

GASEOUS COMPONENTS IN THE ATMOSPHERE AND THE HISTORIC RECORD REVEALED BY ICE CORES

by

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ABSTRACT

The composition of air in bubbles of ice reveals important information on the composition of the atmosphere at the time at which the ice was formed. The enclosed air has essentially an atmospheric composition if the ice formation occurred by dry sintering of snow and firn at low temperatures. The history of atmospheric CO₂ concentration is of special interest due to its present increase and its climatic implications. Currently, CO₂ analysis of air extracted from ice cores seems the best and most direct method of determining the natural CO₂ concentration before 1950 and possible pre-industrial variations. Analyses of ice samples representing the past 40 ka show that there were significant changes in concentration of atmospheric CO₂ at the end, and probably during part, of the last glaciation. $\delta^{13}\text{C}$ measurements on CO₂ extracted from ice cores can indicate possible mechanisms causing these changes in the concentration of atmospheric CO₂.

INTRODUCTION

Precipitations that fell >100 ka ago are preserved in a complete and well-stratified order in the central parts of the large polar ice sheets. Each precipitation event carries information concerning environmental and climatic conditions at the time that it fell and was exposed at the surface. The snow undergoes a metamorphosis from snow to firn, and finally to ice, and during the transition from firn to ice, atmospheric air is enclosed in bubbles. The air which is trapped in the bubbles at the time of ice formation remains at low temperatures as the years pass by. Information on the atmospheric composition obtained by analyzing air extracted from bubbles can be compared with climatic parameters obtained by analyzing the surrounding ice. However, one has to consider that the air is younger than the ice, since the transition from firn to ice occurs from 50 to 3000 a after deposition of the snow (Schwander and Stauffer 1984).

Scientists became interested in the composition of air in bubbles of glacier ice in the last century (Hamberg 1895). Scholander and collaborators (Coachman and others 1956, Scholander and others 1956) made the first comprehensive investigation and invented new methods to extract and analyze air from ice samples. The extraction techniques and analytical methods have been further improved and new analytical techniques are now applied. Most important for the progress of ice-core analysis is, however, the availability of suitable ice samples obtained by core drilling in the central parts of ice sheets.

We used, in our laboratory, samples which were obtained mainly from the deep ice cores from Camp Century, Greenland and Byrd station, Antarctica drilled by Lyle Hansen (Ueda and Garfield 1969) and from Dye 3, Greenland drilled in the course of the Greenland Ice Sheet Program (Gundestrup and others 1984). Important results were obtained with samples from intermediate ice cores from South Pole and Siple stations, Antarctica drilled by the Polar Ice Coring Office, Nebraska. Coordinates, mean annual air temperature and annual accumulation at all these locations are given in Table I.

In our laboratory, gases are extracted using dry extraction systems in which bubbles are opened mechanically at low temperature to release the gas. CO₂ analysis is carried out on ice samples of about 2 g size using a crusher combined with an infrared laser absorption spectrometer (Zumbrunn and others 1982). A new extraction system permits the extraction of gas from samples of up to 800 g (Moor and Stauffer 1984). This amount of extracted gas allows us to measure isotope ratios on the separated CO₂ and trace gases.

2. ICE AS A SAMPLING AND STORAGE DEVICE

When ice is formed by sintering of dry firn, the pore volume becomes separated in isolated bubbles with no further interaction with the atmosphere at the firn/ice transition. The analysis of the N₂/O₂/Ar ratios in air which was extracted from ice samples originating from cold areas without summer melting shows that, within the limits of error, these ratios agree with those found in the atmosphere. This indicates that the trapping of air in ice is essentially a physical process without leading to differentiation of the gas components. However, other components such as CO₂ have specific physico-chemical properties, e.g. a high solubility in water. We expect no deviation of the CO₂ concentration in bubbles of ice sintered from dry firn if both adsorption of air components on the firn grain surfaces and air enclosed during snowflake formation can be neglected.

Klinger and Ocampo (1979) measured the adsorption of CO₂ on ice, and, according to their results, the amount of CO₂ adsorbed on firn grains can be neglected. We have measured the CO₂ concentration of air extracted from firn of 35 m depth at the South Pole (Stauffer and others 1981). The measured CO₂ concentration at this depth agrees within the limits of error with the present atmospheric CO₂ concentration. From these two results we conclude that adsorption effects can be neglected and that air in the open pore space in firn has atmospheric composition.

Measurements on snow and firn samples from North Central station, Greenland show that there is air occluded in firn grains, which is enriched in CO₂ (Stauffer and others 1981). The amount of this air decreases with depth, probably due to a kind of zone refining process paralleling crystal growth. It was mentioned earlier that a small amount of CO₂ remaining in the firn grains could lead to a small but significant increase of the CO₂ concentration in air extracted from ice samples (Stauffer and others 1984). The diameter of firn grains grows by a factor of from 2 to 10 from the surface to bubble close-off depth, depending on temperature and accumulation rate. The grain volume increases therefore by a factor of from 8 to 1000. If we assume that the CO₂ content is 80 $\mu\text{l kg}^{-1}$ in the original nucleus of the firn grain as observed in young firn, and zero in the part accumulated by crystal growth, the CO₂ content at the firn-ice transition will be less than in young firn by a factor of from 8 to 1000. This 0.08 to 10 $\mu\text{l kg}^{-1}$ corresponds to an increase in the measured CO₂ concentration of about 0.8 to 100 ppmv; for polar regions without summer melting it is probably less than 25 ppmv.

TABLE I. CHARACTERISTICS OF DRILL SITES ON THE ANTARCTIC AND GREENLAND ICE SHEETS (Schwander and Stauffer 1984)

Site	Location		Mean annual air temperature (°C)	Annual accumulation water equivalent (m)	Width of age distribution (a)	Difference between age of ice and mean age of air (a)
	(lat)	(long)				
Measured at: Siple station	75°55'S	83°55'W	-24	0.5	22	95
Calculated for						
Vostok	78°28'S	106°48'E	-57	0.022	590	2800
Dome C	74°39'S	124°10'E	-53	0.036	370	1700
South Pole station	90°00'S		-51	0.084	220	950
Byrd station	79°59'S	120°01'W	-28	0.16	54	240
North Central	74°37'N	39°36'W	-31.7	0.11	76	350
Crête	71°07'N	37°19'W	-30	0.265	46	200
Camp Century	77°11'N	61°09'W	-24	0.34	31	130
Dye 3	65°11'N	43°50'W	-19.6	0.5	22	90

The CO₂ concentration in bubbles may be affected, after enclosure, by interactions with the ice itself and with occluded impurities during the long storage times involved.

After isolation from the atmosphere, bubbles shrink due to the hydrostatic pressure of the surrounding ice. Below a certain depth the bubble size decreases faster than would be expected due to the increasing pressure alone. This is because gases start to diffuse into the ice and to be trapped as air hydrates (Miller 1969, Shoji and Langway 1982). After decompression of the ice cores at the surface, air bubbles start to form again. To investigate a possible enrichment or depletion of CO₂ in the air of reformed bubbles, we analyzed samples, using the same ice core from Dye 3, from 1615 m below the surface at times of one week, two months and one year after recovery (Neftel and others 1983). Within the limit of experimental error, the same CO₂ concentrations were measured. Based on measurements on the same ice samples, the permeability of ice at -20°C for CO₂ was estimated to be about $3 \times 10^{-24} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$. The small permeability (of the same order as the permeability of N₂ through iron at 150°C) excludes the possibility of a loss of CO₂ during storage of ice cores, provided the ice is not fractured.

The question of whether CO₂ in bubbles or in the form of air hydrates in the ice may react with impurities in the ice is of special interest, since changes in CO₂ occasionally parallel changes in the dust concentration of ice (Stauffer and others 1981, W Dansgaard personal communication). Concerning the observed transition from low to high CO₂ concentrations at the end of the last glaciation, which will be discussed in section 4, the increase of the CO₂ concentration parallels a decrease of the dust content in all the measured ice cores. We measured the pH value of melted samples from Camp Century and Byrd station after CO₂ was extracted (Stauffer and others 1981). The pH value of all samples measured from Camp Century is

>7 (since it was measured after gas extraction this does not indicate that the ice is alkaline) and is higher for samples from the last glaciation. The samples showing the lowest CO₂ contents have the highest pH values. All samples from Byrd station, on the other hand, show pH values <7.2. They show the same trend concerning CO₂ at the end of the last glaciation as the samples from Camp Century and the total change is of the same magnitude. The increase of the CO₂ concentration in the ice cores from Dome C (Barnola unpublished) and Byrd station occur significantly above the dust increase in the same ice core. We conclude therefore that in this case the change of the CO₂ content is most probably caused by a change of the atmospheric CO₂ concentration. An interaction of CO₂ with impurities in ice cannot be completely excluded and variations of the CO₂ concentration in a certain time interval should be observed in at least two ice cores with different concentrations of impurities before they can be attributed unequivocally to an atmospheric CO₂ concentration change.

3. SOME RESULTS FROM ICE-CORE ANALYSIS

The main components of air: N₂ (78.08%), O₂ (20.95%), Ar (0.93%), and most of the noble gases, are considered to be permanent and their variations during the last 100 ka are expected to be extremely small. Except for water vapour, the first variable gases which attracted general attention were CO₂ and ozone (Junge 1963). Both are important for life and for the radiation balance. Other components present in smaller concentrations and varying, because of differences in natural sources or sinks, or increasing, because of anthropogenic impacts, have attracted attention in recent years. CH₄, N₂O, CO and halocarbons are among the more important.

Scholander and others (1956) reported an O₂ concentration in air extracted from two icebergs which was 0.6 to 0.85% lower than that in the atmosphere. It

was estimated that the icebergs originated from the central part of Greenland and were very old. They speculated that the atmospheric O₂ concentration could have been lower during the beginning of the Pleistocene, owing to reduced photosynthesis.

In air extracted from ice samples from Camp Century, Raynaud and Delmas (1977) found a mean O₂ concentration of 20.87% for samples of Holocene age and 20.69% for samples from the Wisconsin period. They attribute this small but significant difference either to a lower atmospheric O₂ concentration during the Wisconsin or to a change of the adsorption behaviour of O₂ on the surface of firn grains due to different firn temperatures.

Variations of the atmospheric O₂ concentration, due to changes in the activity of photosynthesis and oxidation, are expected to be of the order of 0.01% or less. Precise and reliable measurements of the atmospheric O₂ concentration in the past, based on ice-core analysis, could give an important insight into changes of biological activity and oxidation of organic material. The ratio of the stable isotopes ¹⁸O/¹⁶O may also have varied in the past (e.g. during the last glaciation), because of an indirect interaction with the oxygen in ocean water (Bender personal communication).

Ozone, which is a very reactive gas, might be expected to react with impurities in the firn and in the ice and is therefore probably not suitable for investigation by ice-core analysis.

Most investigations concern the atmospheric CO₂ concentration. The results will be discussed separately in the next section.

The pre-industrial atmospheric concentration of most of the trace gases is not well known or not known at all. Ice-core analyses will help to determine the pre-industrial concentrations of some trace gases as well as the time history of a possible increase. Attempts to measure CH₄, N₂O, CO and halocarbons have been made in different laboratories. Craig and Chou (1982) reported interesting results concerning CH₄. Based on measurements carried out on ice-core samples from Dye 3 they conclude that the atmospheric CH₄ concentration was about 0.7 ppmv during the last 20 ka until about AD 1600. From this time, the CH₄ concentration started to increase linearly, reaching a concentration of about 1.1 ppmv in 1920. There was a faster increase

afterwards, the present (1980) value of the atmospheric CH₄ concentration being about 1.7 ppmv.

We are now measuring the CH₄ concentration in ice cores from South Pole and Siple stations. First preliminary measurements of air extracted with a vacuum melt extraction system confirm the results of Craig and Chou. After the success of the dry extraction system concerning CO₂, we would like to analyse air extracted with this system. However, up to now dry extraction is causing higher and more variable blank values than vacuum melt extraction.

Of special interest are radioactive isotopes in the gas enclosed in bubbles. The best known is ¹⁴C. Results from ¹⁴C measurements on CO₂ extracted from ice samples will be discussed below. Very important for dating purposes are radioactive isotopes of noble gases, since they are not affected by geochemical variations. ³⁹Ar (T_{1/2}= 269 a) measurements have been used for dating ice at different depths (Loosli 1983). ⁸⁵Kr (T_{1/2}= 10.7 a) will be used to check if air in the open pore space of firn is well-mixed down to the transition zone from firn to ice. ⁸¹Kr (T_{1/2} = 2x10⁵ a) will be an ideal isotope for dating very old ice, as soon as progress in the analytical technique allows the use of small ice samples (Kramer and others 1984).

4. RESULTS CONCERNING CO₂ AND THE RATIOS OF CARBON ISOTOPES

4.1. Pre-industrial atmospheric CO₂ concentration

The CO₂ concentration in air bubbles of very cold ice is essentially atmospheric. Small deviations cannot be excluded, e.g. those due to microbubbles. Extraction and analytical methods have to be tested step by step, and absolute calibration of the procedure has not yet been possible, since ice formed during a period with known atmospheric CO₂ concentration is not available. Two laboratories at Bern and Grenoble have compared two different procedures by performing an inter-laboratory calibration, measuring samples from the same ice core (Barnola and others 1983). The results of measurements on sections of ice cores drilled at Dome C (East Antarctica) and Byrd station (West Antarctica) did agree within the error limits of about 3% (9 ppmv absolute). The mean CO₂ concentration of the extracted air was found to be 258 ppmv. Using the same procedures, ice samples from six different locations in Antarctica and Greenland were measured, covering a time interval from

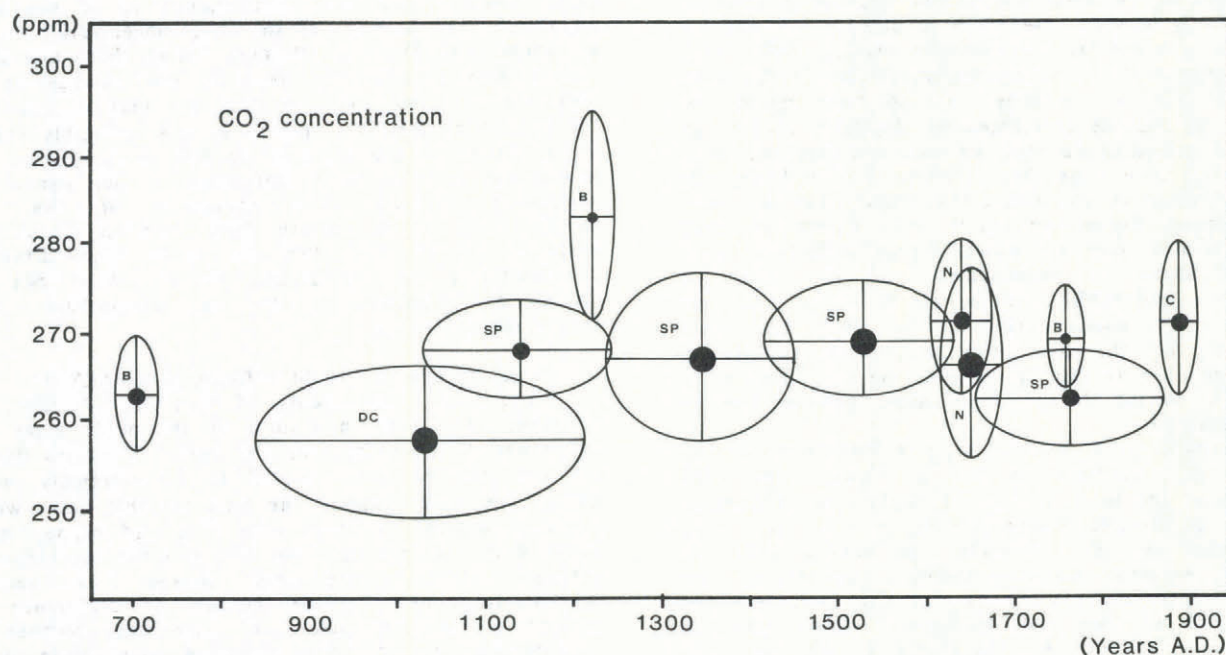


Fig.1. CO₂ concentration of air extracted from 2 g ice samples and measured with an infrared laser absorption spectrometer. Ice samples are from Dome C (DC), South Pole station (SP) Byrd station (B), North Central (N) and Crête (C). Large dots indicate mean values of more than 30 measurements, medium dots of 8 to 30, and small dots less than 8.

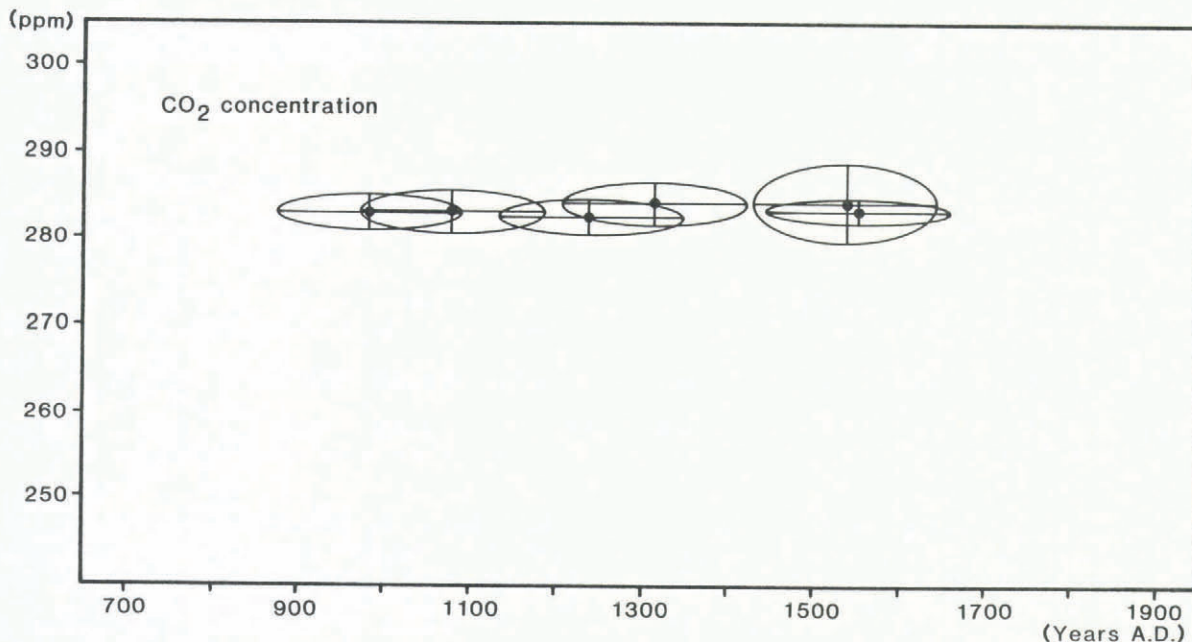


Fig.2. CO₂ concentration of air extracted from 550 g ice samples from South Pole station.

2500 BP to about AD 1850. The results for the mean concentrations occurring at all these locations are in the range of 258 to 270 ppmv. Results from measurements made in Bern are shown in Figure 1.

A new extraction system for much larger ice samples (500 g) was developed in our laboratory at Bern after the inter-laboratory comparison. Measurements of the CO₂ concentration on gases extracted with the new device from samples from South Pole station gave a mean value of 283±2 ppmv (Fig.2). With the system used for the inter-laboratory comparison we found 267±6 ppmv. With the old system, gas released during dry extraction expands into an absorption cell of an infrared laser absorption spectrometer (Zumbrunn and others 1982) where the CO₂ concentration is measured whereas with the new system all extracted gas is collected by condensation at 15 K. Searching for the cause of the discrepancy between the two extraction methods, we observed a small depletion of CO₂ in that fraction of the gas which expands into the absorption cell. The gas has to pass a cold trap where water vapour is transporting CO₂ preferentially, which can lead to a demixing of air by a flux of water vapour. According to recent measurements made in our laboratory, we would have to correct our earlier results to give values about 15 ppmv higher. Tests in the laboratory in Grenoble, however, do not seem to justify a correction of their earlier results (D Raynaud personal communication). Further comparisons with the laboratory in Grenoble are planned. The uncertainty concerns only the absolute values; we have great confidence in results showing variations, especially if they are measured on the same core. Recent measurements in Grenoble and in Bern have also shown that there are variations of the pre-industrial atmospheric CO₂ concentration in the range of 10 ppmv. Comparisons have therefore to be done for the same time interval.

Neighbouring air bubbles in an ice sample may have different ages, since one bubble may have been isolated at the beginning and an adjacent one at the end of the enclosure process. The time resolution, i.e. the width of the age distribution of the enclosed air, is determined by the duration of the gas enclosure process which depends on firn temperature and annual accumulation rate (Schwander and Stauffer 1984) (Table I). Samples from locations with high annual accumulations are best suited to yield good time resolutions which are necessary to investigate, for example, the anthropogenic increase of the atmospheric CO₂ concentration. From the first measurements of samples from Siple station (West Antarctica) we estimate that the history of the CO₂ increase during the last 150

a can be reconstructed with a time resolution of about 20 a and that the results will be overlapping or adjacent to results from direct measurements on Mauna Loa started in 1958. The results are, however, preliminary and it is too early to report on them in this paper.

4.2. Large variations at the end of and during the last glaciation

There is evidence from different ice cores that the atmospheric CO₂ concentration was lower by 70 to 100 ppmv during the last glaciation than in the pre-industrial period of the Holocene (Oeschger and Stauffer in press, Barnola unpublished). We will discuss the chronology of the increase at the end of the last glaciation and the possibility of large variations of atmospheric CO₂ concentration during glaciation as reported by Stauffer and others (1984, 1985) (Fig.3).

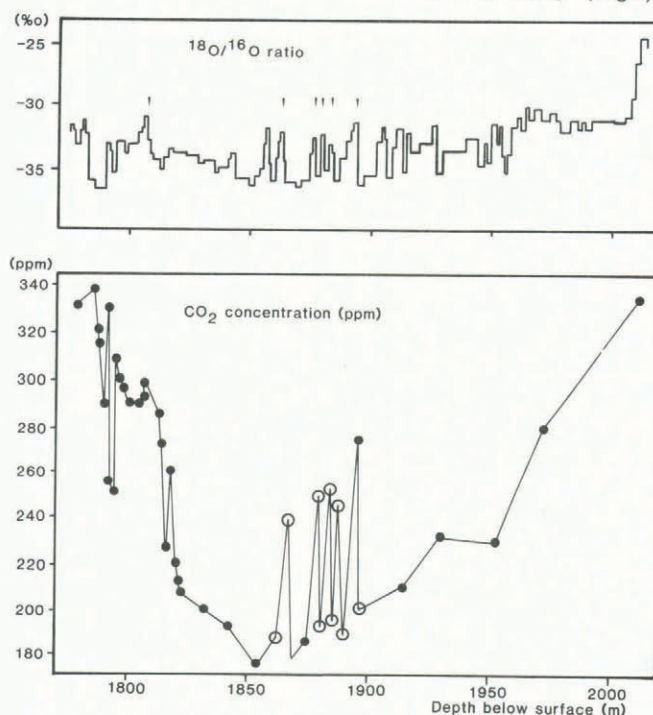


Fig.3. ¹⁸O/¹⁶O ratio and CO₂ concentration measured on the deep ice core from Dye 3. ¹⁸O/¹⁶O results according to Dansgaard and others (1982), CO₂ results indicated by dots according to Stauffer and others (1985) and by circles according to Stauffer and others (1984).

TABLE II. ¹⁴C AGE OF TWO ICE SAMPLES FROM DYE 3 (Andrée and others 1984). THE CORRECTION OF THE ¹⁴C AGES TAKES INTO ACCOUNT ¹³C CORRECTIONS AND ¹⁴C PRODUCTION VARIATIONS

	Mean depth	Amount of ice	Amount of CO ₂	¹⁴ C age uncorrected	¹⁴ C age corrected		Age determined by	
					air	ice	seasonal variations	ice-flow model
	(m)	(kg)	(cm ³ (STP))	(a)	(a)	(a)	(a)	(a)
Sample 1	1668	10.2	0.24	6420±650	7550±660	7640±660	8304±50	8132
Sample 2	1732	11.2	0.28	7930±660	9025±660	9115±660	9019±50	9362

There are two main questions concerning the increase at the end of glaciation: how fast was the increase, and did the CO₂ increase occur before or after the climatic shift indicated by increasing δ¹⁸O values?

The possibility of a rapid increase around 13 ka BP has been reported, based on measurements of samples from an ice core drilled at Dye 3 during the Greenland Ice Sheet Program (Stauffer and others 1985). This ice core has a good time resolution at the depth where the transition from Wisconsin to Holocene is observed, and is of excellent quality. At Dye 3 the mean annual air temperature at present is -20°C, and summer melting occurs regularly. We considered the possibility of this apparently rapid CO₂ increase at the glacial/post-glacial transition being caused by the influence of meltwater leading to elevated CO₂ concentrations in ice as unlikely, based mainly on δ¹⁸O measurements. Possibly we have underestimated the influence of the larger solar insolation during summer at the end of the last glaciation. Blatter and others (1984) calculated for the summer season at 60°N and 10 ka BP a solar insolation for a clear sky of 22.04 MJ m⁻² d⁻¹, compared to the present value of 20.67 MJ m⁻² d⁻¹. This indicates that the summer temperature compared to the mean annual temperature was higher than at present. The formation of meltwater in summer cannot, therefore, be excluded in spite of low δ¹⁸O values. There could be an increasing influence of meltwater due to the climatic warming indicated by increasing δ¹⁸O values observed in the Dye 3 ice core at 1810 m depth.

New measurements on ice samples from Byrd station do not provide further evidence for a very rapid atmospheric CO₂ increase, but do not disprove it either, as samples from the most important core section are no longer available. Results from ice samples from Dome C indicate that the increase occurred in two steps. The CO₂ concentration increased, according to Barnola (unpublished), from 200 to 230 ppmv about 16 ka BP, and from 230 ppmv to a value above the pre-industrial concentration about 11 ka BP. The second increase occurred probably very rapidly.

In order to investigate the detailed chronology of the CO₂ increase, an ice core from a very cold location with a good time resolution (high accumulation) and good quality is needed. The question of a possible time lag between increase of CO₂ and climatic change is related to this chronology, and cannot be answered yet. An ice core drilled in central Greenland would be well suited to solve these problems.

The question arises if meltwater could be responsible for the elevation of CO₂ values during short periods of warmer climate, as observed on ice samples from Dye 3 representing a period from about 30 to 40 ka BP (Stauffer and others 1984) (Fig.3). The solar insolation calculated by Blatter and others (1984) for the summer season is 20.99 MJ m⁻² d⁻¹ for 40 ka BP, and 20.38 MJ m⁻² d⁻¹ for 30 ka BP. The insolation was slightly higher than it is today but lower than it was at the end of the glaciation. Traces of meltwater in periods of relatively warm climate indicated by higher δ¹⁸O

values cannot be excluded, but only a meltwater formation of the same order as exists today would cause the large increase observed. We still consider that the influence of meltwater is unlikely to be great.

The question of whether the rapid changes of the CO₂ content are due to changes of atmospheric CO₂ concentration has to be answered by analyses of ice-core samples from other locations. We measured samples from Byrd station from a small section where elevated CO₂ values were expected based on δ¹⁸O measurements. No such elevated values were found, but this could be due to an error in the estimated age of the core section. A more complete survey of the Byrd core will be done within the next six months.

4.3. First ¹³C/¹²C results

The stable isotope ratio of CO₂ (¹³C/¹²C) extracted from ice samples provides a clue in the investigation of possible reasons for atmospheric CO₂ concentration changes. CO₂ produced from living biomass as well as from fossil fuels has a significantly lower δ¹³C than atmospheric CO₂; on the other hand, CO₂ variations due, for example, to temperature changes in the ocean would not significantly influence δ¹³C.

The ¹³C/¹²C and ¹⁸O/¹⁶O ratios of CO₂ extracted from ice samples from South Pole and from Byrd station have been measured (Friedli and others 1984). Air is extracted from samples of about 500 g by dry extraction (Moor and Stauffer 1984). The CO₂ is separated from the air by condensation at the temperature of liquid nitrogen. The δ¹³C and δ¹⁸O values of the CO₂ samples, of typically 15 μl STP volume, are measured in a MAT 250 triple collector mass spectrometer. The overall precision, including extraction, separation and analysis, is estimated to be 0.22‰ for δ¹³C and 0.45‰ for δ¹⁸O.

The mean δ¹³C for nine samples from South Pole, with ages between 500 and 1000 a BP is -6.69‰ and the mean δ¹⁸O is -31.4‰. The δ¹³C results have to be corrected for a contribution by N₂O which has the same isotopic mass and which was not separated. The corrected δ¹³C value is -6.34±0.3‰, assuming an N₂O concentration of 286 ppbv. This is about 1‰ higher than the result of -7.34‰ for modern (1978) atmospheric air reported by Keeling and others (1980).

This result can be compared to model calculations for the δ¹³C change (Siegenthaler and others 1978). A change of 1‰ is, according to these calculations, compatible with a relatively wide range of pre-industrial CO₂ concentrations and confirms that the observed CO₂ increase is due to an input of CO₂ from burning of fossil fuel and from the biomass. δ¹⁸O of atmospheric CO₂ is about 0‰. The negative values of our samples are probably caused by oxygen exchange between CO₂ and water, either in the ice or during the extraction.

The uncorrected mean δ¹³C for three 50 ka BP CO₂ samples from an ice core from Byrd station is -7.58‰, which is about 1‰ more negative than the value for the South Pole samples. Based on model calculations one would not expect more negative δ¹³C during times of lowered atmospheric CO₂ concentration.

The result from the Byrd samples is, however, much less reliable than the one from the South Pole samples due to the less favourable core quality.

4.4. ^{14}C dating of CO_2 extracted from ice samples

^{14}C dating of ice is an important technique as it supplements dating methods based on counting annual layers and ice-flow calculations. ^{14}C results will be especially useful for comparing climatic events at the end of the last glaciation recorded in ice cores with records of climatic events in peat bogs and other sediments.

The use of an accelerator mass spectrometer (AMS) permits the measurement of ^{14}C concentration on very small samples. Andrée and others (1984) have performed ^{14}C analyses with AMS on CO_2 extracted from ice core samples from Dye 3. For one ^{14}C sample, 12 subsequent extraction runs with the new dry extraction device are necessary. The air released is collected and CO_2 is separated afterwards by condensation of CO_2 and pumping off other gases. The conversion of CO_2 to an amorphous carbon deposit, needed for the AMS measurement, is performed in a glow discharge. During the conversion of only $0.3\text{ cm}^3\text{ CO}_2$, contamination with modern CO_2 cannot at present be avoided causing relatively large errors. If CO_2 samples of the same size without ^{14}C are converted, the measured ^{14}C concentration of the deposit varies between 5 and $20^0/00$ of modern carbon. Due to the high and variable background only relatively young ice samples can be dated up to now. In Table II ^{14}C ages of two ice samples from Dye 3 are compared with ages obtained by other methods.

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