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CO_2 evolution during the last millennium as recorded by Antarctic and Greenland ice

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ABSTRACT

In order to study in detail the pre-industrial CO_2 level (back to about 900 AD) and its temporal variations, several ice cores from Greenland and Antarctica were analysed in two laboratories, and compared with previous records. The agreement between the two laboratories and between the different cores of the same hemisphere is good. However, the comparison of the northern hemisphere (Greenland) and southern hemisphere (Antarctica) records shows values 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. Based on our present knowledge of the carbon cycle, an inter-hemispheric gradient of 20 ppmv is unrealistic. Thus, in the oldest part of the record, at least one profile should not represent the true atmospheric CO_2 concentrations. A companion paper by Anklin et al. (submitted), discusses the possible processes which can alter the atmospheric CO_2 once trapped in the ice. Due to the fact that the impurity content is one order of magnitude lower in the Antarctic than in the Greenland ice, we are much more confident in the Antarctic record. The new results from D47 and D57 (Adélie Land) presented in this paper, confirm the CO_2 fluctuation of about 10 ppmv at the end of the 13th century, previously observed by Siegenthaler et al. (1988) on an ice core drilled at South Pole. This fluctuation corresponds to a small imbalance of the carbon cycle ($\sim$0.3 GT C/yr), but its duration led to a significant cumulative input into the atmosphere. The changes observed in the pre-industrial level are discussed in terms of climatic noise and variability.

1. Introduction

The analysis of air trapped in polar ice reveals past changes of the air composition and a recent review of the ice record of greenhouse gases and its reliability can be found in Raynaud et al. (1993). The variability of the natural carbon cycle, under climatic conditions similar to the present day one is an important question regarding the prediction of the future atmospheric CO_2 level. This problem can be approached by detailed reconstructions of the atmospheric CO_2 evolution during pre-industrial times, based on ice cores analysis. For this purpose, two ice cores from Antarctica and two from Greenland were analysed in two laboratories, the LGGE in Grenoble and the Physics Institut of the University of Bern. The Antarctic results are compared with previous published records covering the same period and with the Greenland ones. The Antarctic record is then discussed in terms of atmospheric CO_2 changes during pre-industrial times and interarction between carbon cycle and climate.

2. Analytical procedures

In the two laboratories, the CO_2 is extracted from the ice using dry extraction methods, where the sample is crushed under vacuum and at low temperature to avoid any melting. In Bern, about

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10 g of ice are crushed between needles, while in Grenoble, the sample of about 40 g of ice and stainless steel balls are placed in a container and shaken. In the two cases about 75 % of the gas is released, the main difference between the two methods is that in Bern small chips of about 1 mm length are obtained and in Grenoble, the result is a fine powder plus un-crushed pieces of ice. The air released is then analysed by infra red laser absorption spectrometry in Bern and by gas chromatography in Grenoble. The analytical accuracy of a single measurement is about ± 3 ppmv in both laboratories. In this study, 3 to 8 samples per level have been measured in Bern, and 2 to 4 in Grenoble. It has been shown that artefacts occur in the CO_2 measurements when a large amount of water vapor was present in the extraction line (Zumbrunn et al., 1982; Barnola et al., 1987). In Bern, the water vapor pressure is kept at a minimum in the analytical system by drying the air in a cold trap (-70°C), isolated from the measuring cell during the CO_2 measurement (Neftel et al., 1985). In Grenoble, all the ice container is kept at -50°C and the CO_2 concentration is calculated using the dry air pressure given by the O_2-N_2 chromatographic peak.

In the firn air study of Schwander et al. (1993), the Grenoble results were higher than Bern's by about 1.5 ppmv. A recent calibration between the Grenoble and NOAA standards (T. Sowers personal communication) has shown that the Grenoble standard was overestimated by 0.39 %, reducing the difference to nearly zero. Nevertheless, the comparison of the results presented here on the same Greenland levels suggests that the Grenoble values are higher than the Bern one's by about 2 ppmv. At this stage, considering the precision of the measurements (~ 3 ppmv), the origin of this small discrepancy is still uncertained.

3. Characteristics of the different cores

The main features of the different cores are reported in Table 1.

The temperature of the different drilling sites range from -24 to -51°C. Due to these low temperatures, the snow melting at the surface is excluded at South Pole and very rare in the other locations. For example, only one melt layer has been observed at Siple at 7 m depth (Neftel et al., 1985) and one at 38 m depth at Summit. Different drilling systems have been used, including thermal and electromechanical equipments, operating in a dry hole or in a hole filled with kerosene.

As we want to compare in detail results coming from different cores, the chronologies have to be well-established, and it is the subject of the following sections.

Table 1. *Characteristics of the different cores analysed*

	Eurocore GRIP	D47	D57	Siple*	South Pole*
location	72°34′ N 37°38′ W	67°23′ S 138°43′ E	68°11′ S 137°33′ E	75°55′ S 83°55′ W	90° S
temperature	−32°C	−25.8°C	−32°C	−24°C	−51°C
accumulation rate (kg/m^2 yr)	209	268 (276–174)	171 (173–156)	500	80
ice dating	seasonal variations	volcanoes	volcanoes	seasonal variations	volcanoes
gas dating	firn air and porosity	gas content	gas content	porosity	porosity
age difference	210 yrs	162–214 yrs	270–287 yrs	83 yrs	950 yrs
age width	15 yrs	25–40 yrs	35–40 yrs	22 yrs	220 yrs
drilling type	EM, D/F	T, F	EM, D	EM, D	EM, D

EM: electromechanical drill; T: thermal drill.
D: dry hole; F: hole fill with fluid.
* CO_2 data are from Neftel et al. (1985), Friedli et al. (1986) and Siegenthaler et al. (1988).

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3.1. Dating the Greenland cores

The ice from the Summit cores (EUROCORE and GRIP) have been dated with an accuracy of about 2 years by counting annual layers and using volcanic horizons as control (H. B. Clausen personnal communication). The gas age at the close-off has been calculated with a diffusion model checked by measuring trace gas concentrations in the air from the open pores of the firn (Schwander et al., 1993). The gas is isolated from the atmosphere at 70 m, where the ice is 220 years old. At this depth, due to the molecular diffusion of the different gases in the firn, the air is already about 10 years old, and thus, the gas is younger than the surrounding ice by about 210 years.

3.2. Dating the Siple and South Pole cores

The Siple ice core has been dated by counting the seasonal variation of ECM (Electrical Conductivity Measurement) down to a depth of 114 m and by extrapolation below that depth. The age difference between the ice and the gas (83 years) has been calculated to be the age of the ice at the close-off depth, determined by the porosity measurements of Schwander and Stauffer (1984), minus 10 years (Neftel et al., 1985). This 10 years adjustment has been originally introduced to match the Siple CO_2 record against the atmospheric one, but it also corresponds to the diffusion time measured on the Summit core and thus seems justified. At South Pole, the ice has been dated using the Tambora volcanic horizon (1816) revealed by the ECM record (Schwander, 1984). The age difference between the ice and the gas (950 years), has been evaluated from the porosity results obtained on the Siple core (Schwander and Stauffer, 1984).

3.3. Dating the D47 and D57 cores

The two Adélie Land ice cores (D47 and D57) have been dated using different volcanic horizons revealed by the ECM records, since no continuous record of seasonal variations have been obtained. Also, these cores come from a coastal area, where horizontal ice flow is not negligeable, so we can expect a decreasing trend of the accumulation rates with depth. For D47, we have used an ice flow model (Ciais, 1991) forced by the Tambora eruption and an event dated at South Pole in 1450 AD. For D57 we have used the work of Kirchner (1988), who compared the ECM and chemical profiles from D57 (Zanolini, 1982) and South Pole (Delmas et al., 1992). To date the core, we have used a linear relationship between accumulation rate, a (Kg/m^2 yr), and depth, h (m of water equivalent), taking the Tambora (1815 AD) and the unknown eruption of 1259 AD (Langway et al., 1988) as markers:

$$a_{D57}(h) = 173 - 0.111 * h.$$

To calculate the age difference between the ice and the gas we have taken the age of the ice at the close-off density (estimated from the total gas content measurements of Martinerie et al., 1992). As the characteristics of these cores are not drastically different from the Summit core, we have considered the same diffusion time of the air in the firn, that is 10 years. A firn densification model (Barnola et al., 1991) has been used to take into account the influence of the accumulation rates on the firn density profiles. The accumulation rate and age values reported in the Table 1 are those corresponding to the upper and lower parts of the records.

The accuracy of these chronologies is good down to the last volcanic horizon, which correspond, for the gas to about 1630 AD for D47 and 1530 AD for D57, and more difficult to ascertain below. Nevertheless, for D47 few sections of δD seasonal variation have been measured (Ciais, 1991). Based on the variability of the accumulation rates thus deduced, we can estimate that the uncertainty of the ice dating increases with depth and is about ± 50 years in the lowest part of the record. Since D57 is located in the same area, a similar uncertainty can be expected.

3.4. Temporal representativity of the air samples

Because the air trapping is not an instantaneous process, each air sample represents a mean value over a time width which depends on the diffusion rate of the gas in the firn and on the density interval where the bubble close-off occurs. The age width (15 years) of the Summit cores (EUROCORE and GRIP) has been taken as twice the standard deviation of the age distribution resulting from the diffusion model of Schwander et al. (1993). Due to the lack of data, the age widths reported for the other sites are, based on the Siple porosity study (Schwander and Stauffer, 1984), the times required to the firn to densify from 0.8 to 0.83 density. This method does not consider

any diffusion process of air in the firn. Whether the decreasing diffusion rate of the air towards the base of the firn (Schwander et al., 1993), or the gradual enclosure of the pores is the dominant process for the age distribution depends on climatic conditions (mainly on the accumulation rate and temperature). But, in any case, the diffusion process will reduce the estimated age width and, at least for Siple, D47 and D57, the real value would be very close to the one of the Summit cores. In the case of South Pole, the firn densification model of Schwander et al. (1993) suggests that the age width could be as short as 100 years (J. Schwander, personal communication) instead of 220 years (Schwander and Stauffer, 1984).

4. Comparison of the records

4.1. The Antarctic records

The CO_2 results obtained in Grenoble on the D47 and D57 cores (this work) are reported in Table 2 and plotted with the Bern results from Siple (Neftel et al., 1985; Friedli et al., 1986) and South Pole (Siegenthaler et al., 1988) in the Fig. 1. The agreement between the different records is very good indicating that neither the drilling type (thermal or electromechanical), the climatic conditions (in the range from -24 at Siple to $-51°C$ at South Pole) nor the time of core storage (up to 10 years for D57) have strongly affected the CO_2 concentrations.

Fig. 1 also shows a smoothed curve based on a 100-year running mean of the yearly interpolated data. Apart from the anthropogenic CO_2 increase beginning around 1800 AD, the characteristics of the profile are, a CO_2 level of about 277 ppmv before the 13th century followed by a CO_2 increase to a maximum of about 285 ppmv occuring during the 14th century and then a slow decrease to a level of 279 ppmv during the 18th century. This oscillation has already been noticed on the South Pole core alone by Siegenthaler et al. (1988) and, although the water vapor affected the absolute values, the decreasing trend between the 14th and the 18th century was also observed on previous measurements made on the D57 core by Raynaud and Barnola (1985).

4.2. The Greenland records

In Fig. 2, the CO_2 results obtained in Bern and in Grenoble on the EUROCORE and GRIP cores are plotted together with the smoothed Antarctic profile.

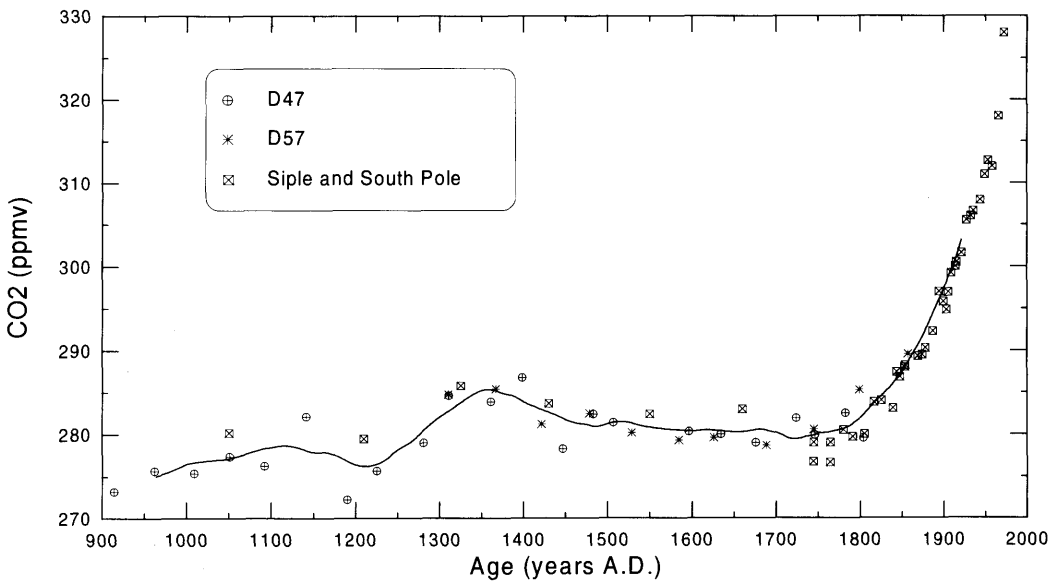

Fig. 1. CO_2 results from Antarctic ice cores. The Siple and South Pole results are from Neftel et al. (1985), Friedli et al. (1986) and Siegenthaler et al. (1988). The smoothed curve is based on a 100 years running mean (see text).

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Table 2. *CO_2 results from D47 and D57 (Adélie Land) ice cores*

Depth (m)	Ice age (yr BP)	Gas age (yr AD)	CO_2 (ppmv)	Depth (m)	Ice age (yr BP)	Gas age (yr AD)	CO_2 (ppmv)
D47				D47			
108	315	1804	279.5	285	1039	1091	276.3
114	337	1782	282.5	294	1080	1051	277.4
124	374	1746	279.9	303	1123	1009	275.4
130	396	1724	281.9	313	1170	962	275.7
143	445	1675	279	323	1219	914	273.2
154	487	1634	280	D57			
164	526	1596	280.3	95	390	1857	289.6
187	617	1507	281.4	105.4	449	1799	285.3
193	642	1483	282.4	115.8	503	1745	280.6
202	678	1447	278.3	126.4	560	1688	278.7
214	728	1398	286.8	138	623	1626	279.6
223	765	1361	283.9	145.6	665	1585	279.3
235	816	1311	284.6	155.7	721	1529	280.2
242	846	1281	279	165	772	1478	282.5
255	903	1225	275.7	175.8	829	1422	281.2
263	939	1190	272.2	185.5	885	1367	285.4
274	988	1141	282.1	195.3	942	1310	284.8

As already mentioned, the Bern and Grenoble values are very similar, the mean difference being of the order of 2 ppmv. The scatter of the profile is higher than the Antarctic one's and exhibits a slow decrease of the CO_2 concentrations from 295 ppmv around 1100 AD to about 280 ppmv at the end of the 18th century followed by the anthropogenic increase. The agreement between the CO_2 measurements obtained on the two Summit cores, EUROCORE (dry drilling hole) and

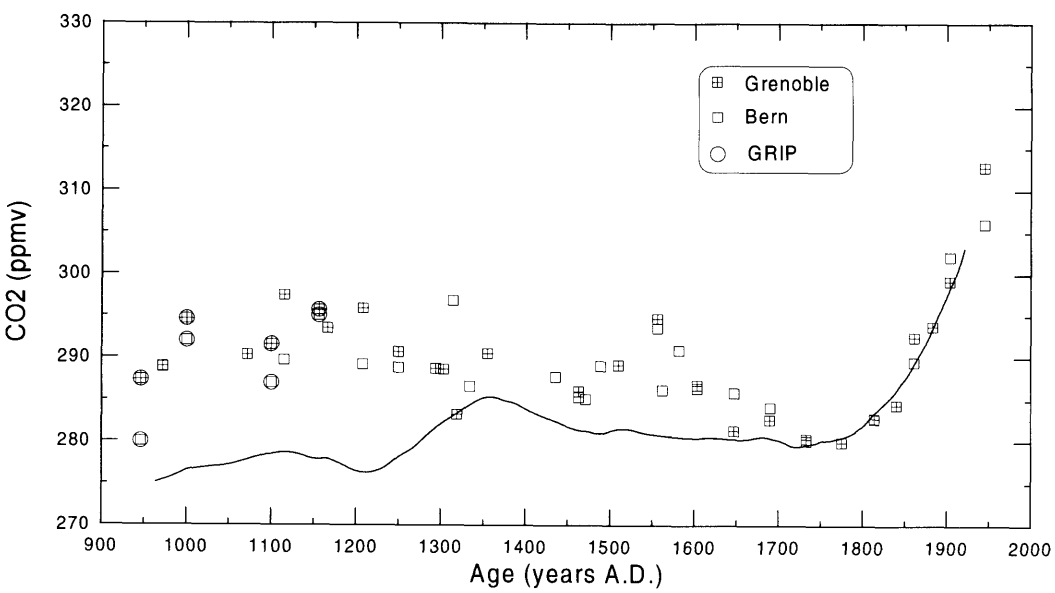

Fig. 2. CO_2 results from the Greenland (Summit) EUROCORE and GRIP cores. The GRIP results are indicated by the circles superimposed on the two laboratories symbols. The smoothed curve is from Fig. 1.

GRIP (Drilling hole filled with fluid), is very good. We have also to note that our set of results agree well with the CO_2 profile going back to 1530 AD (Wahlen et al., 1991), obtained on the GISP 2 core drilled 30 km from GRIP. The agreement between the different cores and laboratories indicates that all these results give the true CO_2 concentrations in the air bubbles of the ice in the area of Summit in central Greenland.

4.3. *Comparison of the Greenland and Antarctic records*

From the comparison between the Greenland record and the smoothed Antarctic profile (Fig. 2), it appears that the difference between the 2 sets ranges from nearly 0 ppmv in the youngest part of the records (back to about 1700 AD) up to about 20 ppmv at the beginning of the millennium.

Under present day conditions, the difference between high latitudes from northern hemisphere and Antarctica (South Pole) is about 3.5 ppmv (during the last 15 years this difference has always been lower than 5 ppmv) (TRENDS 1991). During the pre-industrial time, the large anthropogenic CO_2 emissions in the northern hemisphere were absent and a lower latitudinal gradient is expected. Furthermore, an extrapolation back to zero fossil fuel emission made by Siegenthaler and Sarmiento (1993) indicates that during the pre-industrial times, the interhemispheric gradient could have even been negative in the order of -1 ppmv. Therefore within the time period investigated, a maximum difference of 5 ppmv between Greenland and Antarctic cores can be reasonnably explained. This is a much lower value than the difference found for the oldest part of the records shown on Fig. 2.

Since the EUROCORE, D47 and D57 have been analysed, in Grenoble, at the same time, the difference cannot arises from a drift of the experimental procedure. Also, the good agreement between our two laboratories, using different analytical systems, confirms the higher CO_2 levels measured in the Greenland cores. At least one of the record (Antarctic or Greenland) has been modified by some process and does not reflect the real atmospheric concentrations anymore. Since the temperatures of the 4 sites studied are low enough, we can exclude a major influence of the surface melting. Also, any artefacts linked with the drilling systems are also excluded, since the agreement within the two sets (EUROCORE-GRIP and D47-D57-South Pole) of results is good. As other carbon content impurities are also included in the ice, chemical reactions leading to a CO_2 production are not completly excluded and the

Table 3. *CO_2 results from Summit, Greenland, ice cores (EUROCORE and GRIP)*

Depth (m)	Ice age (yrs AD)	Gas age (yrs BP)	GREN (ppmv)	BERN (ppmv)	Depth (m)	Ice age (yrs BP)	Gas age (yrs AD)	GREN (ppmv)	BERN (ppmv)
79.6	254	1945	312.8	306	194.3	763	1436		287.7
89.6	291	1904	299.2	302.1	213.9	837	1355	290.5	
94.6	316	1883	293.8		215.6	865	1334		286.6
99.5	335	1861	292.5	289.5	219.4	880	1319	283.2	
104.5	358	1840	284.4		220	885	1314		296.8
110.5	385	1814	282.8	282.7	222.7	888	1303	288.6	
119.3	423	1775	279.9		225.5	905	1294	288.7	
129.2	468	1733	280.3	280.1	233.7	940	1250	290.7	288.8
139.1	508	1690	282.6	284.1	243.1	981	1208	295.9	289.2
149	554	1647	281.3	285.9	252	1021	1166	293.5	
159	603	1603	286.8	286.4	254.1*	1044	1156	295.7	295
162.5	617	1582		290.9	262.3	1084	1115	297.4	289.7
167.2	637	1562		286.2	265.1*	1095	1100	291.6	287
168.8	644	1556	294.7	293.5	272.8	1127	1072	290.3	
178.7	689	1510	289.1		287.1*	1200	1000	294.6	292
182.9	710	1489		289	292.6	1227	972	288.9	288.8
186.5	728	1471		285.1	298.1*	1254	946	287.4	280
188.6	734	1463	286	285.3					

The 18 depths corresponding to the GRIP samples are marked by *.

companion paper of Anklin et al. (submitted), discuss the possible processes which can alterate the atmospheric CO_2 records. It is important to note that, due to the age difference between the ice and the gas, any reaction involving impurities deposited with the snow fall will not affect the CO_2 concentration at the same gas age in the different cores. This argument is not valid for the Greenland record, since the cores have been drilled very close from each others (less than 100 m), but for the Antarctic record the agreement between the different cores covering a large range of trapping time, from 83 years at Siple to 950 years at South Pole, excludes a strong influence of this type of reaction. Furthermore, the impurity content of the Antarctic ice is much lower than in Greenland ice, reducing the risk of chemical contamination of the Antarctic record. For all these reasons, we strongly believe that the Antarctic profile represents a real record of the atmospheric CO_2 evolution during the last millennium.

5. Pre-industrial fluctuations of the atmospheric CO_2

In 1988, Siegenthaler et al. published the South Pole results plotted in Fig. 1 and suggested that a CO_2 fluctuation of 10 ppmv happened around the 13th century. The main conclusion of their paper was that a cumulative input in the atmosphere of about 40 GT of carbon could have occurred between 1200 and 1350 AD, at a maximum rate of about 0.4 GT C per year and, based on $^{13}C/^{12}C$ results, they suggested that this input had a biospheric origin.

Our new results from D47 confirm this fluctuation, but, on the smouthed curve shown on Fig. 1, its amplitude is reduced to 7.5 ppmv. This can be due, at least partly, to the fact that, to take into account the age width of the air trapped in the South Pole core, Siegenthaler et al. (1988) deconvoluted the CO_2 signal using an overestimated age width of 220 years.

Fig. 3 shows the CO_2 variation rate, versus time, deduced from the smoothed curve of Fig. 1. During the pre-industrial time, the variation rates range from -0.05 to $+0.1$ ppmv/yr and the mean value during the CO_2 increase centered around 1300 AD is about 0.08 ppmv/yr. By analogy with the present-day situation, we use the concept of airborne fraction, defined as the ratio between the atmospheric increase and the cumulative input during a certain period, to transform this atmospheric increase in term of flux. Assuming as a rough estimate, an airborne fraction of 0.5, a varia-

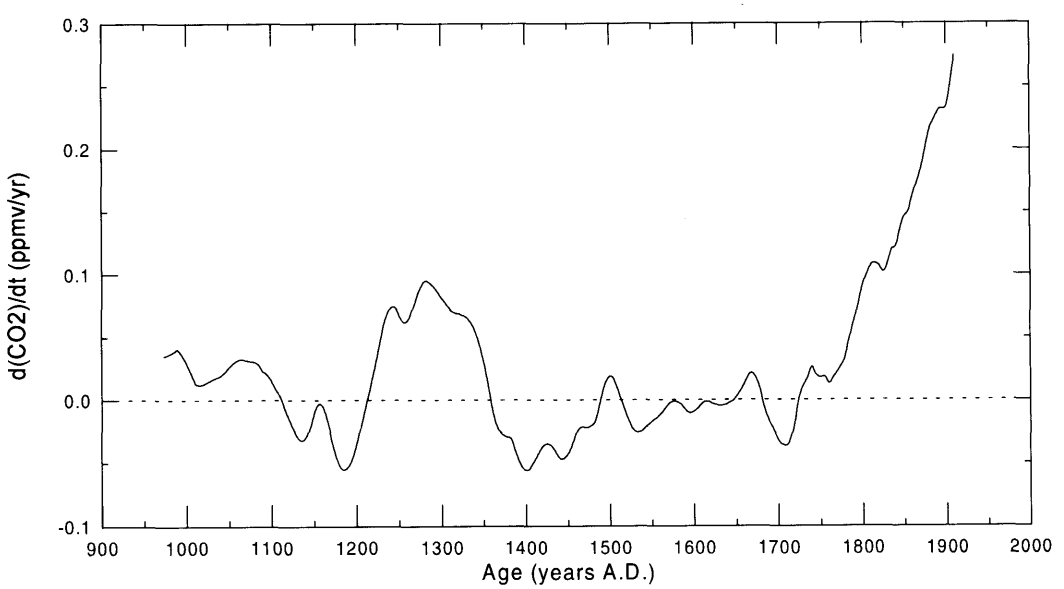

Fig. 3. Atmospheric CO_2 variation rate during the last millennium, based on the smoothed curve of the Fig. 1.

tion rate 0.08 ppmv/yr would correspond to a flux into the atmosphere of about 0.3 GT C/yr. This flux value is slightly lower than the maximum of 0.4 GT C/yr deduced by Siegenthaler et al. (1988) using an oceanic box model.

An imbalance of 0.3 GT C over one year is very small compared to about 175 GT of carbon exchanged seasonnally between the atmosphere and the ocean-continental biosphere system during pre-industrial times (Siegenthaler and Sarmiento, 1993). In term of year to year change it is also smaller than the inter-annual CO_2 fluctuations estimated to be up to 2 GT C under present day conditions, after removing the increasing trend due to fossil fuel consumption (Siegenthaler and Sarmiento, 1993). But the important feature of the Antarctic ice record is the duration of the carbon cycle desequilibrium, more than one century, and the cumulative input into the atmosphere, $\sim$40 GT C. Indeed, during the last millennium climatic fluctuations which could have affected the carbon cycle occurred (Crowley and North, 1991), and the decreasing trend between the end of the 14th and the 18th century could be due to the Little Ice Age. On the other hand, the fact that very similar values are recorded during the 18th (the end of the little ice age) and before the 12th century (during the medieval climatic optimum), indicates that the CO_2-climate relationship is not simple or that these climatic changes are not of global significance.

In fact, models of the different reservoirs of the carbon cycle suggest that the disequilibrium observed can be produced with only small climatic change and even with only interannual noise. Dai and Fung (1993) modeled the natural biospheric fluxes forced by the climate perturbation between 1940 and 1988. The results show the possibility for high variations in plant productivity and soil respiration and for a continuous biospheric sink of up to 1 GT C/yr between 1950 and 1984, that is during 34 years. Oceanic models (Mikolajewicz and Maier-Reimer, 1990; Mysak et al., 1993) can produce low frequency responses to a white noise climatic forcing. The Hamburg ocean general circulation model, driven with a superimposed fresh water flux white noise, produces a response showing an oceanic variability in a frequency band around 320 years (Mikolajewicz and Maier-Reimer, 1990). The coupling of the same OGCM with a carbon cycle model exhibits atmospheric CO_2 changes up to 10 ppmv on similar time scales (Heimann et al., submitted). These changes appear to result from changes in upwelling and vertical mixing and the associated perturbations in the marine biological pump. In any case, the biosphere appears as an important candidate for regulating the atmospheric CO_2 during periods showing only small climatic fluctuations.

6. Conclusion

Based on the CO_2 profiles from Greenland and Antarctic ice cores covering the last millennium, we confirm the pre-industrial atmospheric CO_2 value of $\sim$280 ppmv during the 18th century and the records indicate clearly the start of the anthropogenic increase. The pre-industrial value depends neither on the drilling site and conditions nor on the analytical procedures used in the two laboratories involved. Nevertheless, the cores drilled in the area of Summit in Greenland show higher values (up to about 20 ppmv) than the Antarctic cores when going back in time. This difference cannot be interpreted in term of atmospheric pre-industrial inter-hemispheric gradient, and is most probably due to chemical reactions between the different impurities included in the ice, as discussed in the companion paper by Anklin et al. (submitted). The fact that there are much less impurities in the Antarctic ice than in Greenland ice, and the good agreement between cores from very different locations, indicate that the Antarctic record represents the atmospheric CO_2 evolution during the last millennium. Within this period, the new results presented in this paper show a CO_2 increase from about 277 ppmv, before the 13th to about 285 ppmv during the 14th century followed by a slow decrease until the 18th century. This feature confirms the results of Siegenthaler et al. (1988) highlighting a cumulative input into the atmosphere of about 40 GT of carbon occurring during the 13th century. Model calculations suggest that the oceanic or continental biospheric reservoir can produce such an input under small climatic variations or noise.

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REFERENCES

Anklin, M., Barnola, J. M., Schwander, J., Stauffer, B. and Raynaud, D. 1995. Processes affecting the CO_2 concentrations measured in Greenland ice. *Tellus*, submitted.

Barnola, J.-M., Raynaud, D., Korotkevitch, Y. S. and Lorius, C. 1987. Vostok ice core provides 160,000 year record of atmospheric CO_2. *Nature* **329**, 408–414.

Barnola, J.-M., Pimienta, P., Raynaud, D. and Korotkevich, Y. S. 1991. CO_2-climate relationship as deduced from the Vostok ice core: A re-examination based on new measurements and on a re-evaluation of the air dating. *Tellus* **43B**, 83–90.

Ciais, P. 1991. *Forages profonds et sites côtiers en Antarctique: Données isotopiques et climat des 15.000 dernières années.* Thesis, Univ of Paris VI, nouvelle thèse, 390 pp.

Crowley, T. J. and North, G. R. 1991. Paleoclimatology, *Oxford monographs on geology and geophysics*, no. 18, Oxford University Press, Clarendon Press, pp. 92–109.

Dai, A. and Fung, I. 1993. Can climate variability contribute to the "missing" CO_2 sink? *Global Biogeochemical Cycles* **7**, 599–609.

Delmas, R. J., Kirchner, S., Palais, J. M. and Petit, J.-R. 1992. 1000 years of explosive volcanism recorded at South Pole. *Tellus* **44B**, 335–350.

Friedli, H., Lötscher, H., Oeschger, H., Siegenthaler, U. and Stauffer, B. 1986. Ice core record of the $^{13}C/^{12}C$ ratio of the atmospheric CO_2 in the past two centuries. *Nature* **324**, 237–238.

Heimann, M., Maier-Reimer, E. and Mikolajeviez, U. Global Change Institut, Snowmass (USA) 1993. *The Carbon Cycle*, submitted.

Kirchner, S. 1988. *Chimie de la neige (Na, Cl, NO_3, SO_4) à la station Pôle Sud.* Thesis, Univ of Paris VII, nouvelle thèse, 239 pp.

Langway, C. C., Clausen, H. B. and Hammer, C. U. 1988. An inter-hemispheric volcanic time marker in ice cores from Greenland and Antarctica. *Ann. Glaciol.* **10**, 102–108.

Martinerie, P., Raynaud, D., Etheridge, D. M., Barnola, J.-M. and Mazaudier, D. 1992. Physical and climatic parameters which influence the air content in polar ice. *Earth and Planetary Science Letters* **112**, 1–13.

Mikolajevicz, U. and Maier-Reimer, E. 1990. Internal secular variability in an ocean general circulation model. *Climate Dynamics* **4**, 145–156.

Mysak, L. A., Stocker, T. F. and Huang, F. 1993. Century-scale variability in a randomly forced, two-dimensional thermohaline ocean circulation model. *Climate Dynamics* **8**, 103–116.

Neftel, A., Moor, E., Oeschger, H. and Stauffer, B. 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature* **315**, 45–47.

Raynaud, D. and Barnola, J.-M. 1985. An Antarctic ice core reveals atmospheric CO_2 variations over the past few centuries. *Nature* **315**, 309–311.

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.

Schwander, J. 1984. *Lufteinschluss im Eis von Grönland und der Antarktis. Messung der elektrischen Leifähigkeit von Eisproben für klimatologische Anwendungen.* Inaugural Dissertation der philosophischwissenschaftichen Fakultät der Universität Bern zur Elangung der Doktorwürde. Druckerei der Universität Bern, 80 pp.

Schwander, J. and Stauffer, B. 1984. Age difference between polar ice and the air trapped in its bubbles. *Nature* **311**, 45–47.

Schwander, J., Barnola, J.-M., Andrié, C., Leuenberger, M., Ludin, A., Raynaud, D. and Stauffer, B. 1993. The age of the air in the firn and the ice at Summit, Greenland. *J. Geophys. Res.* **98**, 2831–2838.

Siegenthaler, U., Friedli, H., Lötscher, H., Moor, A., Neftel, A., Oeschger, H. and Stauffer, B. 1988. Stable-isotope ratio and concentration of CO_2 in air from polar ice core. *Ann. of Glaciol.* **10**, 151–156.

Siegenthaler, U. and Sarmiento, J. L. 1993. Atmospheric carbon dioxyde and the ocean. *Nature* **365**, 119–125.

TRENDS '91: Keeling, C. D. et al., Bacastow, R. B. et al. and Conway, T. J. et al., 1991. *Trends '91* (Boden, T. A., Sepanski, R. J. and Stoss, F. W. eds.). CDIAC, Oak Ridge National Laboratory, Tennessee.

Wahlen, M., Allen, D., Deck, B. and Herchenroder, A. 1991. Initial measurements of CO_2 concentrations (1530 to 1940 AD) in air occluded in the GISP 2 ice core from central Greenland. *Geophysical Research Letters* **18**, 1457–1460.

Zanolini, F. 1982. Conductimétrie et chimie de la glace à D57 (Terre Adélie), application à la recherche du paléovolcanisme. *Bulletin PIRPSEV* **76**, 84 pp.

Zumbrunn, R., Neftel, A. and Oeschger, H. 1982. CO_2 measurements on 1 cm^3 ice samples with an IR laserspectrometer (IRLS) combined with a new dry extraction device. *Earth and Planetary Science Letters* **60**, 318–324.