

INFORMATION ON THE CO₂ CYCLE FROM ICE CORE STUDIES

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ABSTRACT. Information on the history of the atmospheric CO₂ content and the ¹³C/¹²C and ¹⁴C/C ratios is recorded in natural ice. Measurements on samples from very cold accumulation regions show that CO₂ is occluded not only in air bubbles, but also in the ice lattice. The two CO₂ components are of similar size. It is very difficult to measure CO₂ in the bubbles and CO₂ in the ice lattice separately. By melting the samples and extracting the evolving gases in two fractions, it is possible to estimate CO₂ concentration in the bubbles and the ice lattice. Enrichment or depletion of CO₂ in the bubbles by exchange with the ice is difficult to estimate. Information about this effect is expected from ¹³C/¹²C analysis on the extracted CO₂ fractions.

To investigate whether atmospheric CO₂ content was different during the last glaciation than during the present one, sets of 16 and 20 samples distributed over the last 40,000 years from the two deep ice cores from Camp Century (North Greenland) and Byrd Station (West Antarctica) were measured. The time scales for the two cores are based on a rheological model. Results and conclusions are:

- The data series from both cores show similar trends correlated to a certain degree to the δ¹⁸O profiles.
- For both cores, the values for the CO₂ concentration of the first fraction, considered to best represent the atmospheric composition, show lower values during glaciation than in the Holocene, with a minimum before the end of glaciation.
- Low CO₂ concentrations in the first fractions (200ppm) of certain samples are a strong indication that the atmospheric CO₂ concentration during last glaciation was lower than during the postglacial. These low concentrations indicate that, at that time, CO₂ concentration in the atmosphere could have been lower than today by a factor of 1.5. Possible explanations for such a change in atmospheric CO₂ content as well as its influence on atmospheric ¹⁴C/C ratio and on the radiation balance is discussed.

INTRODUCTION

Probably the only way to directly reconstruct the history of the atmospheric CO₂ content and the ¹³C/¹²C and ¹⁴C/C ratios is by measuring natural old ice samples. Ice formed by sintering of dry cold snow contains air with atmospheric composition in its bubbles. Until a few years ago, attempts to determine ancient atmospheric CO₂ contents by measuring CO₂ contents of the air occluded as air bubbles in natural ice seemed to be unfeasible (Scholander and others, 1961; Matsuo and Miyake, 1966; Raynaud and Delmas, 1977). CO₂/N₂ ratios much higher than the atmospheric one had been measured, indicating the presence of additional CO₂ adsorbed or dissolved in the ice lattice, present in micro-bubbles or as HCO₃⁻, or CO₃⁻, or originating from oxidation of organic debris. However, measurements on samples from very cold accumulation regions show that CO₂ in ice is of the same order of magnitude as that in bubbles. Considering the long periods involved, CO₂ in the two phases may exchange to a certain degree.

Based on these observations, we started CO₂ measurements on ice-core samples from Greenland and Antarctica to investigate if the CO₂ content of ice formed during the last glaciation or during the climatic optimum is similar to, or different from, that of newly formed ice.

The trapping mechanisms for CO₂ in ice

The origin of CO₂ extracted from ice cores is important. Components of CO₂ are: 1) CO₂ occluded during formation of snow crystals, 2) CO₂

trapped by freezing of melt layers on the surface in the accumulation area, 3) CO_2 trapped on the surface of snow crystals and firn grains, 4) organic and inorganic carbon containing dust either deposited directly or with snow at the firn surface, 5) occlusion of air at the transition from firn to ice.

Air can circulate in the firn. Measurements on firn samples indicate a loss of CO_2 during the sintering process probably due to diffusion of CO_2 out of the grains. The transition from firn to ice in Greenland takes place at typical depths of around 70m. During this process, air gets trapped as air bubbles. ^{39}Ar measurements (Loosli and Oeschger, 1980) show that most of the air trapped at the firn ice transition has been in contact with the free atmosphere till the final occlusion. The age of the occluded air is, therefore, younger than that of the ice matrix. For Greenland, the typical age difference is 200 years. Measurements on samples of young ice from different cold accumulation regions show that the amount of CO_2 in the ice lattice is about equal to that in the bubbles. Considering the long periods involved, there probably has been an exchange between the two CO_2 components.

Extraction and measurement technique

Measurements of the CO_2 content of ice cores are very delicate. Complications are caused by contamination of the surface of the ice cores, by the release of additional CO_2 from the walls of the extraction system, and by incomplete extraction (Stauffer and Berner, 1978).

It took many years to develop a reliable extraction and measuring technique. Many tests show that contamination probably is small (<5 percent). Reproducibility tests also show satisfactory results although it cannot be expected that even two adjacent ice cores will contain the same information. In addition, the extraction procedure provides information on the partitioning of the CO_2 into two CO_2 components, *ie*, CO_2 in the bubbles and CO_2 in the ice lattice. The procedure is as follows:

Samples of 300g of ice are melted in vacuum and the gases produced by the explosion of air bubbles on the melting ice surface are pumped by a Toeppler pump into a sample container. Before all the ice is melted, a first extraction fraction, which is considered representative of the composition of the gases in the bubbles, is separated. Extraction of the gases is continued for several hours until CO_2 no longer escapes. Based on the analyses of the two extraction fractions, the amount of CO_2 contained in the air bubbles and in the ice lattice is estimated. Analysis of the gas composition (N_2 , O_2 , Ar, CO_2) is made by gas chromatography. The accuracy of the CO_2 /total gas ratio measurements is 1.5 percent.

The measuring program

Our experiments provided us with information on analysis and data interpretation of variations on the order of 30 percent of atmospheric CO_2 content in a relatively small number of samples. The limit of detectability of fluctuations can be reduced significantly by measuring a greater

number of samples covering the time span of interest. We decided to measure samples for a period of major climatic change, possibly leading to a change in the atmospheric CO₂ content. Ice cores suited for such a study are available thanks to the pioneering work of B L Hansen and C C Langway. Teams of U S scientists were successful in 1966 in drilling to bedrock of the Greenland ice cap in Northwest Greenland (Station Camp Century) and in 1967/68 to bedrock of the West Antarctic ice shield at Byrd Station. From both deep ice cores, C C Langway provided carefully selected samples covering the last 40,000 years. Sixteen samples were measured for one ice core, 20 samples for the other.

RESULTS

Figures 1 and 2 give the measured gas content, total extracted CO₂ (ml STP CO₂/kg ice) and the CO₂ content of the first extraction fraction (ppm of extracted gas). The total gas contents of the two cores show variations which are partly attributed to gas loss through fractures. Changes in crystal structure and altitude of the accumulation region

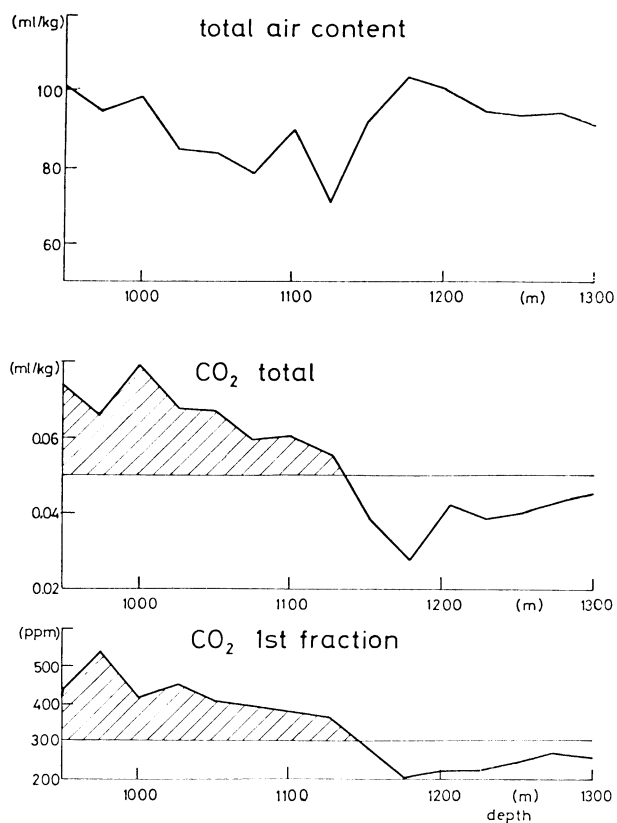


Fig 1. Camp Century Core: total gas content, total extracted CO₂ and CO₂ content of the first extraction fraction versus depth.

may also be influential (Raynaud and Lorius, 1977). In the middle of the two figures the total gas content (ml STP/kg ice) of the ice and, at the bottom, the CO_2 concentration (ppm of extracted gas) of the first fractions are plotted versus depth. The hatched areas indicate values of total CO_2 concentrations in ice and in the first extraction fraction above 0.05ml CO_2 /kg ice and 300ppm, respectively. The white area is chosen for values below these levels. Both ice cores clearly demonstrate a change from values below these levels to values above it. The 0.05ml/kg and the 300ppm level are crossed at depths of approximately 1100m for both cores.

DISCUSSION AND CONCLUSION

Measurements of the total amount of CO_2 (ml/kg ice), of the first fraction (ppm), and estimates of the amount of CO_2 in the ice lattice, are plotted in figures 3 and 4 together with the $\delta^{18}\text{O}$ record for the Camp Century and the Byrd Station core (Dansgaard and others, 1971; Johnsen and others, 1972). The dating is based on model calculations by Hammer and others (1978) and Johnsen and others (1972). The first fractions show

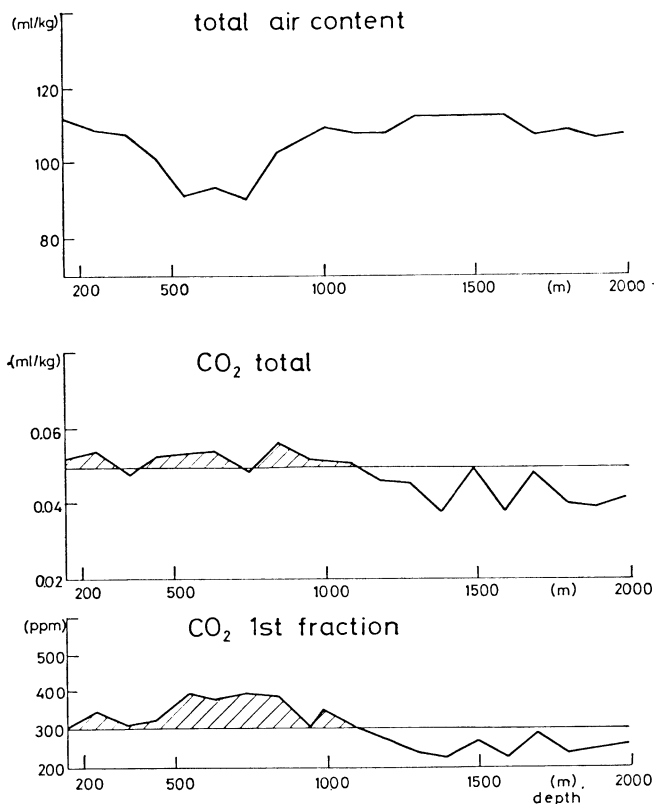


Fig 2. Byrd Core: total gas content, total extracted CO_2 and CO_2 content of the first extraction fraction versus depth.

similar trends. Low values during the last glaciation are followed by higher Holocene values. The change in CO₂ content parallels the $\delta^{18}\text{O}$ transition. Similar minimum values (200 to 230ppm) are found for the last glaciation for both cores. First fraction measurements on young ice (shown here only for the Byrd core) give values around 300ppm for both cores. For most of the Holocene, however, the Camp Century core first fractions contain more CO₂ than those of the Byrd core. See also Berner, Stauffer and Oeschger (1978) for the Camp Century core.

The question must be answered whether the general CO₂ trend in the ice core is mainly due to: 1) a change in atmospheric CO₂ content, or 2) a climatic effect on CO₂ enclosure.

The most probable explanation for the general trend — low values during glacial and higher values during postglacial — is a corresponding change in the atmospheric CO₂ content. The difference between the two profiles in part of the Holocene may be due to a contribution of CO₂ trapped in melt layers during the climatic optimum or due to another climatic effect on CO₂ enclosure at Camp Century. Atmospheric CO₂

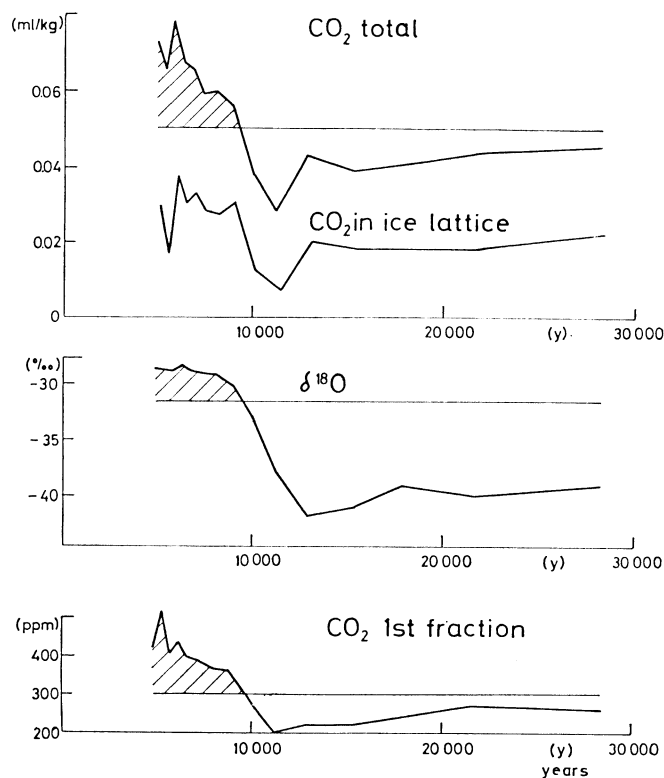


Fig 3. Camp Century Core: measured CO₂ content of the first fraction and estimated CO₂ content of the ice lattice; comparison with $\delta^{18}\text{O}$ profile (Dansgaard and others, 1971). Ages are calculated according to Hammer and others (1978).

concentration during the climatic optimum was, therefore, not necessarily higher than the present one.

A possible explanation for a CO_2 change in the atmosphere

The partial pressure of CO_2 in the atmosphere depends on total CO_2 , alkalinity, and temperature of the ocean surface (Broecker, 1974, Keeling, 1973). During the last glaciation, the ocean volume was smaller by about 3 percent and the ocean surface temperature lower by about 2.3°C . For the first effect, a CO_2 increase by about 1 percent for the second, a decrease by about 6.4 percent can be estimated using chemical equilibria. This results in an overall estimated decrease of the atmospheric CO_2 content during last glaciation by about 5.4 percent, *ie*, these effects cannot account for the suggested difference.

A possible explanation for a change in atmospheric CO_2 content is that it strongly depends on total CO_2 content of the ocean surface. Due to the buffer effect, a relative change in total CO_2 in the ocean surface leads, for constant alkalinity, to a tenfold relative change in the atmospheric CO_2 content. The total CO_2 is determined partly by marine

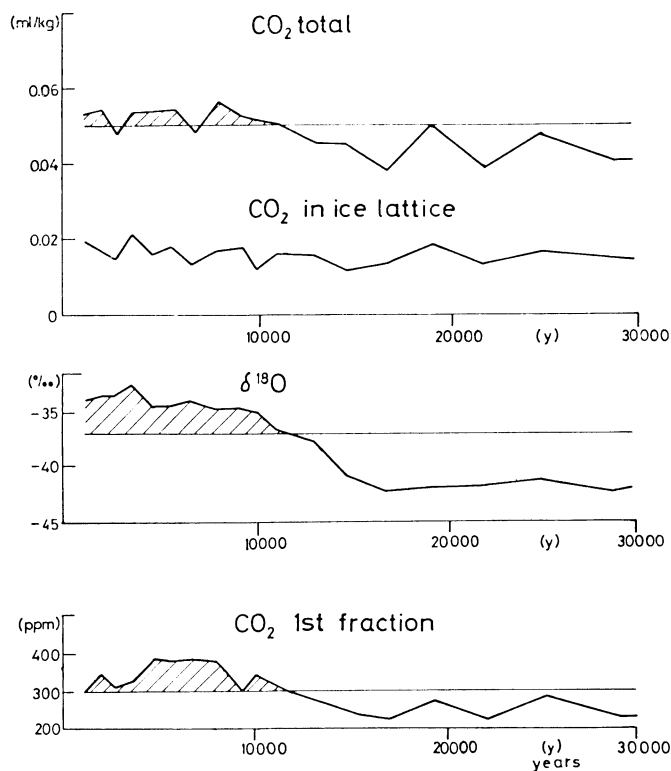


Fig. 4. Byrd Core: measured CO_2 content of the first fraction and estimated CO_2 content of the ice lattice; comparison with $\delta^{18}\text{O}$ profile (Johnsen and others, 1972). Ages are calculated according to Johnsen and others (1972).

biospheric activity which leads to a depletion at the ocean surface compared to the ocean average. A relatively slight change in biospheric activity could, therefore, lead to a significant decrease in atmospheric CO₂.

Influences of a change from 200ppm to 300ppm on the environmental system

Atmospheric ¹⁴C/C ratio

Siegenthaler, Heimann, and Oeschger (1980) discuss the influence of a change in atmospheric CO₂ content on the atmospheric ¹⁴C/C ratio. They show that the exchange flux between the atmosphere and the ocean is proportional to atmospheric CO₂ content. An atmospheric CO₂ content smaller by a factor of 1.5 than the pre-industrial one, therefore, would mean a reduction of the exchange flux by this factor and a corresponding increase of the difference between the atmospheric and the mixed layer ¹⁴C/C ratio. This difference is estimated for the pre-industrial system to be about 5 percent. A reduction of the atmospheric CO₂ content by a factor of 1.5 would increase it to 7.5 percent. The influence on the average oceanic ¹⁴C/C ratio would be negligible. Atmospheric ¹⁴C/C ratio, therefore, would be higher by 2.5 percent, corresponding to an error in age of 200 years. These calculations hold if all the other system parameters are unchanged.

Average global temperature

An atmospheric CO₂ concentration of 200ppm would mean a significantly lower CO₂ greenhouse effect. To estimate the order of magnitude of the influence on global temperature, we use a Gray Model as published in the JASON Report (Chamberlain, 1979). Using the relationship between surface temperature and CO₂ content we find that, for the lower atmospheric CO₂ content of 200ppm, radiative equilibrium would be reached for a 1.4°C lower surface temperature. Model calculation of the expected temperature distribution for a two-fold atmospheric CO₂ increase indicates strong enhancement of the temperature increase in polar areas due to positive albedo feedback and the more pronounced stratification of the atmosphere (Manabe and Wetherald, 1975). A similar enhancement of temperature increase over ice caps probably accompanied the suggested CO₂ increase from 200 to 300ppm after the last glaciation. Much more data is needed to determine whether the probable shift in atmospheric CO₂ at the end of last glaciation, due to its positive feedback, merely reinforced the climatic change or whether it even induced it.

Future work

The data presented here illustrates the importance of natural ice samples for studies of the CO₂ cycle and its fluctuations. Much more information is needed to answer questions regarding the scatter of data from the same epoch and the relationship to other parameters measured on the same samples.

^δ¹³C measurements on both fractions will provide information on: 1) atmospheric ^δ¹³C variations, 2) origin of the CO₂ (air, carbonate,

organic), and 3) physico-chemical processes during precipitation formation, transition from firn to ice and in the ice due to recrystallization.

Measurements of $^{14}\text{C}/\text{C}$ ratio on CO_2 extracted from large amounts of ice in bore holes have been made for several years (Oeschger and others, 1977). They confirm that the CO_2 extracted with the air at the time of occlusion in the ice had $^{14}\text{C}/\text{C}$ ratios close to the atmospheric ratios. The recently developed accelerator based mass-spectrometrical ^{14}C measuring technique enables ^{14}C measurements on samples of 30kg of ice. From such measurements, we expect information on, 1) atmospheric ^{14}C variation (extension of the tree-ring record), and 2) origin of the two CO_2 fractions.

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DISCUSSION

Berger: Why is there a different age for the changeover in the CO₂ fraction and δ¹⁸O ratio at Byrd Station (Antarctica) and Camp Century (Greenland)?

Stauffer: The age calculations are based on a rheological model for the ice flow. In the case of Camp Century, the dating is pretty accurate. Hammer (1978) claims an error of less than 3 percent at an age of 10,000 years. In the case of Byrd Station, the age calculations are very uncertain and an error of several thousand years is possible. Therefore, it is uncertain if the transition from lower to higher δ¹⁸O values, respectively, CO₂ contents occurred at a different time.

Roether: Not knowing your procedure in detail, I would suspect that a clear distinction between your first and second fractions in extracting the CO₂ from the ice is difficult. An alternative might be to try to understand the mechanisms by which CO₂ is originally trapped into the ice lattice. One might then be able to estimate the trapped amount of CO₂ from, eg, the ice structure, and thus obtain the bubble fraction of the CO₂ from the measured totals.

Oeschger: The following studies should give information on the origin of the ice lattice fraction: CO₂ measurements on snow and firn combined with chemical analyses, measurements of the isotopic composition of the extracted CO₂, laboratory measurements on artificially produced snow and ice samples, etc.

Begemann: Why is a different CO₂ content of the atmosphere *not* reflected by the CO₂ in the ice lattice?

Oeschger: We also looked at this question. If Henry's law would hold for the CO₂ fraction in the ice, the varying CO₂ content of the atmosphere *should* be reflected. But the CO₂ in the ice lattice may be due to decomposition of organic debris and/or CO₂ trapped in refrozen melt layers, *ie*, phenomena not directly related to the atmospheric CO₂ content.

Vogel: How much N₂ and Ar is in the second fraction?

Oeschger: From measurements of snow and firn samples, we can estimate that the second fraction contains no more than 0.5 to 1ml air (N₂ + Ar + O₂).