

STABLE-ISOTOPE RATIOS AND CONCENTRATION OF CO₂ IN AIR FROM POLAR ICE CORES

by

U. Siegenthaler, H. Friedli, H. Loetscher, E. Moor, A. Neftel, H. Oeschger and B. Stauffer

(Universität Bern, Physikalisches Institut, CH-3012 Bern, Sidlerstraße 5, Switzerland)

ABSTRACT

Analyses of air trapped in an ice core from the South Pole indicate that the CO₂ concentration may have increased by about 10 ppm and that the ¹³C/¹²C ratio decreased slightly in the thirteenth century. These changes, if really of atmospheric origin, must be due to a significant input into the atmosphere of CO₂, either of biogenic or of oceanic origin.

¹⁸O/¹⁶O ratios in CO₂ from different ice cores are much lower than those which have been observed in atmospheric carbon dioxide. A possible explanation is that the CO₂ has equilibrated isotopically with the ice. We have calculated equilibrium isotope-fractionation factors between ice and carbon dioxide and found that the observed ¹⁸O/¹⁶O ratios of CO₂ are indeed near isotopic equilibrium with the ice. This indicates that an exchange of oxygen atoms probably occurs between ice and included CO₂.

1. INTRODUCTION

In the past few years, experiments have been successful in measuring the CO₂ concentration of air trapped in bubbles in old polar ice. In this way, it has been possible to reconstruct the anthropogenic CO₂ increase, and it has been found that atmospheric CO₂ levels were lower in glacial than in postglacial time. There are also indications of natural CO₂ variations during the past millennium (Raynaud and Barnola 1985), and we present data here that point to a CO₂ input into the atmosphere during the thirteenth century. For a better understanding of the observed variations, it is of interest to know the carbon-isotopic composition of the trapped CO₂. Since biomass and fossil fuels have relatively low $\delta^{13}\text{C}$ values, of about -25‰ (compared with $\delta^{13}\text{C} \approx -7\text{‰}$ for atmospheric CO₂), a CO₂ increase due to input of biospheric or fossil fuel CO₂ is accompanied by a decrease in $\delta^{13}\text{C}$. On the other hand, a CO₂ change due to a net transfer between ocean and atmosphere is expected to have little influence on $\delta^{13}\text{C}$.

We have developed a method for extracting the CO₂ from air trapped in ice and for measuring its carbon- and oxygen-isotope ratios by mass spectrometry (see section 2). We applied this method in order to determine the $\delta^{13}\text{C}$ trend accompanying the CO₂ increase over the past 200 years (Friedli and others 1986). In this paper (section 3) we reconsider a series of CO₂ and $\delta^{13}\text{C}$ results obtained from samples spanning the period of about 1000–1800 A.D., taken from an ice core from the South Pole (Friedli and others 1984).

In addition to $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ was routinely determined in our measurements. Atmospheric CO₂ has a $\delta^{18}\text{O}$ value (versus PDB standard) near 0‰. However, we found values in CO₂ extracted from ice of *c.* -20 to -30‰ , which shows that the oxygen-isotope composition must have changed between the time the air was trapped in the firn and the time it was measured in the laboratory. We suggest that CO₂ equilibrated isotopically with the ice — in other words, that an exchange of oxygen atoms took place. This is discussed in section 4.

2. EXPERIMENTAL METHODS

The procedures for extracting the enclosed air from the ice and for separating CO₂ from air have been described previously (Moor and Stauffer 1984, Friedli and others 1984). Briefly, the first step involves crushing the ice sample (typically about 700 g) in an evacuated, all-metal extraction system at -20°C and collecting the air by condensation at a temperature of 15 K. After measurement by gas chromatography of the CO₂ concentration, CO₂ is separated at liquid-nitrogen temperature; volumetric determination of the quantity of CO₂ makes it possible to check the separation efficiency, or, where no result from gas chromatography is available, to measure the CO₂ concentration. The CO₂ sample (typically 15 μl STP) is then transferred to the mass spectrometer (MAT 250), which is equipped with a small-volume inlet system. Achieved overall precision (1 standard deviation) for $\delta^{13}\text{C}$ is 0.10‰ in good conditions. For $\delta^{18}\text{O}$ the standard deviation is larger, nearly 1‰. The reason must be oxygen-isotope exchange of the CO₂ with water films adsorbed at the walls of sample-containers and extraction systems. (The precision of the ¹⁸O analysis by mass spectrometry alone is 0.1–0.2‰ for samples of about 15 μl STP.)

The results of mass spectrometry have to be corrected to take into account the influence of N₂O, which is separated from air simultaneously with CO₂ in our freezing-out method. N₂O has the same main isotopic masses (44, 45 and 46) as CO₂ and, if the N₂O/CO₂ mixing ratio is known, the correction can be determined (Mook and van der Hoek 1983). We have determined the corrections for our mass spectrometer, and we have developed a method for approximate determination by mass spectrometry of the N₂O/CO₂ ratio, by measuring the abundance of mass 30 which corresponds to the molecule fragment NO⁺ (Friedli and Siegenthaler, in press). In the course of our work we found that N₂O was produced in a Penning cold-cathode manometer (it must have been formed from N₂ and O₂ in the electric discharge). For the early isotope results (samples from South Pole) we cannot give a precise correction for this effect, so they are less accurate than our later data (samples from Siple Station).

For testing the whole experimental procedure, we routinely processed artificial standard air, and during some measuring periods we noticed systematic deviations in the isotope results of the order of 0.1–0.2‰, the cause of which we could not identify. The question thus arises whether $\delta^{13}\text{C}$ results for samples should be corrected accordingly or not. Such deviations found in "standard-air" samples affect the data for the South Pole series, as discussed in the next section. For the Siple Station series ($\delta^{13}\text{C}$ trend over the past 200 years) (Friedli and others 1986), the standard-air measurements fortunately did not exhibit systematic deviations, only the usual scatter around the mean.

3. CO₂ and $\delta^{13}\text{C}$ RESULTS FROM A SOUTH POLE ICE CORE

Figure 1 shows CO₂ results, obtained by gas chromatography and by volume, and $\delta^{13}\text{C}$ results for samples from a core drilled in 1982 at the South Pole; the $\delta^{13}\text{C}$ data have

already been published by Friedli and others (1984). Between A.D. 1210 and 1310 the CO₂ concentration increases from 280 to 286 ppm and slowly decreases afterwards. The gas ages given here are based on the assumption that the air in the firn is well mixed. Because of uncertainties about this assumption and about the ice dating, we estimate the error in the gas ages to be about half a century. With reference to the analytical precision, this increase is significant, and it is shown independently by the gas-chromatography and the volumetric concentration measurements. The δ¹³C data in Figure 1b were corrected by +0.25‰ to allow for the presence of N₂O, with an assumed N₂O concentration of 285 ppb (the data given in Friedli and others (1984) were not corrected). In Figure 1c, average δ¹³C values for the four groups of samples

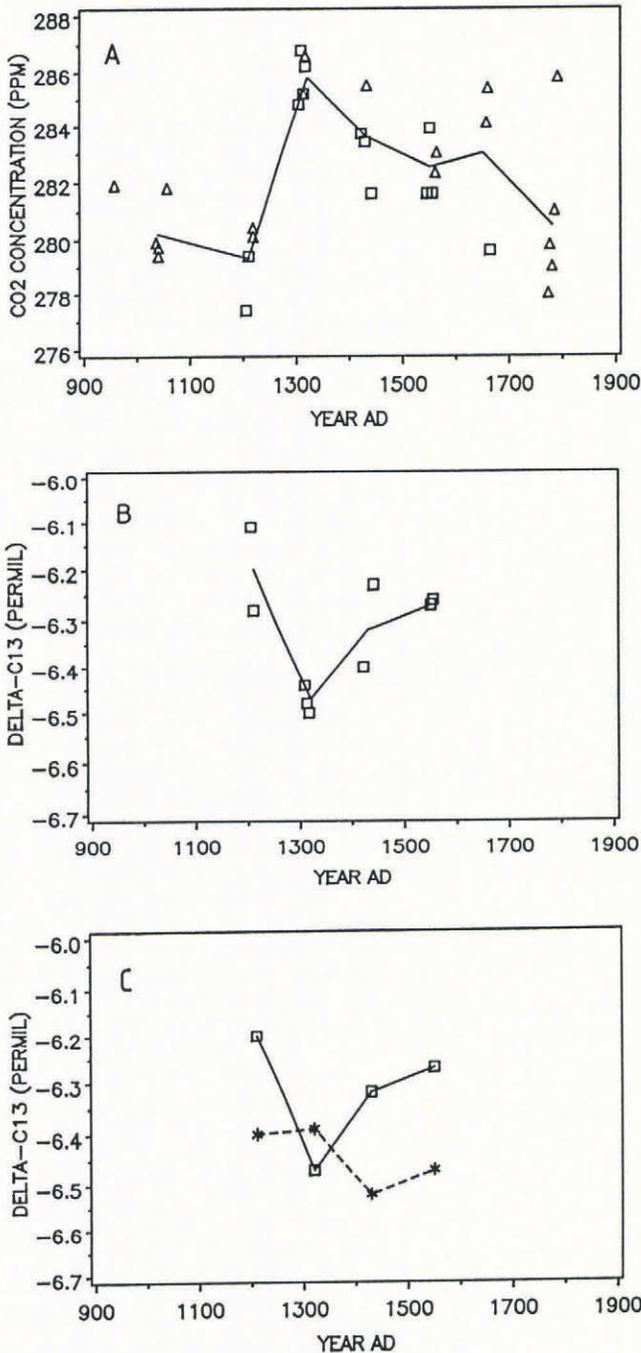


Fig.1. Analytical results versus average gas age for samples from the South Pole ice core. (a) CO₂ concentration, measured by gas chromatography (triangles) and volumetrically (squares). The solid line connects average values for different age intervals. (b) δ¹³C results (standard-air corrected, cf. text); the solid line connects average values. (c) Average δ¹³C results, solid line: standard-air corrected; dashed line: not standard-air corrected.

centering on A.D. 1210, 1310, 1430 and 1550 are shown. As mentioned above, the standard-air isotope results were not constant during that period, so standard-air corrected data are also given in Figure 1c. These corrected data vary antiparallel to the CO₂ concentration, reaching a minimum in A.D. 1310. It is not possible to decide whether the δ¹³C data are more reliable with or without standard-air correction, so we will consider both possibilities.

If the CO₂ results reflect a true atmospheric variation (which can only be determined by measuring more samples from other ice cores covering the same period) then an input of CO₂ into the atmosphere must have occurred in the thirteenth century. In the following we will estimate the size of this input. First, the fact must be taken into account that the air enclosed at a specific depth is not the same age in all the bubbles, because closing of pores at the firn-ice transition occurs over a finite range of densities. Schwander and Stauffer (1984) estimate that at the South Pole the width of the gas-age distribution, defined as the time during which between 10 and 90% of the final volume of bubbles were trapped, is 220 years. Therefore, variations in atmospheric composition which occur over characteristic times less than 220 years will be suppressed in the ice. Neftel and others (in press) developed a method for back-calculating the atmospheric concentration history from the ice-core record; by frequency filtering they avoid unrealistic high-frequency oscillations in the atmospheric concentration. Figure 2 shows the result of such a back-calculation, using a Gaussian curve for the age-distribution curve of the trapped air. The calculated atmospheric increase is 10 ppm instead of the measured 6 ppm, and there is a slight decrease in concentration before the increase; if the atmospheric CO₂ level had been constant before increasing, then the air with the average trapping-time of A.D. 1210 should, because of the broad age distribution, already have had slightly enhanced concentration.

The increase by 10 ppm corresponds to a change in the atmospheric CO₂ mass of about 20 GTC (1 GTC = 10⁹ metric tons of carbon). In addition, the enhanced atmospheric concentration must have brought about a net CO₂ flux into the ocean. If N_a is the atmospheric CO₂ mass, deduced from the ice-core measurements, the input rate p(t) can be calculated from a CO₂ balance for the atmosphere:

$$\frac{dN_a}{dt} = p(t) - F_{ao}(t) \tag{1}$$

We calculated the induced flux into the ocean, F_{ao}, using the box-diffusion model of Oeschger and others (1975), calibrated by means of bomb-produced ¹⁴C and starting from an assumed steady state at 280 ppm; the procedure has been described in detail by Siegenthaler and Oeschger (1987). This is how we calculate p(t), which may represent an input from land vegetation or soils or from a restricted part of the world ocean.

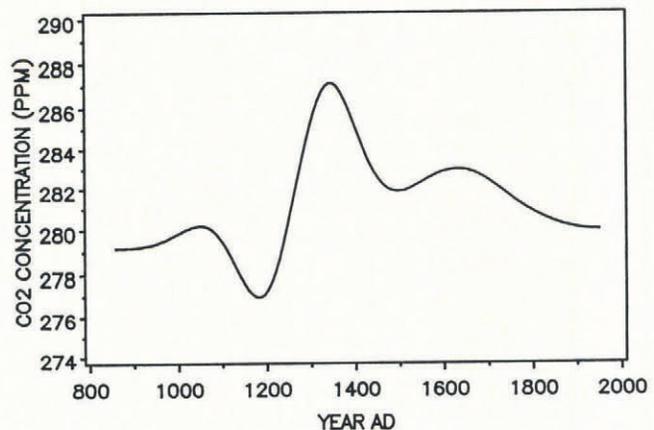


Fig.2. Atmospheric concentration, calculated by deconvolving the ice-core record for the finite time interval of air occlusion.

In Figure 3, the input rate $p(t)$, calculated from the model, and the cumulative input

$$P_{\text{cum}}(t) = \int_{t_0}^t p(t)dt$$

are shown. According to these results, a cumulative input of about 45 GTC over the period A.D. 1200–1350, or about 35 GTC net from A.D. 1000 to 1350, would have been necessary to cause the observed concentration change, and the annual emission amounted to up to $0.4 \text{ GTC year}^{-1}$. (For comparison: nowadays about 5 GTC year^{-1} of CO_2 are produced by fossil-fuel burning.)

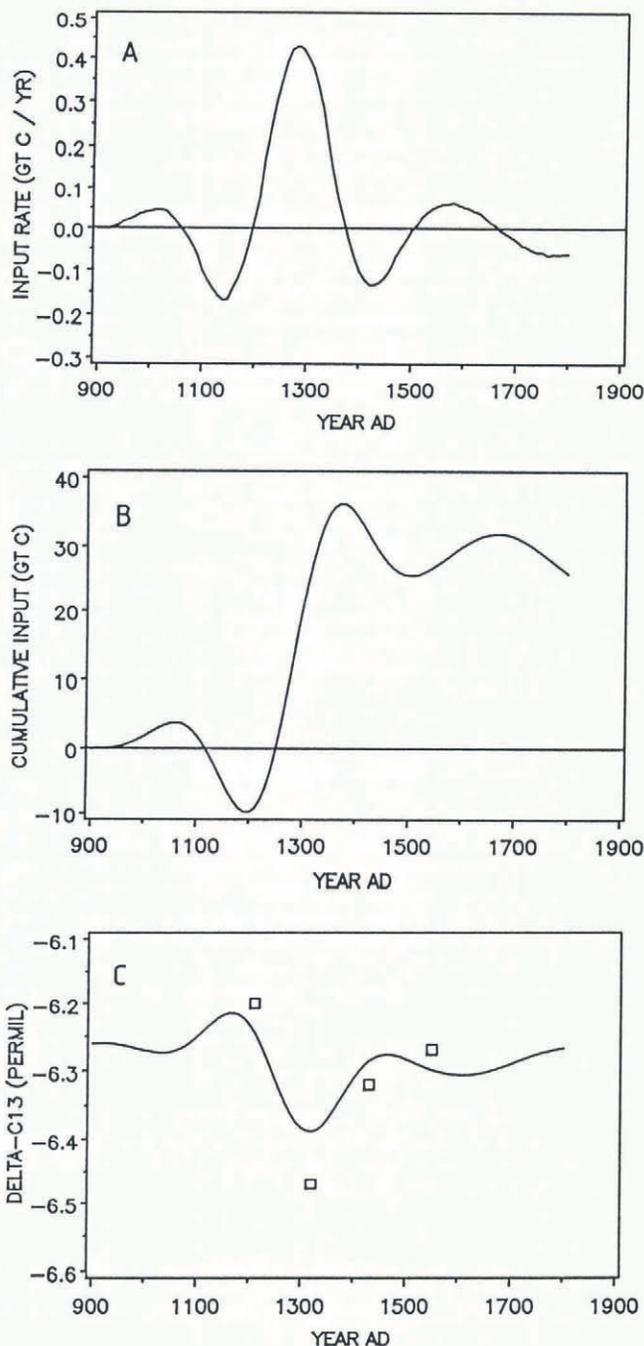


Fig. 3. (a) CO_2 input rate (GTC year^{-1}) to produce the atmospheric CO_2 variations (cf. Fig. 2), calculated using the carbon-cycle model. (b) Cumulative CO_2 input (GTC). (c) Solid curve: atmospheric $\delta^{13}\text{C}$ variation calculated from the model, for the assumption that the input was of biospheric origin; squares: observed $\delta^{13}\text{C}$ values (standard-air corrected).

Before discussing the results further, we must emphasize that all the estimates are based on the hypothesis that the CO_2 variation observed in the ice cores indeed reflects an atmospheric change. However, we cannot exclude the possibility that it is an artefact, due to the enclosure process or ice-gas interaction, until further high-precision measurements have been made on a different ice core. This should be kept in mind for what follows.

The presumed input in the thirteenth and early fourteenth centuries could originate from the biosphere or from some region of the ocean. The amount of roughly 40 GT corresponds to about 6% of the global pre-industrial live land biomass, and to about 2% of the total biomass including soils, which are quite appreciable fractions. The period in which the CO_2 input would have occurred coincides roughly with a late-medieval warm phase as registered in England, so one might speculate that the enhanced temperature could have led to higher soil respiration rates and thus to a net transfer to the atmosphere of carbon from soils. It has been well established in experiments that on a short-term (monthly) basis CO_2 production in the soil is correlated with (monthly) temperature (Dörr and Münnich 1987), but it is not clear whether the net production also varies significantly with temperature over the time-scale of a century. In theory, human activity like deforestation and agricultural expansion in Europe and the Mediterranean region could also be responsible for the increase in CO_2 , but the cumulative input seems rather large for that to be the case.

A biospheric input would cause a decrease in $\delta^{13}\text{C}$ in atmospheric carbon dioxide. Figure 3c shows the isotopic variation calculated with the carbon-cycle model, based on the assumption that the CO_2 input of Figure 3a consisted of biospheric CO_2 with $\delta^{13}\text{C} = -25\text{‰}$. The measured $\delta^{13}\text{C}$ values (shown as squares in Fig. 3c, standard-air corrected data) agree qualitatively with the curve calculated on the model, but show a larger variation. A deconvolution for the finite air-trapping interval does not make much sense because there are not enough data, but the atmospheric variation must have been even larger than that. The starting $\delta^{13}\text{C}$ value for the model has been chosen to match the observed values approximately. The data which had not been standard-air corrected (cf. Fig. 1), however, would not exhibit a decrease at A.D. 1310.

The presumed CO_2 input might also be of oceanic origin, due to a fluctuation in the carbonate chemistry of surface waters in response to a change in the circulation or climate of the ocean. Such a change would certainly seem to be possible. A high-precision record of atmospheric $\delta^{13}\text{C}$ could provide a test: no measurable $\delta^{13}\text{C}$ change would have occurred if the CO_2 input had been of oceanic origin, since carbon in surface water and in the atmosphere are in isotopic equilibrium. Since we are not absolutely certain that the standard-air correction can indeed be applied to our data, we cannot exclude the possibility that the $\delta^{13}\text{C}$ of the atmosphere was constant, i.e. that the CO_2 input came from the ocean.

Another possibility might be that the input was of volcanic origin, e.g. due to the large eruption in A.D. 1259 (Langway and others 1988, this volume). Average volcanic CO_2 emissions are estimated at $0.07 \text{ GTC year}^{-1}$ (Bernier and others 1983), of which, however, a large part goes directly into the ocean. Thus the 40 GTC would correspond to the amount emitted on average into the atmosphere over 1000 years or more. A direct estimate indicates a CO_2 amount of 0.005 GTC for the large eruption of Lakagígur (Laki) in 1783 (Thorarinsson 1969). Thus a volcanic origin does not appear to be likely for the production of 40 GTC within a century or less.

In conclusion, the data from the South Pole ice core point to a possible net injection into the atmosphere of about 40 GTC of biospheric, perhaps of oceanic, origin over the period A.D. 1200–1350. We cannot state with certainty that this input really did occur, since we cannot exclude the possibility that the observed CO_2 increase is an artefact due to some interaction between ice and trapped air, nor can we check whether the applied $\delta^{13}\text{C}$ correction is really appropriate. However, the CO_2 change in the ice is clearly outside the range of experimental error, and the corrected $\delta^{13}\text{C}$ data are consistent with the assumption that the concentration changed as the result of carbon input

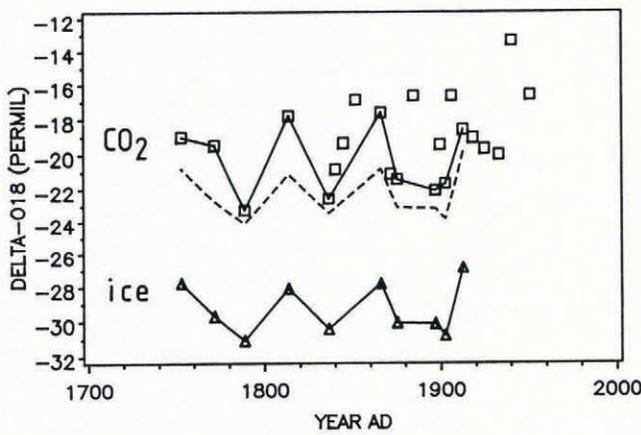


Fig.4. From top to bottom: $\delta^{18}\text{O}$ (versus PDB standard) of CO_2 from the Siple Station ice core (squares; the solid line connects those results for which the $\delta^{18}\text{O}$ in ice has also been measured); $\delta^{18}\text{O}$ of hypothetical CO_2 in isotopic equilibrium with the ice (dashed line); $\delta^{18}\text{O}$ (versus SMOW standard) for ice (triangles). Horizontal axis: average gas age.

from the biosphere. The question of natural CO_2 variations during the Holocene is very important for the understanding of the global carbon cycle, and our data show that a search should be undertaken for such variations by means of high-precision studies on other ice cores from suitable locations like Siple Station.

4. $\delta^{18}\text{O}$ OF CO_2 FROM POLAR ICE

4.1 Equilibrium $^{18}\text{O}/^{16}\text{O}$ fractionation between CO_2 and ice

As mentioned in the Introduction, we found $\delta^{18}\text{O}$ values of -20 to -30‰ (versus PDB) in CO_2 extracted from polar ice, instead of about 0‰ as observed in modern atmospheric CO_2 (Mook and others 1983, Friedli and others, in press). Figure 4 shows the $\delta^{18}\text{O}$ of CO_2 , and of the corresponding ice samples from which the CO_2 was extracted, for the ice core from Siple Station, Antarctica. For this core, the CO_2 and $\delta^{13}\text{C}$ trend of the past 200 years was reconstructed (Neftel and others 1985, Friedli and others 1986). The horizontal axis gives the estimated mean time of gas enclosure. Note that the results for CO_2 are given versus PDB- CO_2 , whereas those for ice are given versus Standard Mean Ocean Water (SMOW). The relation between the two standards is explained below.

The isotopic composition of the CO_2 samples is clearly correlated with that of the surrounding ice. A plausible explanation is that there was an isotopic equilibration between CO_2 and ice in the ice sheet. Isotopic equilibrium between two substances, 1 and 2, can be described by a (temperature-dependent) fractionation factor α : $\alpha(1-2) = R_1/R_2$, where $R_i = ^{18}\text{O}/^{16}\text{O}$ ratio of substance i . For obvious reasons, $\alpha(\text{CO}_2\text{-ice})$ has never been measured, but it can be estimated from equilibrium-fractionation factors between other pairs of substances, noting that if there is thermodynamic equilibrium between substances 1 and 2 and between substances 2 and 3, then there must also be equilibrium between substances 1 and 3. Thus we can write:

$$\alpha(\text{CO}_2\text{-ice}) = \alpha(\text{CO}_2\text{-water}) \alpha(\text{water-vapour}) \alpha(\text{vapour-ice}) \quad (2)$$

The α s at the right-hand side have all been determined experimentally, with the following results (T = absolute temperature):

$$\ln \alpha(\text{CO}_2\text{-water}) = -20.6/T^2 + 17.9942/T - 19.97 \times 10^{-3} \quad (3)$$

(Bottinga, quoted by Friedman and O'Neil 1977).

$$\ln \alpha(\text{water-vapour}) = 1137/T^2 - 0.4156/T - 2.067 \times 10^{-3} \quad (4)$$

(Majoube 1971[a])

TABLE I. $^{18}\text{O}/^{16}\text{O}$ FRACTIONATION FACTORS, ADJUSTED TO SMOW SCALE FOR WATER AND PDB SCALE FOR CO_2 .

Station	Temperature	$\alpha^*(\text{CO}_2\text{-ice})$	$\alpha^*(\text{CO}_2\text{-water})$
South Pole	-51°	1.01471	-
Byrd (50 000 B.P)	-35°	1.00998	-
Siple	-24°	1.00719	-
	0°	1.00213	1.00505

$$\ln \alpha(\text{vapour-ice}) = -11.839/T + 28.782 \times 10^{-3} \quad (5)$$

The last equation is adapted from Majoube (1971[b]), but the constant term has been changed by 0.56×10^{-3} so that Equations 4 and 5 yield $\alpha(\text{ice-water}) = 1.00291$ at 0°C , which is the result of our own experiments (Lehmann and Siegenthaler, in preparation).

According to Equation 2 we then obtain:

$$\ln \alpha(\text{CO}_2\text{-ice}) = 1116.4/T^2 + 5.7396/T + 6.745 \times 10^{-3} \quad (6)$$

By calculating $\alpha(\text{CO}_2\text{-ice})$ we have extrapolated the two fractionation factors (3, 4) (which were measured only for positive Celsius temperatures) for temperatures $<0^\circ\text{C}$. Obviously, some uncertainty is introduced by this extrapolation. We estimate that the error of $\alpha(\text{CO}_2\text{-ice})$ should be smaller than $\pm 1\text{‰}$ at temperatures down to at least -35°C .

Since $\delta^{18}\text{O}$ of CO_2 is expressed versus the standard PDB, it is convenient to take this into account by dividing $\alpha(\text{CO}_2\text{-ice})$ by the conversion factor between PDB- CO_2 and SMOW- CO_2 of 1.04142 (see Friedman and O'Neil 1977): $\alpha^*(\text{CO}_2\text{-ice}) = \alpha(\text{CO}_2\text{-ice})/1.04142$.

Values for α^* are given in Table I for several temperatures, chosen to include the mean annual temperatures of Siple Station, Antarctica (-24°C), South Pole (-51°C) and an estimated temperature of about -35°C at Byrd Station, Antarctica, 50 000 years ago (the approximate age of our samples).

4.2 Observed $\delta^{18}\text{O}$ relation between CO_2 and ice

In Table II, average $\delta^{18}\text{O}$ values are given for CO_2 and for ice. For Siple Station, $\delta^{18}\text{O}(\text{CO}_2)$ includes only values where $\delta^{18}\text{O}(\text{ice})$ was also determined (which is the case for only about half of all the samples). For South Pole and Byrd Station, we had to estimate $\delta^{18}\text{O}(\text{ice})$ from curves measured by Grootes and Stuiver (1988, this volume) (South Pole) and Johnsen and others (1972). Also in Table II, the observed ratios of the $^{18}\text{O}/^{16}\text{O}$ ratios in CO_2 and ice are compared with the (adjusted) fractionation factors α^* from

TABLE II OBSERVED MEAN $\delta^{18}\text{O}$ VALUES IN CO_2 EXTRACTED FROM ICE; α^* = EQUILIBRIUM $^{18}\text{O}/^{16}\text{O}$ FRACTIONATION FACTOR $\text{CO}_2\text{-ICE}$, ADJUSTED FOR CHANGE OF STANDARD.

	Siple	South Pole	Byrd
$\delta^{18}\text{O}(\text{CO}_2)$ (‰, vs PDB)	-20.4	-31.7 ± 0.8	-31.8 ± 0.9
$\delta^{18}\text{O}(\text{ice})$ (‰, vs SMOW)	-29.2	-50.5 ± 1	-40 ± 1
α^*	1.0072	1.0147	1.0100
Degree of equilibration ($\delta(\text{CO}_2) - \delta(\text{atm})$) / ($\delta(\text{eq}) - \delta(\text{atm})$)	0.92	0.87	1.04

Table I. In addition, the degree of equilibration is indicated, defined by

$$(\delta^{18}\text{O}(\text{CO}_2) - \delta^{18}\text{O}(\text{atm})) / (\delta^{18}\text{O}(\text{eq}) - \delta^{18}\text{O}(\text{atm})),$$

where $\delta^{18}\text{O}(\text{atm}) = 0\text{‰}$ is the value in atmospheric air and $\delta^{18}\text{O}(\text{eq})$ is the expected value of CO_2 in isotopic equilibrium with the ice. The degree of equilibration for the three stations is roughly between 90 and 100%. The $\delta^{18}\text{O}$ values of CO_2 at Siple Station are well correlated with $\delta^{18}\text{O}(\text{eq})$ (Fig.4). From all these results, we conclude that the oxygen-isotope ratio in CO_2 extracted from polar ice is essentially determined by equilibration with the surrounding ice. This is surprising, since we would not expect a significant exchange with solid ice.

Before discussing the results further, we must consider the possibility that the equilibration took place in the laboratory, with water vapour originating from the ice sample, during the time between air extraction and CO_2 separation (typically 3–5 d, sometimes up to a few weeks). Indeed, $\delta^{18}\text{O}$ measurements on atmospheric CO_2 samples exhibit relatively large scatter that must be due to oxygen-isotope exchange with water films on the walls of the sample-flask during storage (Francey and Goodman 1985). However, our own results on tropospheric air samples, which were stored for periods from days to weeks (Friedli and others, in press), showed that the degree of isotopic equilibration was always very small, generally of the order of 10%. The possibility of oxygen-isotope exchange can also be checked from our tests, in which gas-free single-crystal ice were milled in the presence of artificial standard air. Although the $\delta^{18}\text{O}$ values of CO_2 from such samples exhibited considerable scatter ($1\sigma = 0.9\text{‰}$), they were not shifted systematically towards the expected value for isotopic equilibrium with ice-derived water vapour. We conclude that exchange with water films at sample-container walls probably affects the reproducibility of the $\delta^{18}\text{O}$ results of CO_2 , but does not determine the absolute values. Therefore the $\delta^{18}\text{O}$ shift in CO_2 must indeed be due to the exchange of oxygen atoms between CO_2 and ice.

Bender and others (1985) measured the $\delta^{18}\text{O}$ of molecular oxygen trapped in old ice and found a shift from glacial to postglacial time. In connection with our results for CO_2 , it is important to emphasize that O_2 and CO_2 behave differently with reference to isotopic exchange. CO_2 equilibrates isotopically with liquid water over a short period, whereas it is well known that atmospheric oxygen is not in isotopic equilibrium with ocean water. Obviously, O_2 is much more inert than CO_2 with reference to exchange with water, and the results of Bender and others suggest that this is also the case for exchange with ice.

4.3 Implications for CO_2 -ice interaction

The amount of ice needed to equilibrate the included CO_2 is quite small: in 1 kg of ice, typically 90 ml STP of air are trapped, or, for a concentration of 280 ppm, 1.1×10^{-6} mol CO_2 , so that the mole ratio CO_2/ice is 2×10^{-8} . For a bubble density of 600 per cm^3 of ice (Schwander unpublished) and a typical value of 90 ml STP of enclosed air per kg of ice, the radius of an average bubble is 0.17 mm at a pressure of 7 bar (actually, the bubble pressure varied between 1 and about 15 bar for the samples from Siple Station as well as those from the South Pole). Under these conditions, an ice shell of 0.1 nm thickness around each gas bubble contains the same number of H_2O molecules as there are CO_2 molecules in the bubble at a CO_2 concentration of 280 ppm. For the observed degree of equilibration of $\geq 90\%$, the CO_2 must equilibrate with an amount of H_2O at least ≈ 10 times larger (on a molar basis), i.e. with an ice shell around the bubble ≥ 1 nm thick. This is only of the order of ten molecular layers, and even that is small compared with the diffusion length of a H_2O molecule in ice during 1 s, $\sqrt{2Dt} \approx 35$ nm (with $D \approx 6 \times 10^{16} \text{ m}^2 \text{ s}^{-1}$ at -20°C (Hobbs 1974)). Thus the CO_2 molecules clearly can come into contact with more than enough H_2O molecules to equilibrate; the question is whether they react with them at all.

How fast is the observed equilibrium achieved? There is no shift away from the equilibrium value in the Siple Station series when progressing from older to younger samples (Fig.4), so the equilibration time at -24°C seems to

be short when compared with the age of the youngest air sample, which is about 70 years.

In liquid water the isotopic equilibration proceeds via the hydration reaction, $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$. Equilibration in water is certainly much faster than in ice and the question arises, whether a liquid-like layer at the air bubble-ice interface could be responsible for the isotopic equilibration process. According to Hobbs (1974), the thickness of the liquid-like layer is of the order of 1 nm at -7°C . It decreases rapidly with decreasing temperature and is negligible at the ice temperature prevailing at the South Pole as well as at Siple Station. However, we cannot fully exclude the possibility that equilibration in the liquid-like layer played a role during storage or transport of the ice cores at temporarily higher temperatures.

ACKNOWLEDGEMENTS

We wish to thank K Hänni for his help with the mass-spectrometry measurements, and M Lehmann for discussion about oxygen-isotope fractionation factors. C Hammer suggested considering a volcanic origin for the thirteenth-century CO_2 input. This work was supported by the Swiss National Science Foundation.

REFERENCES

- Bender M, Labeyrie L D, Raynaud D, Lorius C 1985 Isotopic composition of atmospheric O_2 in ice linked with deglaciation and global productivity. *Nature* 318(6044): 349–352
- Berner R A, Lasaga A C, Garrels R M 1983 The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *American Journal of Science* 283: 641–683
- Dörr H, Münnich K O 1987 Annual variations in soil respiration in selected areas of the temperate zone. *Tellus* 39B(1–2): 114–121
- Francey R J, Goodman H S 1985 Systematic error in, and selection of, in-situ $\delta^{13}\text{C}$. In Francey R J, Forgan B W (eds) *Baseline Atmospheric Program (Australia) 1983–1984*. Department of Science/Bureau of Meteorology: 27–36
- Friedli H, Siegenthaler U In press Influence of N_2O on isotope analyses in CO_2 and mass-spectrometric determination of N_2O in air samples. *Tellus*
- Friedli H, Moor E, Oeschger H, Siegenthaler U, Stauffer B 1984 $^{13}\text{C}/^{12}\text{C}$ ratios in CO_2 extracted from Antarctic ice. *Geophysical Research Letters* 11(11): 1145–1148
- Friedli H, Löttscher H, Oeschger H, Siegenthaler U, Stauffer B 1986 Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries. *Nature* 324(6094): 237–238
- Friedman I, O'Neil J R 1977 *Compilation of stable isotope fractionation factors of geochemical interest*. Washington, DC, United States Government Printing Office
- Grootes P M, Stuiver M 1988 Oxygen-isotope records covering the last 2 ka at South Pole. *Annals of Glaciology* 10: 203
- Hobbs P V 1974 *Ice physics*. Oxford, Clarendon Press
- Johnsen S J, Dansgaard W, Clausen H B, Langway C C Jr 1972 Oxygen isotope profiles through the Antarctic and Greenland ice sheets. *Nature* 235(5339): 429–434
- Langway C C Jr, Clausen H B, Hammer C U 1988 An inter-hemispheric time-marker in ice cores from Greenland and Antarctica. *Annals of Glaciology* 10: 102–108
- Majoube M 1971[a] Fractionnement en oxygène 18 et en deutérium entre l'eau et sa vapeur. *Journal de Chimie Physique* 68(10): 1423–1436
- Majoube M 1971[b] Fractionnement en ^{18}O entre la glace et la vapeur d'eau. *Journal de Chimie Physique* 68(4): 625–636
- Mook W G, Hoek S van der 1983 The H_2O correction in the carbon and oxygen isotopic analysis of atmospheric CO_2 . *Isotope Geoscience* 1: 237–242
- Mook W G, Koopmans M, Carter A F, Keeling C D 1983 Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric carbon

- dioxide. 1. Results from land stations. *Journal of Geophysical Research* 88(C15): 10915-10933
- Moor E, Stauffer B 1984 A new dry extraction system for gases in ice. *Journal of Glaciology* 30(106): 358-361
- Neftel A, Moor E, Oeschger H, Stauffer B 1985 Evidence from polar ice cores for the increase in atmospheric CO₂ in the past two centuries. *Nature* 315(6014): 45-47
- Neftel A, Oeschger H, Staffelbach T, Stauffer B In press CO₂ record in the Byrd ice core 50,000-5,000 years BP. *Nature*
- Oeschger H, Siegenthaler U, Schotterer U, Gugelmann H 1975 A box diffusion model to study the carbon dioxide exchange in nature. *Tellus* 27(2): 168-192
- Raynaud D, Barnola J M 1985 An Antarctic ice core reveals atmospheric CO₂ variations over the past few centuries. *Nature* 315(6017): 309-311
- Schwander J Unpublished Lufteinschluss im Eis von Grönland und der Antarktis. Messung der elektrischen Leitfähigkeit von Eisproben für klimatologische Anwendungen (Ph.D. thesis, Universität Bern, 1984)
- Schwander J, Stauffer B 1984 Age difference between polar ice and the air trapped in bubbles. *Nature* 311(5981): 45-47
- Siegenthaler U, Oeschger H 1987 Biospheric CO₂ emissions during the past 200 years reconstructed by deconvolution of ice core data. *Tellus* 39B(1-2): 140-154
- Thorarinsson S 1969 The Lakagigar eruption of 1783. *Bulletin Volcanologique* 33: 910-929