Reconstruction of the atmospheric CO₂ concentration history from an Antarctic deep ice core, Dome Fuji using a wet extraction technique: analysis procedures, dating of air in ice and concentration variations

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Abstract: In order to deduce the atmospheric CO₂ concentration variations over the past 320 kyr, air samples were extracted from the Dome Fuji deep ice core using a wet extraction method, and their CO₂ concentration values were determined with a reproducibility of 1.0 ppmv. By measuring the CO₂ concentrations of firn air samples collected at Dome Fuji, it was found that the effective bubble close-off depth can be defined by the mid-point of the close-off zone. For dating the air in the ice core, the age difference between ice and air (Δage) was estimated by using a densification model to be between 1000 and 5000 years, showing small and large values during the interglacial and glacial periods, respectively, due primarily to variations of precipitation. The CO₂ concentration variations with a mean time resolution of about 1.1 kyr over the last three glacial-interglacial cycles showed a good correlation with those of δ¹⁸O, which suggests that the Southern Ocean played an important role in the variation of the atmospheric CO₂ concentration during the last three glacial-interglacial cycles.

Keywords: CO₂, Dome Fuji, wet extraction

1. Introduction

The Antarctic ice sheet preserves the past atmosphere in its bubbles and clathrate hydrates. In order to know past variations of atmospheric compositions such as CO₂ and CH₄, various Antarctic ice cores have been analyzed (Barnola et al., 1987; Etheridge et al., 1996; Fischer et al., 1999; Indermühle et al., 1999, 2000; Machida et al., 1996; Monnin et al., 2001; Neftel et al., 1985; Petit et al., 1999; Raynaud et al., 2000; Smith et al., 1999; Stauffer et al., 1998). However, concentration data covering the period older than the last glacial period have been obtained only from the Vostok record (Petit et al., 1999).

We analyzed a deep ice core drilled at Dome Fuji (77°S, 39°E), Antarctica (Dome-F Deep Coring Group, 1998) using a wet extraction technique, to deduce temporal variations of atmospheric components over the glacial-interglacial timescale. The wet extraction method,
in which an ice sample is melted to extract air, is generally thought to suffer from CO$_2$ contamination caused by acid-carbonate reactions in melt water. On the other hand, this method has the advantage of completely extracting air from an ice sample so that the extracted air is free from a clathrate hydrate effect which can cause dry extraction methods to yield an artifact for the measured value of CO$_2$ concentration (Stauffer and Tschumi, 2000).

Air occluded in an ice core is younger than the surrounding ice, because the air is isolated from the atmosphere near the bottom of the firm. Therefore, to compare time variations of air components deduced from ice with those of isotopic and chemical compositions of ice, it is necessary to know the age difference between ice and air ($\Delta$age) at each depth. $\Delta$age is determined on the basis of the ages of air and ice at the close-off depth (Schwander et al., 1993). To know the close-off depth and the age of air in the firm at Dome Fuji under the present condition, we collected air samples from the open pore spaces of the firm covering from the surface to 104 m, and then analyzed them for the CO$_2$ concentration. Since $\Delta$age varies with time due to changes of temperature and accumulation rate, its past values were estimated using a firm densification model (Schwander et al., 1997).

From comparison of the CO$_2$ concentrations deduced from the Dome Fuji core with those from other Antarctic ice cores, as well as with concentrations of Ca$^{2+}$ and acidity of the Dome Fuji core, we have found that our wet extraction method is applicable to deducing past atmospheric CO$_2$ concentrations from this ice core (Kawamura et al., 2003). This paper provides a detailed description of our wet extraction technique, analytical procedure of CO$_2$ concentration in extracted air, analytical results for CO$_2$ concentration in the firm air and its application to the estimation of $\Delta$age, and calculation of $\Delta$age using a firm densification model. The atmospheric CO$_2$ concentrations deduced from the Dome Fuji core are also discussed in comparison with $\delta^{18}$O variations of the core.

2. Experimental procedures

2.1. Air extraction and CO$_2$ concentration analyses

In this study, each ice sample was melted in an evacuated chamber, and air released was collected into a sample tube. Figure 1 shows our wet extraction system schematically. The system consists of four parts: an extraction chamber for melting an ice sample, a tubing system with two water traps, a sample tube, and an evacuation system with a water trap. Except for water traps 1 and 3, which are made of Pyrex glass, all parts of the extraction system including valve seats are made of stainless steel. Viton O-rings and nickel gaskets are used for connecting parts with each other. The sample tube is 35 cm long and 6.3 mm in outer diameter with an inner volume of about 6 ml; one end is closed by welding, and a metal diaphragm valve is attached to the other end. The extraction device used in this study is the same as that in Nakazawa et al. (1993a, b), but a closed cycle refrigerator (JANIS Research) was used to cool the sample tube, instead of liquid helium. Before assembling the device, the extraction chamber was washed with detergents, pure water and acetone. Then, the extraction chamber, the tubing system and the sample tubes were heated at 150°C, and humidified pure air flowed slowly through their insides for several days to precondition the inner walls. After these processes, all components were assembled and then evacuated for a few weeks at 150°C with a turbo molecular pump for further cleaning of their insides. The system was installed in our air-conditioned laboratory room. Prior to extraction, the extraction chamber
was cooled to –15 to –20°C in a cold room, and the sample tube was evacuated to lower than 10⁻³ Pa using a turbo molecular pump at 90°C for more than 2 hours.

The air extraction procedures are as follows. An ice sample of 300–350 g was cut off from a 50 cm-long piece of the ice core using a bandsaw in the cold room at about –20°C. The ice sample was used not only for analysis of the CO₂ concentration but also for those of concentrations of CH₄ and N₂O, stable isotopic ratios of N₂ and O₂, O₂/N₂ ratio and total air content. After removing a surface layer of 1–2 mm thickness (corresponding to 30–50 g of ice) with a degreased cutter knife, the ice sample was placed in the extraction chamber, and the chamber was sealed with a copper gasket. Then, the extraction chamber and the sample tube were connected to the tubing system and the whole device except for the sample tube was evacuated for more than 90 min with a turbo molecular pump through water trap 3 cooled by liquid nitrogen, immersing the lower part of the chamber into an alcohol bath at –15°C. The evacuation was made for further cleaning of the ice sample by sublimating 2 g of ice from its surface, as well as for removing ambient air from the extraction system. The pressure of water vapor sublimated from the ice sample during the evacuation was about 40 Pa, which was monitored with a Pirani gauge. After the evacuation, water traps 1 and 2 were cooled to –100°C, the valve located between water traps 2 and 3 was closed, the valve of the sample tube was opened, and the cold alcohol bath was replaced with a Dewar vessel with hot water. Air released by melting the ice sample was continuously collected into the sample tube cooled at about –263°C by the closed cycle refrigerator, after passing through water traps 1 and 2. In general, the air pressure in the system increased rapidly to about 200 Pa at the beginning of melting of the ice sample, stagnated at around 100 Pa for several minutes, and decreased rapidly to 1 Pa or lower when the melting was finished. After confirming the

Fig. 1. Schematic diagram of the wet extraction system used in this study.
collection of the air by reading the Pirani gauge, the valve of the sample tube was closed, and then the sample tube was disconnected from the extraction system after introducing pure nitrogen gas into the system. The sample tube was laid in our laboratory room for a night before analysis, to assure that air components sublimed in the tube were mixed well.

The CO$_2$ concentration of the sample air was determined by using a gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector (FID). The sample air was introduced into a 1 ml-sample loop of the gas chromatograph at ambient pressure, and then led to two Porapak N columns by switching a multi-port valve to separate CO$_2$ from other air components. CO$_2$ was detected by the FID after being converted to CH$_4$ by Ni catalyst with hydrogen.

CO$_2$ standard gases used in this study were air-based mixtures, and they were classified into two categories, primary and working. The CO$_2$ concentration of the sample air was determined using three working standard gases whose concentrations were 204.5, 249.4 and 299.6 ppmv. The working standard gases were prepared volumetrically and their CO$_2$ concentrations were calibrated against the primary standard gases by using a non-dispersive infrared analyzer (Horiba AIA-210R). The primary standard gases were prepared gravimetrically using 3-stage dilution, with uncertainty of 0.03% in CO$_2$ concentration (Nakazawa et al., 1992; Tanaka et al., 1987).

Prior to analysis of the sample air, three working standard gases were measured several times to relate the CO$_2$ concentration to the chromatogram area. In order to compensate for the temporal drift of the detector response, the working standard gases were measured once every 2 or 3 sample analyses. The concentration of each air sample was determined from the chromatogram areas measured for the sample and three working standards, assuming a quadratic calibration curve between the chromatogram area and the CO$_2$ concentration. The reproducibility of our gas chromatograph analyses was estimated to be about 0.3 ppmv (one standard deviation), by determining the CO$_2$ concentration of a standard gas repeatedly. Some air samples extracted from the Dome Fuji ice core showed chromatogram areas smaller than that of the working standard gas with 204.5 ppmv. In this case, their CO$_2$ concentrations were calculated using two standard gases with 204.5 and 249.4 ppmv, on the assumption that the calibration curve goes through the origin. We confirmed that this assumption is plausible, by determining the CO$_2$ concentration of the standard gas with 204.5 ppmv using the remaining two standard gases.

In order to assess the effect of CO$_2$ desorbed from or adsorbed on the inner surfaces of the extraction system on the measured CO$_2$ concentration, we repeatedly injected about 21 ml of a standard gas into the extraction chamber without water and collected it into the sample tube by the same procedure as actual air extraction. The CO$_2$ concentration of the standard gas samples thus collected differed from its original value by –0.4 ppmv on average, with a standard deviation of 0.7 ppmv. This slightly negative change suggests selective adsorption of CO$_2$ on the inner wall of the extraction system and/or the sample tube.

Since the solubility of CO$_2$ in water is higher than those of other air components, imperfect degassing from melt water of the ice sample would lower the CO$_2$ concentration. Kawamura et al. (2003) examined this effect by using a simple thin film model. A brief description of the procedure and supplementary explanation are as follows. The CO$_2$ flux from air to water is expressed as
\[ F = v (C_{eq} - C_w), \]  

where \( F \) is the CO\(_2\) flux (mol cm\(^{-2}\) s\(^{-1}\)), \( v \) is the transfer velocity of CO\(_2\) through the water boundary layer (cm s\(^{-1}\)), \( C_{eq} \) is the CO\(_2\) concentration in water in equilibrium with air (mol cm\(^{-3}\)), and \( C_w \) is the actual CO\(_2\) concentration in water (mol cm\(^{-3}\)). CO\(_2\) fluxes from air to water for the duration of melting of the ice sample were calculated with a time step of 1 s, and they were integrated over 5 min to estimate the amount of CO\(_2\) remaining in water. The essential input parameters for the model were the temperature and amount of the melt water, the air pressure during the melting of ice, the amount of extracted air and the CO\(_2\) concentration in the air, and they were assumed to be 0°C, 300 cm\(^3\), 1.5 hPa, 25 cm\(^3\)\textsubscript{STP} and 250 ppmv, respectively. The area of the air-water interface was set to 85 cm\(^2\), which is the cross sectional area of the extraction chamber. Since the transfer velocity is difficult to assess, the respective values of \(1\times10^{-2}\) and \(1\times10^{-3}\) cm s\(^{-1}\) were employed as upper and lower bounds, based on previous observations. The former is an overestimation considering that it corresponds e.g. to a sea surface at 20°C with wind speed at 10-m height of 10 m s\(^{-1}\) (Liss, 1988) or to a turbulent water surface in a rapidly stirred vessel (Davies and Rideal, 1963). The latter is roughly equivalent to a sea surface at 20°C with wind speed at 10-m height of 5 m s\(^{-1}\) (Liss, 1988). The solubility effect on the CO\(_2\) concentration, thus estimated, ranged between 3.3 and 0.6 ppmv. These values were obtained by assuming that the contact area between air and water was equal to the cross sectional area of the extraction chamber. However, the actual contact area should be smaller because of the existence of the ice sample. If we can assume the contact area to be the open cross sectional area of the extraction chamber at the beginning of ice core melting, the value was reduced to about 2 ppmv, even employing \(1\times10^{-2}\) cm s\(^{-1}\) for the transfer velocity.

2.2. Sampling and analysis of firn air

Firn air samples at Dome Fuji were collected by the 39th Japanese Antarctic Research Expedition team in December 1998, using a device similar to that used by Schwander \textit{et al.} (1993). The air sampling procedure was as follows. After drilling down to an assigned depth, a bladder was inserted into the borehole and then inflated at the bottom by feeding air from the surface through a plastic tube connected to the top of the bladder. To remove contaminated air which was brought into the borehole by the drill and bladder, about 0.25 m\(^3\) of air was sucked from the bottom of the borehole through another plastic tube which penetrates the bladder. Then, fresh firn air was pumped up and pressurized into a stainless steel flask to about 1.0 MPa. The air was sampled at 15 different levels from the surface to 104 m. It was impossible to pump up air at 108 m.

The air samples collected were analyzed at Tohoku University for several gas components. Their CO\(_2\) concentrations were determined by the same procedure as used for the air samples from the ice core. To assess the overall precision of our firn air analysis, we compared the CO\(_2\) concentrations of two air samples collected at the surface of the Dome Fuji site with the results of direct atmospheric observations at Syowa Station by the National Institute of Polar Research and Tohoku University (Morimoto \textit{et al.}, 2003) for the same period. The CO\(_2\) concentrations of the surface air samples agreed well with those of the direct observations within 0.7 ppmv.
3. Results and discussion

3.1. Vertical profile of CO2 concentration in firn and its implication for Δage

The CO2 concentrations of the firn air samples collected at Dome Fuji are shown in Fig. 2. The CO2 concentration is 365.4 ppmv at the surface and decreases gradually with increasing depth to 345.0 ppmv at 95 m, and then rapidly to 332.2 ppmv at 104 m. Taking account of the fact that the atmospheric CO2 concentration has been increasing for the last 2 centuries, the observed concentration profile implies that older air exists in the deeper layer, as a result of slow gas movement in firn which is driven by molecular diffusion. The contribution of gravitational separation to the CO2 concentration in firn (Schwander, 1989) is estimated from the measured values of δ15N of the collected air samples (our unpublished data) using the equation

\[ \frac{\Delta C}{C} = \frac{\delta^{15}N}{1000} (m - 29), \]  

where \( C \) is the CO2 concentration and \( m \) (g) is the molecular weight of CO2. The values calculated using this equation varied from 0 ppmv at the surface to +2.7 ppmv at the deepest sampling depth. This result indicates that the gravitational correction is important for reconstructing the past atmospheric CO2 concentrations precisely from the Dome Fuji ice core.

The change in CO2 concentration is remarkable for the depth interval below 95 m. The apparent downward speed of CO2 was estimated to be 6.5 m yr\(^{-1}\) for 0–90 m and 1.0 m yr\(^{-1}\) below 95 m, by comparing the CO2 concentrations in the firn, corrected for the gravitational separation, with the atmospheric CO2 concentrations at Syowa Station (Aoki et al., 2000; Morimoto et al., 2003; Nakazawa et al., 1991) and the South Pole (Keeling et al., 1995). The CO2 concentration at 104 m was found to correspond to the atmospheric value in 1975. The slow gas movement in the deepest layers of firn is attributable to bubble formation in the close-off zone at 90–108 m (Hondoh et al., 1999). The gas diffusivity in the close-off zone is significantly reduced due to decreased open porosity and increased tortuosity of the open pore. However, the downward speed of CO2 in the close-off zone is still much higher than that of firn itself, which is only about 0.03 m yr\(^{-1}\). This suggests that the non-diffusive layer (Etheridge et al., 1996; Schwander et al., 1997) does not exist at Dome Fuji, probably due to

![Fig. 2. Vertical profile of the CO2 concentration in firn at Dome Fuji in December 1998.](image)
low annual accumulation which leads to no clear seasonal layering in the firm.

\[ \Delta \text{age} \] can be calculated by subtracting the transport time of CO\textsubscript{2} from the ice sheet surface to the close-off depth by diffusion from that of the firm layer by densification. By assuming that non-diffusive zone does not exist in the firm at Dome Fuji, we can define the effective close-off depth as the midpoint of the close-off zone in which pore space is gradually transformed into bubbles. This depth was found to be 99 m at Dome Fuji (Hondoh et al., 1999). Since the age of ice at this depth (over 2 kyr at the present condition) is larger by 2 orders of magnitude than the age of air, \( \Delta \text{age} \) for the Dome Fuji core can be approximated by the age of ice at the close-off depth.

3.2. Temporal variation of \( \Delta \text{age} \) at Dome Fuji

The age of air in ice (\( a_{\text{air}} \)) at a certain depth is determined by the age of ice (\( a_{\text{ice}} \)) and \( \Delta \text{age} \),

\[ a_{\text{air}} = a_{\text{ice}} - \Delta \text{age}. \] (3)

The relationship between the depth and the age of ice for the Dome Fuji ice core was derived by using a one-dimensional ice flow model with two reference points and an estimated history of the accumulation rate (Watanabe et al., 2003a). From this relationship, the age of ice at a depth of 2500 m was estimated to be 323 kyr BP. As described above, \( \Delta \text{age} \) is essentially determined by the age of ice at the effective close-off depth. To estimate \( \Delta \text{age} \) in the past, it is necessary to know the temporal variations of density at the effective close-off depth, density profile of firm and snow accumulation.

The past density values at the effective close-off depth at Dome Fuji were estimated by using an empirical relationship between temperature and density at the bottom of the close-off zone, which was derived by Martinerie et al. (1994) from the data at various Antarctic and Greenland sites. However, the following correction was applied in this study. The present density value calculated using this relationship for Dome Fuji was 842 kg m\textsuperscript{-3}. This value is equal to the density at 109 m which is close to the bottom of the close-off zone (Dome-F Ice Core Research Group, 1998; Hondoh et al., 1999), and is larger by 22 kg m\textsuperscript{-3} than the observed density at the effective close-off depth of 99 m. Assuming that this difference has not changed over the last 320 kyr, we subtracted 22 kg m\textsuperscript{-3} from the values calculated by using the equation given in Martinerie et al. (1994). The past surface temperatures and accumulation rates were estimated from \( \delta^{18}O \) of the Dome Fuji ice core, using the respective empirical relationships of the annual mean temperature and accumulation rate to \( \delta^{18}O \) of surface snow around Dome Fuji (Satow et al., 1999). Using these values as input data, the vertical density profiles and \( \Delta \text{age} \) in the past were estimated by a dynamic densification model (Schwander et al., 1997), with minor modifications of some constants of equations (see Appendix).

As seen in Fig. 3, \( \Delta \text{age} \) over the past 320 kyr calculated for the Dome Fuji core varied between 1 and 5 kyr, showing clear glacial-interglacial cycles. The values were 1–2 kyr for the past four interglacial periods and 4–5 kyr for the past three glacial maxima. Such a large fluctuation is caused primarily by the variation of the accumulation rate and partly by the variation of the close-off depth.

We examined the sensitivity of the calculated results to the constants employed for the densification model, by comparing \( \Delta \text{age} \) calculated using the respective original and modi-
Compared with $\Delta$age calculated employing the original constants, the modified constants yielded smaller values by 290 and 670 years for the average Holocene and last glacial maximum (LGM) conditions, respectively. We also compared the effective close-off depths derived from the densification model with diffusive column heights (Schwander et al., 1997; Sowers et al., 1992) estimated from measured $\delta^{15}$N of N$_2$ (our unpublished data). For the Holocene, the effective close-off depth was found to be deeper by 7 m, on average, than the diffusive column height, which could be explained by the existence of a well-mixed layer in the uppermost part of the firm. However, the difference between both factors increased greatly in the glacial periods, e.g. 37 m in the LGM. If this difference is ascribed to overestimation of the close-off depth by the densification model, it is expected that $\Delta$age for the LGM would be overestimated by 1.4 kyr, under the assumption that the firm density profile in the LGM can be reproduced well by the densification model.

### 3.3. Atmospheric CO$_2$ variation during the last three glacial-interglacial cycles

Figure 4 shows the concentration variations of atmospheric CO$_2$ over the past 320 kyr reconstructed from the Dome Fuji core. The measured values of the CO$_2$ concentration were corrected for the gravitational enrichment in firm using $\delta^{15}$N in N$_2$ measured for the respective ice samples (our unpublished data). Kawamura et al. (2003) compared the CO$_2$ concentrations, thus obtained, with those from the Vostok (Petit et al., 1999), Taylor Dome (Indermühle et al., 1999, 2000) and Dome C (Monnin et al., 2001) ice cores using dry extraction methods, and discussed the possibility of CO$_2$ production by chemical reactions in meltwater during the wet extraction procedure. They indicated from the comparison that our results reconstruct the atmospheric CO$_2$ variation fairly well for the past 65 kyr. They also found that our values for the LGM were higher by 10–20 ppmv than those from the other cores, possibly due to CO$_2$ chemically produced in the melt water. It was also shown that the CO$_2$ concentrations derived from the Dome Fuji core for the past 320 kyr are in good agreement with those from the Vostok core, with systematic differences of about 20 ppmv for the periods around the last interglacial period.

As seen in Fig. 4, the CO$_2$ concentration varied between 186 and 300 ppmv over the last 320 kyr, showing clear evidence for glacial-interglacial variations with high values in the interglacial periods and low values in the glacial periods. Since the $\delta^{18}$O value of ice can be used as a proxy for temperature, the values of $\delta^{18}$O measured for the Dome Fuji core...
(Watanabe et al., 2003b) are also shown in Fig. 4. From the comparison between the CO₂ concentration and \( \delta^{18}O \) values, it is evident that their variations are similar to each other. It is seen in Fig. 4 that the CO₂ concentration increases rapidly by 80–100 ppmv at the last three glacial terminations. The maximum CO₂ concentrations in the early Holocene and the last three interglacial periods (corresponding to marine isotope stages (MIS) 5.5, 7.5 and 9.3) are 272, 300, 278 and 299 ppmv, respectively. The maximum CO₂ concentrations in MIS 5.5 and 9.3 are higher than those in the early Holocene and MIS 7.5. A similar relationship is also found in the \( \delta^{18}O \) record. During the glacial periods, the CO₂ concentration decreases gradually from high values in the interglacial periods to low values of 200 ppmv or less around the glacial maxima. More detailed inspection of the data indicates that some of the relatively large \( \delta^{18}O \) increases with short time periods seem to be accompanied by CO₂ increases of 20–60 ppmv (e.g. at about 62, 86, 212, 252, 276 and 302 kyr BP).

The records of \( \delta^{18}O \) in ice from the Dome Fuji, Vostok, Taylor Dome (Grootes et al., 2001; Steig et al., 2000) and Byrd (Blunier and Brook., 2001; Johnsen et al., 1972) cores showed similar long-term variations for the last glacial period. These variations are also similar to those of sea surface temperature (SST) in the Southern Ocean estimated from deep-sea cores (Pichon et al., 1992; Waelbroeck et al., 1995). Therefore, the above-mentioned features in the Dome Fuji record could support the idea that the Southern Ocean played an important role in the CO₂ concentration variations during the glacial-interglacial cycles (Indermühle et al., 2000; Petit et al., 1999). The Southern Ocean might have contributed to low atmospheric CO₂ concentrations in the glacial periods through dust-induced intensification of biological pump (Broecker and Henderson, 1998) or expansion of the sea ice area around Antarctica (Stephens and Keeling, 2000), in addition to changes in solubility induced by the SST variation.

The variations of CO₂ and \( \delta^{18}O \) around the four interglacial periods are enlarged in Fig. 5. It is clearly seen that the CO₂ concentration increases almost in parallel with \( \delta^{18}O \) during the last three glacial-interglacial transitions, although it is difficult to discuss the phase events.
relationship between both factors precisely because of the error in the estimated Δage and the insufficient time resolution of the CO₂ data. The rapid increase of the CO₂ concentration at the end of each glacial period would have contributed to the temperature rise. On the other hand, the decreases of the CO₂ concentration at the end of the interglacial periods, i.e. during about 118–111, 225–215 and 312–304 kyr BP, lag behind the δ¹⁸O changes by several kyr. This fact implies that CO₂ did not cause the temperature change during these periods but the global carbon cycle was affected by climate change.

4. Conclusions

In order to reconstruct concentration variations of atmospheric CO₂ over the last three
glacial-interglacial cycles, we analyzed a deep ice core drilled at Dome Fuji, Antarctica using a wet air extraction technique. To estimate the bubble close-off depth at the site, which is important for deriving Δage, air samples were collected from the firn and analyzed for the CO₂ concentration. The analytical results of the firn air suggested that molecular diffusion is the most important process for gas movement in the firn column at Dome Fuji, and that an apparent non-diffusive zone does not exist in the close-off zone. The effective bubble close-off depth was estimated on the basis of the firn air analyses to be the midpoint of the close-off zone. For dating air occluded in the Dome Fuji core, temporal variations of Δage were estimated by using a densification model. Δage, thus obtained, ranged between 1000 and 5000 years, showing small values during the interglacial periods. Such a large fluctuation is found to be caused primarily by the variation of accumulation rate, and secondarily by that of the close-off depth. By considering both the ice age and Δage, the CO₂ concentrations for the past 320 kyr were reconstructed from the Dome Fuji core at a mean time resolution of about 1.1 kyr, with higher resolution at shallower depth. The CO₂ concentration values, thus obtained, varied between 186 and 300 ppmv, showing a clear glacial-interglacial variation with high values in the interglacial periods and low values in the glacial periods. The comparison of the CO₂ concentration with δ¹⁸O in ice suggests that the Southern Ocean played an important role in the interglacial-glacial variation of the atmospheric CO₂ concentration. It was also shown that the CO₂ concentration increased almost in parallel to that of δ¹⁸O during the glacial terminations, suggesting a contribution of CO₂ to the temperature rise through its radiative forcing. The CO₂ concentration decreased at the end of the interglacial periods, following after the δ¹⁸O decrease. This implies that the carbon cycle on the Earth’s surface was changed by global climate change in those times.

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References

Dome-F Ice Core Research Group (1998): Preliminary investigation of paleoclimate signals recorded in the ice core
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(Appendix: Firn densification model)

The past values of Δage at Dome Fuji were estimated by using a dynamic densification model including heat transfer in ice sheet (Schwander et al., 1997), which is based on a densification model by Pimienta and Barnola (Barnola et al., 1991). For the model calculation, the upper part of the ice sheet at Dome Fuji was divided into 12010 layers so that the thickness of each layer was equal to annual thickness for the upper 12000 layers and 100 m for the remaining lower 10 layers. The time step was set to 1 year. The past data of surface temperature and accumulation rate required by the model as input data were estimated from δ18O in ice (see text). The surface density was set to the present value of 300 kg m⁻³, assuming that

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its value has not changed over the period covered by this study.

In this study, we modified some constants in equations given by Schwander et al. (1997) so that the density profile calculated under the present temperature and accumulation rate was close to the observational results. For firm densities $\rho < 520$ kg m$^{-3}$ ($\rho < 550$ kg m$^{-3}$ in Schwander et al. (1997)), the following equation was used:

$$\frac{d\rho}{dt} = k_0 A(\rho_{ice} - \rho),$$  \hspace{1cm} (4)

where

$$k_0 = C \exp\left(-\frac{10160}{RT}\right).$$  \hspace{1cm} (5)

Here, $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the temperature (K), $A$ is the accumulation rate (kg m$^{-2}$ s$^{-1}$), $\rho_{ice}$ is the density of pure ice (kg m$^{-3}$), and $C=0.015$ ($C=0.011$ in Schwander et al. (1997)). For 520 $< \rho < 800$ kg m$^{-3}$,

$$\frac{d\rho}{dt} = k_1 \rho f \Delta p^\mu,$$  \hspace{1cm} (6)

where

$$k_1 = 25400 \exp\left(-\frac{60000}{RT}\right),$$  \hspace{1cm} (7)

$$f = 10^{\left(\frac{a}{\rho_{ice}}\right)^{1.5} + \left(\frac{\rho}{\rho_{ice}}\right)^{1.5} + \left(\frac{\rho}{\rho_{ice}}\right)^{10^{\nu}}},$$  \hspace{1cm} (8)

with $\alpha=-29.166$, $\beta=84.422$, $\gamma=-87.2$ and $\delta=30.7$ ($\gamma=-87.425$ and $\delta=30.673$ in Schwander et al. (1997)). $\Delta p$ is the effective pressure (Pa), given by subtracting bubble pressure from over-burdened pressure, and $\mu=3$ (creep exponent). For $\rho < 800$ kg m$^{-3}$, eqs. (5) and (6) were also used, but with

$$f = \varepsilon \cdot \frac{3}{16} \cdot \frac{\left(1 - \frac{\rho}{\rho_{ice}}\right)}{\left(1 - \left(1 - \frac{\rho}{\rho_{ice}}\right)^{\frac{1}{3}}\right)^3},$$  \hspace{1cm} (9)

where $\varepsilon=1.7$ ($\varepsilon=1$ in Schwander et al. (1997)).

For heat transfer in the ice sheet, the equations given in Schwander et al. (1997) were used without modification.