD Thesis, University of Chambéry, France.
- Conrad, R., Seiler, W., Bunse, G. and Giehl, H. 1982. Carbon monoxide in seawater (Atlantic Ocean). *J. Geophys. Res.* **87**, 8839–8852.
- Corazza, E. and Tesi, G. 1995. Tropospheric hydrogen and carbon oxides in Antarctica and in Greenland. *Sci. Tot. Environ.* **160/161**, 803–809.
- Delmas, R. 1993. A natural artefact in Greenland ice-core CO<sub>2</sub> measurements. *Tellus* **45B**, 391–396.
- Etheridge, D. M., Steele, L. P., Langenfelds, R. L., Francey, R. J., Barnola, J. M. and Morgan, V. I. 1996. Natural and anthropogenic changes in atmospheric CO<sub>2</sub> over the last 1000 years from air in Antarctic ice and firn. *J. Geophys. Res.* **101**, 4115–4128.
- Fuhrer, K., Neftel, A., Anklin, M. and Maggi, V. 1993. Continuous measurements of hydrogen peroxide, formaldehyde, calcium and ammonium concentrations along the new GRIP ice core from Summit, central Greenland. *Atm. Env.* **27A**, 1873–1880.
- Haan, D. 1996. *Teneurs en monoxyde de carbone de l'air contenu dans la glace de l'Antarctique et du Groenland*. PhD Thesis, University J. Fourier Grenoble, France.
- Haan, D., Martinerie, P. and Raynaud, D. 1996. Ice core data of atmospheric carbon monoxide over Antarctica and Greenland during the last 200 years. *Geophys. Res. Lett.* **23**, 2235–2238.
- Legrand M., De Angelis, M., Staffelbach, T., Neftel, A. and Stauffer, B. 1992. Large perturbations of ammonium and organic acids content in the Summit-Greenland ice core. Fingerprint from forest fires? *Geophys. Res. Lett.* **19**, 473–475.
- Legrand, M. and De Angelis, M. 1995. Light carboxylic acids in Greenland ice: a record of past forest fires

- and vegetation emissions from the boreal zone. *J. Geophys. Res.* **101**, 4129–4145.
- Legrand, M. and De Angelis, M. 1996. Origins and variations of light carboxylic acids in polar precipitation. *J. Geophys. Res.* **100**, 1445–1462.
- Martinierie, P., Brasseur, G. P. and Granier, C. 1995. The chemical composition of ancient atmospheres: a model study constrained by ice core data. *J. Geophys. Res.* **100**, 14,291–14,304.
- Mopper, K. and Stahovec, W. L. 1986. Sources and sinks of low molecular weight organic carbonyl compounds in seawater. *Mar. Chem.* **19**, 305–321.
- Mopper, K., Zhou, X., Kieber, R.J., Kieger, D. J., Sikorski, R. J. and Jones, R. D. 1991. Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature* **353**, 60–62.
- Neftel, A., Jacob, P. and Klockow, D. 1986. Long-term record of H<sub>2</sub>O<sub>2</sub> in polar ice cores. *Tellus* **38B**, 262–270.
- Novelli, P. C., Steele, P. L. and Tans, P. 1992. Mixing ratios of carbon monoxide in the troposphere. *J. Geophys. Res.* **97**, 20,731–20,750.
- Novelli, P. C., Collins, J. E., Myers, R. C., Sachse, G. W. and Scheel, H. E. 1994. Reevaluation of the NOAA/CMDL carbon monoxide reference gases at NASA, Langley and the Fraunhofer Institut. *J. Geophys. Res.* **99**, 12,833–12,839.
- Rasmussen, R. A., Khalil, M. A. K. and Hoyt, S. D. 1982. Methane and carbon monoxide in snow. *APCA Journal* **32**, 176–178.
- Raynaud, D., Jouzel, J., Barnola, J. M., Chappellaz, J., Delmas, R. J. and Lorius, C. 1993. The ice record of greenhouse gases. *Science* **259**, 926–934.
- Redden, G. D. and Gordon, L. I. 1982. Characteristics of photochemical production of carbon monoxide in seawater. *Trans. Am. Geophys. Union* **63**, 909.
- Savarino, J. 1996. *Chimie de la carotte Eurocore (Groenland central): variabilité des émissions biologiques au cours du dernier millénaire*. PhD Thesis, University J. Fourier Grenoble, France.
- Schwander, J., Barnola, J. M., Andrié, C., Leuenberger, M., Ludin, A., Raynaud, D. and Stauffer, B. 1993. The age of air in the firn and ice at Summit, Greenland. *J. Geophys. Res.* **98**, 2831–2838.
- Sigg, A. and Neftel, A. 1991. Evidence for a 50% increase in H<sub>2</sub>O<sub>2</sub> over the past 200 years from a Greenland ice core. *Nature* **351**, 557–559.
- Staffelbach, T., Neftel, A., Stauffer, B. and Jacob, D. 1991. A record of the atmospheric methane sink from formaldehyde in polar ice cores. *Nature* **349**, 603–605.
- Valentine, R. L. and Zepp, R. G. 1993. Formation of carbon monoxide from the photodegradation of terrestrial dissolved organic carbon in natural waters. *Environ. Sci. Technol.* **27**, 409–412.
- Zika, R. G. 1981. *Marine organic photochemistry*. In: E. K. Duursma and R. Dawson (editors), *Marine organic chemistry*. Elsevier, Amsterdam, 299–325.
- Zumbrunn, R., Neftel, A. and Oeschger, H. 1982. CO<sub>2</sub> measurements on 1 cm<sup>3</sup> ice samples with an IR laser-spectrometer (IRLS) combined with a new dry extraction device. *Earth and Planetary Sciences Letters* **60**, 318–324.
- Zuo, Y. and Jones, R. D. 1995. Formation of carbon monoxide by photolysis of dissolved marine organic material and its significance in the carbon cycling of the oceans. *Naturwiss.* **82**, 472–474.
- Zuo, Y. and Jones, R. D. 1996. Photochemical production of carbon monoxide in authentic rainwater. *Geophys. Res. Lett.* **23**, 2769–2772.