

$^{13}\text{C}/^{12}\text{C}$ RATIOS IN CO_2 EXTRACTED FROM ANTARCTIC ICE

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Abstract. Air is extracted from bubbles of polar ice samples by a dry extraction method, and the $^{13}\text{C}/^{12}\text{C}$ ratio is measured on CO_2 separated from the air.

Ice samples of typically 700 g are crushed at ca. -20°C , the evolving air is trapped cryogenically, and CO_2 is frozen out from this air for mass-spectrometric isotope analysis. First $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results of CO_2 from Antarctic ice cores are presented, and $\delta^{13}\text{C}$ is discussed in relation to atmospheric CO_2 variations. $\delta^{13}\text{C}$ of 400 to 800 year old ice is ca. 1.1 ‰ higher than the 1980 atmospheric value, which agrees well with model-based estimations. The measurement of three ca. 50,000 yr old samples yielded astonishingly low values, but contamination cannot be excluded.

Introduction

The global carbon cycle and its changes, natural and man-made, have been a subject of intense discussions in the past years. Atmospheric CO_2 concentration changes are caused by the transfer of carbon to or from other reservoirs - ocean, land biomass, organic and inorganic sedimentary carbon - and there is often the question as to the role of each reservoir in such changes. Information on this question may be obtained from stable carbon isotope analyses. CO_2 produced from living biomass as well as from fossil fuels has a significantly lower $\delta^{13}\text{C}$ than air- CO_2 ; on the other hand, CO_2 variations due e.g., to temperature changes in the ocean would essentially not influence $\delta^{13}\text{C}$. Therefore, knowledge on the history of $\delta^{13}\text{C}$ in atmospheric CO_2 will help to understand the causes of CO_2 variations.

One of the most promising methods to reconstruct atmospheric CO_2 concentrations in earlier times are measurements on air trapped in polar ice. Such measurements have revealed that at the end of the last glaciation, the atmospheric CO_2 concentration was about 30 percent lower than during the Holocene [Berner et al., 1980; Delmas et al., 1980; Neftel et al., 1982]. ^{13}C analyses on CO_2 from those periods will yield information on the cause of the change [Broecker and Peng, 1984].

CO_2 from fossil fuels as well as from biomass is depleted in ^{13}C by roughly 20 ‰, compared to atmospheric CO_2 . Therefore, the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 must have decreased about parallel to the anthropogenic concentration in-

crease. Thus, the $\delta^{13}\text{C}$ trend of the last centuries is connected to the question of the atmospheric CO_2 concentration history since pre-industrial times. Several authors have attempted to reconstruct the ^{13}C trend of the past 100 to 200 years from tree-rings, but considerable uncertainty has remained. Tree-ring records exhibit relatively high variability introduced by factors other than atmospheric ^{13}C variations; the effects to be studied are about 1 ‰, i.e. small compared to the $^{13}\text{C}/^{12}\text{C}$ fractionation between CO_2 and plant material which apparently is not quite constant. This problem can be avoided by analysing CO_2 extracted from polar ice. In cold ice, air parcels are physically enclosed in bubbles, and fractionation effects are probably negligible. We have carried out such analyses. In this paper we discuss the experimental methods we have used, present first results on the isotopic composition of CO_2 extracted from polar ice and give a preliminary interpretation of the data obtained.

Experimental Methods

The experimental procedure involves three steps:

- extraction of trapped air from an ice sample;
- separation of CO_2 from the air sample;
- mass-spectrometric measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the CO_2 .

To extract the gases from the ice, a dry extraction system is used [Moor and Stauffer, 1985]; it is shortly described in the following. A carefully cleaned ice sample is placed in a stainless steel crusher which then is sealed by metal gaskets. A typical sample is 600 to 800 g of ice, containing ca. 10 % by volume of air. After evacuating the system, the ice is crushed into small chips by a milling cutter. By this process most bubbles are opened. The escaping air is collected in a small container cooled to 15 K by a closed-cycle helium refrigerator. The overall extraction efficiency is about 80 to 90 percent. Special attention has been paid to avoid contamination by organic vapors that would interfere with the mass-spectrometric analyses, as well as by CO_2 adsorbed on the walls of the system. For this purpose we work at a low temperature (-20°C) and keep the extraction time short. As a result contamination by CO_2 makes up less than 0.5 % of a typical CO_2 sample [Moor and Stauffer, 1985]. At the end of the extraction, a fraction of the sample is split off for gas-chromatographic analysis of its CO_2 concentration.

Separation of CO_2 from the extracted air takes place in a glass vacuum system with high-vacuum

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TABLE 1. $\delta^{13}\text{C}$ of CO_2 extracted from air of South Pole (S.P.) and Byrd samples, uncorrected for N_2O .

Site	Depth (meter)	Mean gas age (yr)	$\delta^{13}\text{C}$ (o/oo)
S.P.	160.52 ÷ 160.85	430	-6.71
	160.85 ÷ 161.35	430	-6.72
	171.00 ÷ 171.35	550	-6.68
	172.77 ÷ 173.10	550	-6.85
	182.41 ÷ 182.75	660	-6.67
	182.75 ÷ 182.16	660	-6.65
	183.16 ÷ 183.50	660	-6.61
	192.18 ÷ 192.51	770	-6.73
	192.64 ÷ 193.00	770	-6.56
Byrd	1716.58 ÷ 1717.17	ca. 50,000	-7.89
	1753.87 ÷ 1755.32	ca. 50,000	-7.49
	1755.54 ÷ 1756.35	ca. 50,000	-7.38

O-ring stopcocks. The air sample of typically 50 ml STP is expanded into a 10 liter volume and its size is determined by measuring temperature and pressure. Then the air is pumped with constant flow through a liquid nitrogen trap where CO_2 is frozen out quantitatively. When all the air has passed through the trap (after about 20 min), its temperature is raised to -77°C (dry ice-alcohol bath) for separating CO_2 from water. The CO_2 is then frozen into a 4 ml cold finger where its pressure is measured at room temperature which permits to determine the CO_2 concentration of the air sample and thus to check the efficiency of the separation.

The CO_2 sample, typically 15 μl STP, is transferred to the 0.13 ml cold finger of a triple-collector mass-spectrometer, type MAT 250, where $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are measured simultaneously. To obtain reliable results it is essential to keep the extraction and separation systems and the gas containers thoroughly clean from organic vapors and water. We tested the whole procedure with a standard gas. The results indicate an overall precision of extraction, separation and mass-spectrometric analysis of 0.22 ‰ for $\delta^{13}\text{C}$ and 0.45 ‰ for $\delta^{18}\text{O}$.

For our measurements we selected ice from different depths of a core drilled in 1982 at the South Pole by the Polar Ice Coring Office [Kuivinen, 1983]. The mean annual temperature at the South Pole is -51°C , the mean accumulation rate 8.4 cm water equivalent per year. An ice sample consisted of only one or two large pieces, so that the risk of contamination was kept small. $\delta^{13}\text{C}$ results, referring to the PDB standard, are given in Table 1; the results are not corrected for a bias introduced by N_2O , as discussed in the next paragraph. The accuracy of our $\delta^{13}\text{C}$ calibration versus PDB can be judged from the following results of multiple analyses of international carbonate standards. NBS-20: -1.07 (-1.06 ,

Craig, 1957); NBS-19: $+1.93$ ($+1.95$, Gonfiantini, 1983); NBS-18: -5.01 (5.03); single analyses of CO_2 gas standards yielded -41.52 for NBS-16 (-41.60) and -4.45 for NBS-17 (-4.51). Values in brackets for NBS-20 and NBS-19 are those defining the PDB scale; for the other standards they are mean values of an interlaboratory comparison [Gonfiantini, 1983]. The results show that near $\delta^{13}\text{C} = -7$ ‰, our calibration should be accurate to 0.05 ‰. The CO_2 concentrations of the South Pole samples, as measured by gas chromatography and volumetrically, are all in the range 279 to 289 ppm, which is consistent with other measurements on the same core [Moor and Stauffer, 1984]. The value is higher than results for the pre-industrial CO_2 concentration reported earlier by our laboratory and by the laboratory in Grenoble [Barnola et al., 1983], probably due to experimental effects. More measurements and comparisons with other laboratories are necessary before the new higher value can be accepted with satisfactory reliability.

The bubbles close off only at a certain depth where firn is transformed to ice, and the enclosed air has therefore a younger age than the surrounding ice. Each gas sample contains air from many bubbles which were closed off at somewhat different times and is therefore a mixture of components of slightly different age.

The mean ages of the enclosed air, indicated in Table 1, have been calculated according to Schwander and Stauffer [1984]. The total spread of its age distribution is about 1/3 of the mean age. Besides $\delta^{13}\text{C}$ also $\delta^{18}\text{O}$ of the CO_2 has been measured. The mean $\delta^{18}\text{O}$ value of the nine samples from South Pole is -31.4 ‰ vs. PDB- CO_2 (not corrected for N_2O), with a standard deviation of 2.4 ‰.

We also measured three samples of ice from the last glacial period from Byrd Station, Antarctica ($79^\circ59'\text{S}$, $120^\circ10'\text{W}$). This core was drilled by Lyle Hansen in 1967 [Ueda, 1968]. The mean annual temperature at Byrd Station is -28°C and the estimated mean accumulation rate is 16 cm water equivalent per year. Ice samples from this core have a small cross section, are of fair quality and have been stored for 16 years at different places. The $\delta^{13}\text{C}$ values are shown in Table 1. The age of the Byrd samples of about 50,000 years is estimated according to Dansgaard et al. [1982]. The mean $\delta^{18}\text{O}$ of the three samples is -31.4 ± 1.5 ‰, and the measured CO_2 concentrations are in the range of 202 to 212 ppm.

The mean $\delta^{13}\text{C}$ of the nine samples from the South Pole is -6.69 ‰, with a standard deviation of only 0.08 ‰; interestingly, this scatter is considerably less than the error determined from standard gas analyses (0.22 ‰). From this we conclude that $\delta^{13}\text{C}$ of air- CO_2 did probably not exhibit any significant variations in the about 340 years covered by these samples (mean gas ages 430 to 770 years). An absolute calibration of the procedures has not been possible, since ice

formed during a period of known $\delta^{13}\text{C}$ of the atmospheric CO_2 is not available. If we assume that the mean value does correspond to the original atmosphere and is also representative for the following centuries until the beginning of industrialization, we can compare it with measurements on modern air and tentatively estimate the $\delta^{13}\text{C}$ decrease due to fossil fuel consumption and forest destruction. For this purpose it is necessary to correct for the influence of N_2O on the mass spectrum. N_2O has the same isotopic masses 44, 45 and 46 as CO_2 and cannot be separated from it by freezing, so that the measured ratios of masses 45 to 44, and therefore the $\delta^{13}\text{C}$ values of Table 1 are systematically shifted by an amount proportional to the concentration ratio of N_2O to CO_2 . Weiss [1978] estimated the N_2O concentration of the pre-industrial unperturbed troposphere between 281 and 291 ppb. Taking a mean value of 286 ppb for N_2O and 285 ppm for the pre-industrial CO_2 concentration we obtain, following the procedure of Mook and van der Hoek [1983], a correction of +0.25 ‰. We performed preliminary tests with N_2O - CO_2 mixtures. They confirmed the N_2O correction reported by Mook and van der Hoek. The resulting corrected value is -6.44 ‰, about 1.1 ‰ higher than the result of 7.51 ‰ for modern [1980] South Pole atmospheric air reported by Mook et al. [1983]. It is difficult to estimate the accuracy of this result; tentatively we assume an uncertainty of ± 0.3 ‰ due to possible systematic errors of unknown origin.

Our result can be compared to model calculations for the $\delta^{13}\text{C}$ change [Siegenthaler et al., 1978; Peng et al., 1983]. For the assumption that fossil fuels were the only source of excess CO_2 , these models yield a change until 1980 of -1.0 to -1.1 ‰, i.e., of the same size as our measured value (-1.1 ‰). However, there is no one-to-one relationship between total CO_2 increase since pre-industrial times and $\delta^{13}\text{C}$ decrease, because the uptake of excess CO_2 by the ocean depends on chemical processes, while this is not the case for excursions of $\delta^{13}\text{C}$. Thus, the time of release of the CO_2 into the atmosphere also plays an important role: a relatively large biospheric CO_2 input in the 19th century would have led to a CO_2 increase still well noticeable in 1980, while the $\delta^{13}\text{C}$ perturbation would largely have decayed by that time [Siegenthaler et al., 1978]. Therefore, our $\delta^{13}\text{C}$ result of -6.44 ± 0.3 ‰ for the South Pole samples is compatible with a relatively wide range of pre-industrial CO_2 concentrations and cumulative amounts of CO_2 produced from forest destruction, and it fits very well the CO_2 concentration of 284 ± 5 ppm measured on these samples. For reconstructing the atmospheric CO_2 increase, a detailed time series of the $\delta^{13}\text{C}$ history of the past 150 years will be necessary.

The derived $\delta^{13}\text{C}$ decrease of 1.1 ‰ can be compared to changes estimated from tree-ring records. These range from 0 ‰ [Francey, 1981]

to about 2 ‰ [Freyer, 1979; Peng et al., 1983], with a predominance of values above 1 ‰. Stuiver et al. [1984] measured six trees from isolated sites and partly corrected for growth variations. Their mean $\delta^{13}\text{C}$ change is well comparable with that obtained from the South Pole ice core.

The mean $\delta^{13}\text{C}$ for the three about 50,000 yr old samples from Byrd Station is -7.58 ‰, nearly 1 ‰ more negative than the values for the South Pole samples. Based on theoretical considerations, one would rather expect higher $\delta^{13}\text{C}$ during times of lowered atmospheric CO_2 concentration [Broecker and Peng, 1984; Siegenthaler and Wenk, 1984]. It should, however, be kept in mind that the quality of the Byrd ice samples was not favorable and that therefore the results are less reliable than those of the recently obtained South Pole samples.

$\delta^{18}\text{O}$ of atmospheric CO_2 is about 0 ‰ [Bottinga and Craig, 1960; Mook et al., 1983; Friedli, unpublished results, 1983]. The strongly negative values of our samples, -31 ‰ on the average, were probably caused by oxygen exchange between CO_2 and H_2O , either in the ice or in the extraction systems. An estimate of the equilibrium $^{18}\text{O}/^{16}\text{O}$ fractionation factor between CO_2 and ice indeed leads to an expected value of the observed magnitude. If this isotopic exchange could be confirmed, this would have interesting consequences regarding the interaction between CO_2 and the ice matrix.

Conclusions

The first $\delta^{13}\text{C}$ measurements on CO_2 separated from air extracted from South Pole ice yielded a value 1.1 ‰ higher than $\delta^{13}\text{C}$ of air- CO_2 in 1980, which is well consistent with the measured CO_2 concentration of the samples if compared with model calculations. The South Pole samples yielded a remarkably constant value, from which we conclude that the atmospheric $\delta^{13}\text{C}$ did probably not exhibit any significant change in the time period of ca. 400 to 800 years before present. Before taking the absolute result at face value it is, however, necessary to repeat the measurements on ice from other sites and to eliminate N_2O from the gas.

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