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Atmospheric CO_2 variations over the last three glacial–interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique

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ABSTRACT

A deep ice core drilled at Dome Fuji, East Antarctica was analyzed for the CO_2 concentration using a wet extraction method in order to reconstruct its atmospheric variations over the past 320 kyr, which includes three full glacial–interglacial climatic cycles, with a mean time resolution of about 1.1 kyr. The CO_2 concentration values derived for the past 65 kyr are very close to those obtained from other Antarctic ice cores using dry extraction methods, although the wet extraction method is generally thought to be inappropriate for the determination of the CO_2 concentration. The comparison between the CO_2 and Ca^{2+} concentrations deduced from the Dome Fuji core suggests that calcium carbonate emitted from lands was mostly neutralized in the atmosphere before reaching the central part of Antarctica, or that only a small part of calcium carbonate was involved in CO_2 production during the wet extraction process. The CO_2 concentration for the past 320 kyr deduced from the Dome Fuji core varies between 190 and 300 ppmv, showing clear glacial–interglacial variations similar to the result of the Vostok ice core. However, for some periods, the concentration values of the Dome Fuji core are higher by up to 20 ppmv than those of the Vostok core. There is no clear indication that such differences are related to variations of chemical components of Ca^{2+}, microparticle and acidity of the Dome Fuji core.

1. Introduction

Knowledge of the atmospheric CO_2 variation and its relation to climate in the past is very important for understanding the global carbon cycle and therefore assessing the future climate change due to elevated CO_2 concentrations. In order to elucidate the budget of anthropogenic CO_2, first systematic and precise observations of atmospheric CO_2 were begun at Mauna Loa and the South Pole in the late 1950s (Keeling et al., 1976a; b). Since then a comprehensive monitoring network has been established around the globe (e.g., Conway et al., 1994; Keeling et al., 1995; Nakazawa et al., 1997). Great efforts have been devoted to reconstructing the concentration history of atmospheric CO_2, using various methods such as analyses of atmospheric CO_2 concentration data measured chemically (Fraser et al., 1986), of spectral absorption lines of atmospheric CO_2 (Stokes and Barnard, 1986), of vertical profiles of inorganic carbon concentration in the oceans (Brewer, 1978) and of air occluded in polar

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ice cores. In particular, the analyses of air extracted from Antarctic ice cores have provided high-quality records of the past atmospheric CO_2 variations over timescales from decades to several hundred thousand years (e.g., 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; Smith et al., 1999; Stauffer et al., 1998; see Raynaud et al., 2000 for a recent review). However, only one continuous CO_2 record has been obtained for an extremely long period covering more than one glacial–interglacial cycle (Barnola et al., 1987; Petit et al., 1999) using the deep ice core recovered at the Russian Antarctic station, Vostok (78°27′S, 106°51′E). The Vostok record revealed that the atmospheric CO_2 concentration varied between 180 and 300 ppmv during the past 420 kyr, showing a close correlation with temperature changes estimated from the hydrogen isotopic compositions of ice (Fischer et al., 1999; Petit et al., 1999).

We analyzed a deep ice core drilled at Dome Fuji (77°19′S, 39°42′E; Fig. 1), Antarctica (Dome-F Deep Coring Group, 1998) using a wet extraction technique, to deduce temporal variations of atmospheric CO_2 on the glacial–interglacial timescale. The air samples extracted were also analyzed to estimate past variations of the CH_4 and N_2O concentrations, the isotopic ratios of N_2 and O_2, the O_2/N_2 ratio and the total air content; analyses of these variables will be described elsewhere. Due to low accumulation rates at this site (about 3 cm water equivalent at present), the age of the bottom part of the Dome Fuji ice core is little over 320 kyr BP, which includes the last three glacial–interglacial cycles. The stratigraphy is undisturbed and no upstream corrections are needed, because the drilling was made at the summit of a local dome.

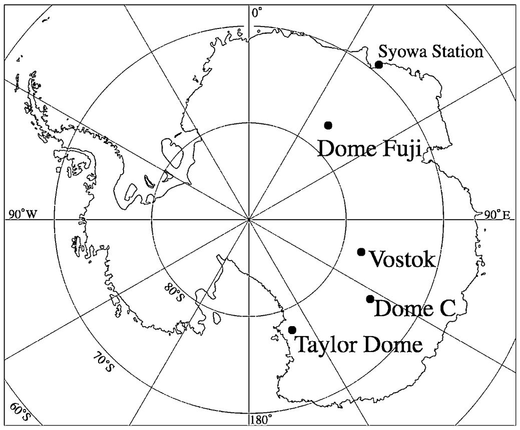

Fig. 1. Locations of the Dome Fuji, Vostok, Taylor Dome and Dome C drilling sites for deep ice cores. Japanese Antarctic station, Syowa is also shown.

It is generally thought that the wet extraction method is prone to the risk of CO_2 contamination caused by acid–carbonate reactions in melt water. However, it can be expected that the influence of CO_2 produced by such reactions may be insignificant for the Dome Fuji core, since Dome Fuji is located far from the coast of the Antarctic Continent and the concentration levels of chemical impurities and dust are low in the core. In contrast to dry extraction techniques, complete air extraction from ice samples is expected using a wet extraction method. This assures that the extracted air is free from any clathrate hydrate effect (Stauffer and Tschumi, 2000) on its components, possibly leading to artifacts in CO_2 concentration.

In this paper, we describe the variations of the atmospheric CO_2 concentration reconstructed from the Dome Fuji deep ice core using the wet extraction technique. The results obtained in this study are also compared with those from other Antarctic deep ice cores, and similarities and differences among these records of the past CO_2 concentration are discussed.

2. Experimental procedures

2.1. *Dome Fuji deep ice core*

The deep ice core used in this study was recovered from Dome Fuji, East Antarctica (Fig. 1). Detailed description of the drilling operation for the Dome Fuji ice core has been given elsewhere (Dome-F Deep Coring Group, 1998). Therefore, only a brief description of the drilling site and the ice core is presented here. The elevation of the ice sheet surface is 3810 m a.s.l., the ice thickness is 3090 m, the average annual mean net accumulation rates measured from 1966 to 1985 is 32 kg m^{-2} yr^{-1}, and the snow temperature at 10 m depth, which corresponds approximately to the annual mean air temperature, is −58 °C. The drilling of the core was started in 1995 using a mechanical drill and n-butyl acetate as borehole liquid, and reached a depth of 2503 m in 1996. The ice core, with a diameter of 9 cm, was cut into sections of 50 cm length each; each piece was subdivided along the core axis into three parts with the respective cross-sectional areas of 60, 25 and 15% of the total. The core samples with the largest cross-sectional area were used in this study. The quality of the core is quite good even in the brittle zone between 500 and 840 m (15–42 kyr BP in age of air). The transition from bubbles to clathrate hydrates begins at about 450 m and ends at about 1200 m (Ikeda-Fukazawa et al., 2001; Narita et al., 1999), corresponding to an air age of 12–73 kyr BP, respectively.

2.2. *Air extraction and CO_2 concentration analyses*

The air extraction device used in this study was the same as in Nakazawa et al. (1993a; b), with the modification that a closed cycle refrigerator was used to cool the sample tubes, instead of liquid helium. The extraction chamber, the tubing and the sampling tubes were washed sufficiently using detergents and pure water. Then, they were heated at 150 °C, and humidified pure air was allowed to flow slowly through their inside for several days to precondition the inner walls. This was also effective in minimizing the deterioration risk of the sample air during its storage inside the sample tube, which is caused by CO_2 produced by the reaction of remaining organic compounds with O_2 in the sample air. After these processes, all components were assembled and then evacuated for a long time at 150 °C for further cleaning of their inside.

We used an ice sample of 300–350 g for the measurements of CO_2, CH_4 and N_2O concentrations, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, $\delta(O_2/N_2)$ and total air content at each depth. After removing a surface layer of a thickness of 1–2 mm from each sample (corresponding to 30–50 g ice) with a degreased cutter knife, we put the ice sample in the extraction chamber cooled at -15 °C and evacuated it for over 90 min. The purpose of the evacuation is to ensure further cleaning of the ice sample by sublimating 2 g of ice from its surface, as well as to get rid of ambient air from the extraction system. Then, the ice sample was melted by immersing the chamber into hot water, and the air released from the ice was collected continuously in the sample tube cooled at -265 °C, after passing through two water traps at -100 °C. The time required for melting the ice sample and transferring the air to the sample tube was shorter than 10 min. After collecting the air, the sample tube was laid in our laboratory room with ambient temperatures for one night to assure that the extracted air components were mixed well before its analysis.

The CO_2 concentration of each air sample was determined by using a gas chromatograph equipped with a flame ionization detector. The sample air was first introduced into a sample loop of the gas chromatograph at ambient pressure, and then to two Porapak N columns by switching a multi-port valve. CO_2 separated from other air components was detected after converting to CH_4 using a methanizer with nickel catalyst. A quadratic calibration curve between chromatogram peak area and CO_2 concentration was used, which was obtained every 2–3 sample analyses from three working standard gases with CO_2 concentrations of 204.5, 249.4 and 299.6 ppmv. When the peak area of CO_2 in the sample was smaller than that of the working standard with 204.5 ppmv, the calibration curve was obtained by applying a quadratic equation to the data measured for the two standards with 204.5 and 249.4 ppmv, under the assumption that the equation goes through the origin. We confirmed, by determining the CO_2 concentration value of the standard gas with 204.5 ppmv using the remaining two standard gases, that this assumption is plausible. The reproducibility of our gas chromatograph analyses was better than 0.2 ppmv. The CO_2 concentrations of the working standard gases were calibrated against our primary standards prepared gravimetrically with uncertainties of 0.1 ppmv.

In order to estimate the overall precision of the ice core analyses, we repeatedly injected about 21 cm^3 of the standard gas into the extraction chamber without water, after evacuating the whole system for longer than 1 h, and collected it in the sample tube by the same procedure as used in the collection of air samples from the ice core. Each standard gas was measured within 1–2 d after their collection for its CO_2 concentration. The change of the CO_2 concentration was -0.4 ppmv on average, with the standard deviation of 0.7 ppmv. The slightly negative change suggests selective adsorption of CO_2 on the inner wall of the extraction system and/or the sample tube.

Since CO_2 is highly soluble in water, it is expected that the CO_2 concentration is lowered by 4 ppmv at most (see Appendix) due to imperfect degassing from the melt water of the ice sample. We also have to examine the effect of chemical reactions in the melt water on the measured values of the CO_2 concentration. However, it is difficult to estimate this effect quantitatively for each ice sample, because chemical properties of the ice core are highly variable even over a short depth interval. Therefore, this effect will be discussed later by comparing our result with those obtained from other Antarctic ice cores using a dry air extraction method, as well as with the concentrations of some chemical components in the Dome Fuji core.

3. Dating of air occluded in Dome Fuji ice core

To determine the age of air in ice (a_{air}) at a certain depth, it is necessary to know the age of ice (a_{ice}) and the age difference between air and its surrounding ice (Δage),

$$a_{\mathrm{air}} = a_{\mathrm{ice}} - \Delta\mathrm{age}. \quad (1)$$

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 at 97.8 and 1852.3 m, which correspond to 2.3 and 141 kyr BP, respectively, and an estimated history of the accumulation rate (H. Shoji, personal communication). From this relationship, the age of ice at a depth of 2500 m was estimated to be 323 kyr BP.

The value of Δage can be calculated by subtracting the transport time of CO_2 from the ice sheet surface to the effective close-off depth by diffusion from the age of ice at that depth. The effective close-off depth is defined as an arithmetic mean of the respective depths where 10 and 90% of finally trapped air are enclosed in bubbles. However, Δage for the Dome Fuji ice core is essentially determined by the age of ice at the effective close-off depth, since the transport time of surface CO_2 to that depth is only about two decades (Schwander et al., 1997), which is negligibly small as compared to the age of ice of over 2 kyr at the effective close-off depth.

To estimate the age of ice at the effective close-off depth in the past, we have to know the temporal variations of the density at that depth and density profile of firn. The past density values at the effective close-off depth at Dome Fuji were estimated by using an empirical relationship between the temperature and the density at the bottom of the close-off zone (Martinerie et al., 1994). However, the density calculated using this method for the present condition was larger by 22 kg m^{-3} than the observed effective close-off depth. Taking this into account, the calculated density values were shifted down by this amount, assuming that such a difference has not been changed over the last 320 kyr. The vertical density profiles in the past were estimated by using a dynamic densification model including heat transfer in the ice sheet (Schwander et al., 1997). The model requires the histories of the surface temperature and the accumulation rate as input data. For this purpose, empirical relations formulated by Satow et al. (1999) between these valuables and $\delta^{18}O$ in ice (Watanabe et al., 1999) were used. In this study, we slightly modified some of the constants in the equations by Schwander et al. (1997) so that the density profile calculated under the present temperature and accumulation rate was close to the observation.

As seen in Fig. 2, the calculated Δage values for the past 320 kyr for the Dome Fuji core vary between 1 and 5 kyr, showing clear glacial–interglacial cycles; the values for the past four interglacial periods were 1–2 kyr, while those for the past three glacial maxima were 4–5 kyr. Such a large fluctuation is caused primarily by the variation of the accumulation rate, and secondarily by the variation of the close-off depth.

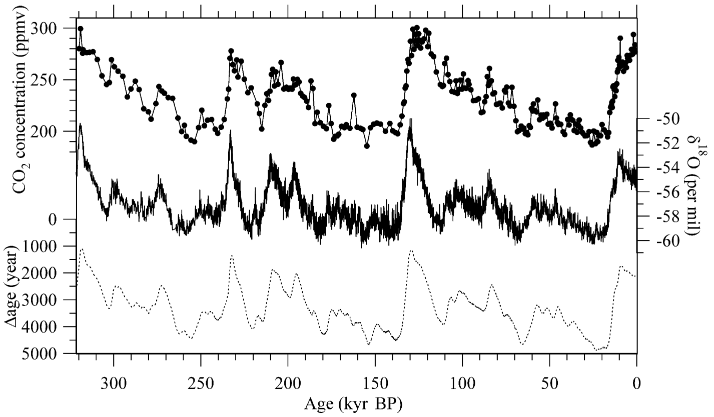

Fig. 2. Variations of the CO_2 concentration over the past 320 kyr deduced from the Dome Fuji ice core (solid circles). The $\delta^{18}O$ values of ice (solid line, Watanabe et al., 1999) and calculated age differences between air and its surrounding ice (dashed line) are also shown.

We examined the sensitivity of the model result to the constants of the above-mentioned equations, by comparing the Δage values calculated with the respective sets of the original and modified constants. The Δage values calculated with the modified constants for the average Holocene and LGM conditions were smaller by about 0.3 and 0.7 kyr, respectively, than those with the original constants. We also found, from the comparison of the effective close-off depths derived from the densification model with the diffusive column heights (Schwander et al., 1997; Sowers et al., 1992) estimated from the measured δ^{15}N of N_2 (our unpublished data), that the differences between both factors increased significantly in the glacial periods, e.g. 37 m in the LGM. If we can ascribe these differences to an overestimation of the close-off depth based on the model, Δage estimated for the LGM would be reduced by 1.4 kyr at most, under the assumption that the density profile of firn was the same as that predicted by the densification model.

4. Results and discussion

Figure 2 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 by 1–2 ppmv for the gravitational enrichment in firn using δ^{15}N in N_2 (Sowers et al., 1992) measured for the respective ice samples (our unpublished data). The CO_2 concentration varied between 190 and 300 ppmv, with high values in the interglacial periods and low values in the glacial periods. From the comparison with the δ^{18}O record of the Dome Fuji ice core (Watanabe et al., 1999), it is obvious that the overall variations of the two components are similar to each other. The timing of the rapid increase in the CO_2 concentration at the end of each glacial period is almost synchronous with δ^{18}O, suggesting that the CO_2 increase made some contribution to the temperature rise during the glacial termination. However, during the period from the interglacial to the glacial maximum, the decrease of the CO_2 concentration is delayed by 6–10 kyr relative to the decrease in δ^{18}O. This may imply that the global carbon cycle changed in response to global climate change. A similar time delay was also observed in the Vostok record (Fischer et al., 1999; Petit et al., 1999; Cuffey et al., 2001).

In order to examine whether the concentration history of atmospheric CO_2 is reconstructed well by the analyses of the Dome Fuji core, the values obtained in this study were compared with those from other ice core studies using dry extraction methods, as well as with concentrations of some chemical components from the Dome Fuji core. In a similar comparison, Anklin et al. (1995) found that the wet extraction method clearly overestimated the CO_2 concentrations for a Greenland core. Its possible causes are attributed to acid–carbonate reactions (Anklin et al., 1995; 1997; Delmas, 1993; Smith et al., 1997a; b) and oxidation of organic compounds (Tschumi and Stauffer, 2000). Since the Dome Fuji ice core is acidic as a whole, with background acidity levels of 2–7 μmol L^{-1} (Fujita et al., 2002a; b), the acid–carbonate reactions may occur in melt water by employing the wet extraction method, if carbonates are present in the core in high enough quantities.

4.1. *Comparison with the results from other cores for the past 65 kyr*

In Fig. 3, the CO_2 concentrations from the Dome Fuji core for the past 25 kyr are compared with those from the Vostok core (Petit et al., 1999), the Taylor Dome core (Indermühle et al., 1999; 2000) and the Dome C core (Monnin et al., 2001). The results from the Taylor Dome and Dome C cores are thought to be fairly reliable, since individual values were determined by measuring six small ice samples taken from

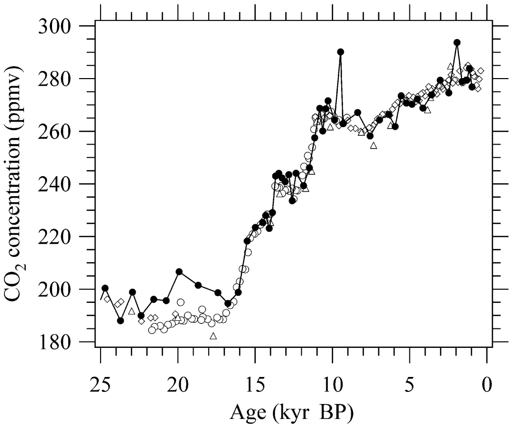

Fig. 3. CO_2 concentrations deduced from deep ice cores drilled at Dome Fuji (solid circles), Vostok (open triangles, Petit et al., 1999), Taylor Dome (open diamonds, Indermühle et al., 1999; 2000) and Dome C (open circles, Monnin et al., 2001) for the past 25 kyr.

neighboring depths, resulting in scattered values with estimated uncertainty of 1.5 ppmv (one standard error). In the Holocene, the CO_2 concentration from the Dome Fuji core decreases from 272 ppmv at 10 kyr BP to 258 ppmv at 7.5 kyr BP, and then increases to the pre-industrial level of about 280 ppmv. Such a behavior of the CO_2 concentration is very similar to that of the Taylor Dome record, except for the two high values of 290 ppmv at 9.5 kyr BP and 293 ppmv at 1.9 kyr BP. These high values are probably due to CO_2 produced during the air extraction procedure. In this regard, our preliminary analyses of the Dome Fuji core using the dry extraction method showed 265 and 279 ppmv for the ice core samples at 9.5 and 1.9 kyr BP, respectively, which are close to the values obtained in the Taylor Dome record.

The comparison of the CH_4 concentrations from the Dome Fuji core (our unpublished data) and the Dome C core (Monnin et al., 2001) suggests that the differences between the air age scales of both cores are less than 300 yr for the period 14–11 kyr BP and less than 500 yr around 17 kyr BP (at the onset of CH_4 increase). During this last glacial termination, the CO_2 concentration from the Dome Fuji core increases rapidly with time, showing that the mean values are 197 and 267 ppmv between 17.4 and 16.1 kyr BP and between 10.8 and 10.3 kyr BP, respectively. A more detailed inspection of the data revealed that the increasing trend of the CO_2 concentration depends on time. The CO_2 concentration increases at a rate of 18 ppmv kyr^{-1} during 16.8–15.5 kyr BP and 7 ppmv kyr^{-1} during 15.5–13.9 kyr BP, rises very fast by 24 ppmv within the following 200 yr (13.9–13.7 kyr BP), becomes stable during 13.7–11.9 kyr BP, and then increases again at a rate of 30 ppmv kyr^{-1} during 11.9–10.8 kyr BP. A similar CO_2 variation was also found in the Dome C record (Monnin et al., 2001). The CO_2 concentrations from the Dome Fuji core are almost consistent with or slightly higher than those from the Vostok core after 17 kyr BP. During 22–17 kyr BP (corresponding to the LGM), the CO_2 values from the Dome Fuji core are systematically higher by 10–20 ppmv than those from the Taylor Dome core, the Dome C core and the Vostok core, possibly due to excess CO_2 produced during the wet extraction procedure.

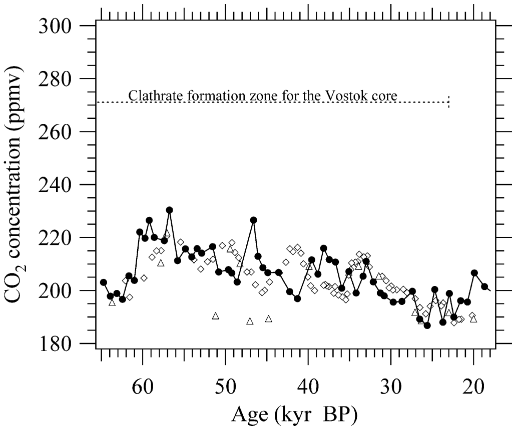

Fig. 4. Same as in Fig. 3, but for the period 20–65 kyr BP.

Figure 4 shows the CO_2 concentrations from the Dome Fuji core during 20–65 kyr BP, corresponding to the latter half of the last glacial period. Also shown are the corresponding results from the Vostok and Taylor Dome cores. The age scale for the Taylor Dome core for this period was adjusted to the GT4 age scale of the Vostok core (Indermühle et al., 2000). The CO_2 variations from the Dome Fuji core are generally in good agreement with those from the Taylor Dome core, except for apparently high values at 57 and 47 kyr BP in the Dome Fuji record. The Dome Fuji record is also in agreement with the Vostok record, but three values at 45, 47 and 51 kyr BP in the Vostok record are lower by as much as 10–20 ppmv. Since these low concentration values are not found in the Taylor Dome record with a higher time resolution, the discrepancy could be ascribed to the underestimation of the Vostok values. The low CO_2 concentration values in the Vostok record are observed at 765, 788 and 835 m (Petit et al., 1999). These depths are included not only in the depth interval where the quality of the ice is rather poor (Barnola et al., 1991), but also in the transition zone from bubbles to clathrate hydrates spanning the interval from 500 to 1250 m (Uchida et al., 1994). We also found, from our preliminary analyses of the Dome Fuji core with the dry extraction method, that at four depths between 845 and 915 m (42–48 kyr BP) in the transition zone but below the brittle zone, the CO_2 concentrations are between 185–191 ppmv, which are clearly lower than the Taylor Dome values. From the measurements of the N_2/O_2 ratio in air from ice cores (Ikeda et al., 1999; Ikeda-Fukazawa et al., 2001), it was found that fractionation of gas components occurs in the transition zone, especially at cold sites such as Vostok and Dome Fuji. If CO_2 is enriched in clathrate hydrates rather than in bubbles, the dry extraction method could yield lower CO_2 concentrations than real, because its air extraction efficiency is higher for bubbly ice than for clathrate hydrate ice. In fact, such a phenomenon was found by Stauffer and Tschumi (2000) for the North GRIP ice core, Greenland. On the other hand, the CO_2 concentration values deduced from the Taylor Dome core are not subject to this problem, since this core contains bubbles only. From the above comparison, we conclude that the CO_2 concentration derived from the Dome Fuji core using the wet extraction method reproduces its atmospheric variations fairly well at least for the last 65 kyr, and that the results presented here give an important upper limit for the reconstruction of past CO_2 concentrations.

To examine the possibility of contamination by CO_2 originating in acid–carbonate reactions during the wet air extraction procedure, the CO_2 concentrations from the Dome Fuji core are compared in Fig. 5 with the Ca^{2+} concentrations in ice (Watanabe et al., 1999) which are generally used as an indicator of the carbonate concentration. Considering high Ca^{2+} concentrations in the Dome Fuji core for the LGM and some other part of the glacial periods, it is remarkable that the influence of excess CO_2, based on the comparison with the other cores, is only about 20 ppmv at most.

As mentioned above, the CO_2 concentrations between 548 and 599 m at Dome Fuji, corresponding to 17–22 kyr BP, are systematically higher by 10–20 ppmv than those from the other cores. The ice in this depth interval was formed during the LGM, and its Ca^{2+} concentration is the highest in the whole record. However, if excess CO_2 is produced only by acid–carbonate reactions, the concentration increase of 10–20 ppmv due to this CO_2 corresponds to 0.04–0.08 μmol L^{-1} of carbonates, which is only 2–4% of the average Ca^{2+} concentration (1.9 μmol L^{-1}) for this depth interval. High Ca^{2+} concentrations are also seen in 460–548 m (13–17 kyr BP), 599–730 m (22–33 kyr BP) and 1060–1130 m (59–65 kyr BP), with the respective mean Ca^{2+} concentrations of 1.3, 1.0 and 1.2 μmol L^{-1}. The CO_2 concentrations from these depths at Dome Fuji agree quite well with those obtained from the other cores, indicating that almost no CO_2 was produced during the wet extraction. During the Holocene period, two high CO_2 concentration values are found in the Dome Fuji record. The Ca^{2+} concentrations at 149.7 and 364.9 m, each separated by less than 10 cm from the depths where the high CO_2 concentration values appear, are 0.07 and 0.04 μmol L^{-1}, respectively. On the other hand, the other Holocene samples with Ca^{2+} concentrations (0.15 μmol L^{-1} on average) several times as high as those at 149.7 and 364.9 m show fairly consistent CO_2 concentrations.

From the above comparisons, it is obvious that excess CO_2 is not well correlated with the Ca^{2+} concentration. This fact may imply that calcium in the Dome Fuji ice core, which is initially emitted mainly as calcium carbonate from continental areas, was mostly neutralized in the atmosphere by acids such as H_2SO_4 during its transport to the central part of Antarctica (Anklin et al., 1995), especially during the glacial periods. Another possible explanation is that calcium carbonate existed as particles in the ice and did not sufficiently dissolve and react during the air extraction (Stauffer and Berner, 1978). However, it may be difficult in both cases to quantify the excess CO_2 using the Ca^{2+} concentration, because the amount of excess CO_2 would be controlled not only by the concentration of calcium carbonate, but also by its dissolution and the relevant reaction rates, which are closely related to factors such as the size of calcium carbonate particles and the acidity of melt water.

We also compared the CO_2 concentration with acidity (Fig. 5; Fujita et al., 2002a; b) and microparticle concentration (Watanabe et al., 1999). The acidity values used for the comparison were estimated from high-frequency-limit conductivity measurements (AC-ECM) with a depth resolution of 1 mm, and their estimated errors were found to depend on depth. As seen in Fig. 5, the values of acidity of the ice samples used in this study range generally between 1 and 6 μmol L^{-1}, with the highest value of 9 μmol L^{-1}. These values are mostly at background levels. Acidity would not be helpful as an indicator for the excess CO_2, because the hydrogen ion concentrations required for producing 10–20 ppmv of the CO_2 concentration are only 0.04–0.08 μmol L^{-1}. In fact, no clear relationship between the excess CO_2 and acidity was found for the Dome Fuji ice core. The microparticle concentration can be used as an indicator for the concentrations of impurities originating in continental areas. The microparticle concentrations around the LGM (14–30 kyr BP) are 50–250 ppb, which are much higher than Holocene levels (0–30 ppb). The CO_2 concentrations for this period agree during 14–17 and 22–30 kyr BP and disagree during 17–22 kyr BP with those from the other cores using the dry extraction methods. This result suggests that it is difficult to derive a relationship between the microparticle concentration and excess CO_2, although the measurements of CO_2 and microparticle concentrations should be done simultaneously for each ice sample to draw a certain conclusion. Since CO_2 is produced by oxidizing organic compounds, such as formaldehyde (HCHO), formic

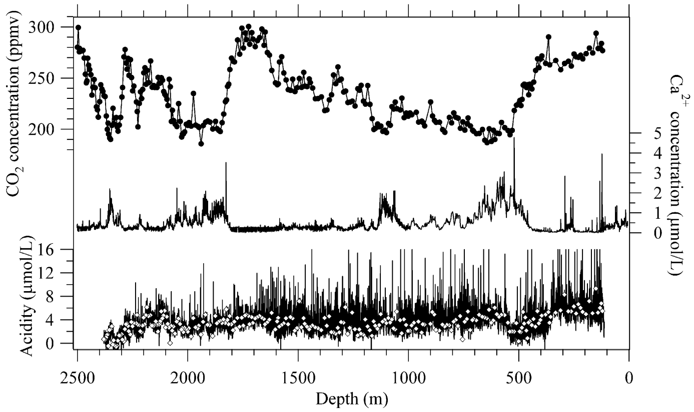

Fig. 5. Comparison of the CO_2 concentration (top) with Ca^{2+} concentration (middle, Watanabe et al., 1999) and acidity (bottom, Fujita et al., 2002a) for the Dome Fuji ice core. The acidity was estimated from high-frequency-limit conductivity measurement (AC-ECM), and the estimated error varies with depth. Solid lines for acidity represent 11 cm-running mean values, and open diamonds indicate the measured values at depths where the CO_2 concentration analysis was made. The acidity values higher than 16 μmol L^{-1} are not shown in this figure.

acid (HCOOH) and acetic acid (CH_3COOH), with hydrogen peroxide (H_2O_2) and others, this process could be another source for the excess CO_2. In this regard, Tschumi and Stauffer (2000) found that the oxidation of organic compounds is at least as important as the acid–carbonate reactions for in situ production of CO_2 in the Greenland ice. Since such reactions could also occur during the wet extraction procedure, the detailed measurements of organic compounds contained in the ice samples would be helpful for examining if they produced CO_2 during the wet extraction process.

4.2. Comparison with the Vostok record for the past 320 kyr

For comparison of the CO_2 concentration for the times older than 65 kyr BP, only the results from the Vostok core are available (Petit et al., 1999; Fischer et al., 1999). The CO_2 concentration values derived from the Dome Fuji core for the past 320 kyr are compared in Fig. 6 with those from the Vostok core. Since the air age scales of Petit et al. (1999) and Fischer et al. (1999) for the Vostok ice core agree with each other to within about 1 kyr, we employed the former scale for the following discussion. The age scales of the Dome Fuji and Vostok cores are in good agreement with each other for the last 180 kyr, but the difference becomes recognizable for the period before about 200 kyr BP. By comparing characteristic features of the CO_2 concentration variations obtained from both ice cores, the age scale of the Dome Fuji core was found to be younger by up to 8 kyr than that of the Vostok core. Petit et al. (1999) evaluated the accuracy of their Vostok GT4 timescale, based on a strong relationship between the variations of $\delta^{18}O$ in air and the summer insolation at 65°N. Using the same approach with our own $\delta^{18}O$ data (unpublished data), we found that the air age scale of the Dome Fuji core employed in this

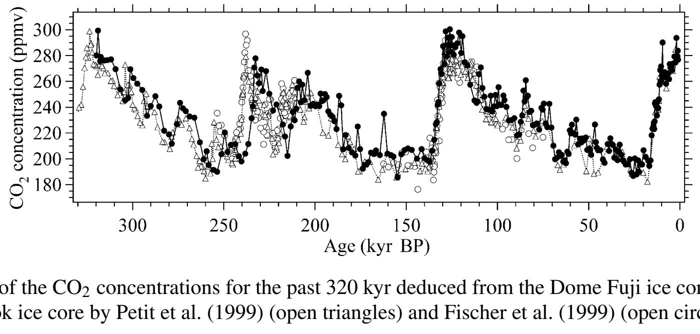

Fig. 6. Comparison of the CO_2 concentrations for the past 320 kyr deduced from the Dome Fuji ice core (solid circles) with those from the Vostok ice core by Petit et al. (1999) (open triangles) and Fischer et al. (1999) (open circles).

study is possibly underestimated by 10–15 kyr for the period before 200 kyr BP.

Except for the difference in the air age before 200 kyr BP, it is obvious that the CO_2 concentration variations from the Dome Fuji and Vostok cores are very similar to each other as a whole. The striking glacial–interglacial variations of the CO_2 concentration, with the rapid increases at the glacial terminations and the gradual decreases toward the glacial maxima after the interglacial periods, are clearly seen in the records from the two ice cores; furthermore, the concentration differences between the glacial maxima and the interglacial periods are also similar for both records. However, the Dome Fuji core shows some spiky high CO_2 concentrations, for example, at 162 kyr BP. We did not find any significant signals of the Ca^{2+} concentration or acidity at depths where these high CO_2 concentrations were observed.

Around the period of about 70–170 kyr BP, which includes the last interglacial period (Eemian), the Dome Fuji values are systematically higher by 10–20 ppmv than the Vostok values (Petit et al., 1999), but such a difference is not found during the other three interglacial periods including the Holocene. In the first part of the last glacial period, the Dome Fuji core and the Vostok core show different mean CO_2 concentrations of 244 and 231 ppmv for almost the same period, i.e. for 95–106 and 92–106 kyr BP, respectively. A high concentration peak is recognizable at around 109 kyr in the Dome Fuji record, but such a peak is not found in the Vostok record. After the penultimate glacial termination, the Vostok record shows CO_2 concentrations of about 290 ppmv at the beginning of the Eemian and then decreases to values of about 260–280 ppmv until 111 kyr BP. On the other hand, the Dome Fuji record shows 280–300 ppmv during 119–130 kyr BP. In the last half of the penultimate glacial period, the Dome Fuji core and the Vostok core yield average concentrations of 205 and 193 ppmv for 138–169 and 138–173 kyr BP, respectively. Before 170 kyr BP, most of local maxima and minima of the CO_2 concentration record derived from the Dome Fuji core agree with those from the Vostok core by Petit et al. (1999) within several ppmv.

The differences between the two CO_2 records may be ascribed to different chemical properties of the Dome Fuji ice core at different depths and/or underestimated CO_2 concentrations of the Vostok core due to some reasons, such as incomplete extraction of air from the ice core. The concentrations of Ca^{2+} and microparticle in the Dome Fuji core for the Eemian are generally at the same level as those for the other interglacial periods, which are lower by one order of magnitude than those in the penultimate glacial maximum. Therefore, it is hard to understand why the systematic differences between the CO_2 records from the Dome Fuji and Vostok cores are observed only in the Eemian and not during the other interglacial periods, and why the differences between the two CO_2 records in the Eemian and the penultimate glacial maximum are of the same degree.

On the other hand, clathrate hydrates gradually return to bubbles during storage of the ice core under relatively warm conditions, e.g. –25 °C which is a typical cold room temperature. If such a phenomenon occurred for the Vostok core, the CO_2 concentrations obtained using the dry extraction method from the ice samples below the transition zone may be affected by incomplete air extraction. In this regard, the CO_2 concentrations derived by Fischer et al. (1999) from the Vostok core are not in agreement for some periods with those by Petit et al. (1999) from the same core. Some differences between both results over short time interval, e.g. around 238 kyr BP, may be due to higher sampling resolution in Fischer et al. (1999). However, some differences, e.g. during 250–254 kyr BP, seem to be real, which may be ascribed to the different dry extraction techniques with different extraction efficiencies.

5. Conclusions

In order to reconstruct the concentration variations of atmospheric CO_2 over the last three glacial–interglacial cycles, we analyzed a deep ice core drilled at Dome Fuji, Antarctica, using a wet extraction technique. Although the wet extraction method has been thought to be unreliable for the CO_2 concentration analyses, the present results succeeded in reconstructing the past atmospheric CO_2 concentration variations fairly well.

Spiky excess CO_2 of up to 20 ppmv were occasionally seen in the Dome Fuji record, and the concentration values in the LGM were systematically higher by 10–20 ppmv than the records from the Taylor Dome, Vostok and Dome C cores. These high values are possibly due to excess CO_2 produced during the air extraction procedure. Therefore, the results obtained in this study can be regarded as an upper limit of estimation of atmospheric CO_2 in the past. However, we found that such high CO_2 concentrations are not related to the concentration of Ca^{2+}, which is generally used as an indicator for the carbonate concentration. This suggests that calcium carbonate originating in land areas was mostly neutralized in the atmosphere during its transport to the central part of Antarctica, or that calcium carbonate existed as particles in the ice and did not sufficiently dissolve and react during the wet extraction. On the other hand, it was also suggested that the dry extraction method might not always be suitable for analyzing CO_2 concentration of ice samples containing clathrate hydrates.

Systematic differences between the CO_2 concentrations from the Dome Fuji core and the Vostok core were found especially around the Eemian, but their causes remain uncertain. They may be ascribed to different chemical properties of the Dome Fuji ice core at different depths. It may also be possible that the Vostok record underestimates the CO_2 concentration from the ice samples containing clathrate hydrates, due to incomplete air extraction. To solve this discrepancy, analyses of the Dome Fuji core with a high extraction efficiency dry extraction device is required. Such analyses would also contribute to a better understanding not only of the past variations of atmospheric CO_2 but also of the global carbon cycle over the glacial–interglacial cycle.

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7. Appendix: Estimation of CO_2 dissolution in water during wet extraction

The amount of CO_2 dissolved in melt water of the sample ice was simply estimated using a thin film model. The CO_2 flux from air to water can be expressed as

$$F = v(C_{\mathrm{eq}} - C_{\mathrm{w}}), \tag{A.1}$$

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 to be in equilibrium with air (mol cm^{-3}), and C_{w} is the actual CO_2 concentration in water (mol cm^{-3}). The transfer velocities obtained from laboratory experiments, wind tunnel studies and ocean observations are of the order of 10^{-2} to 10^{-3} cm s^{-1}, showing larger values for rougher water surface (Davies and Rideal, 1963; Liss, 1988). In the present calculation, we assumed v to be 1×10^{-2} cm s^{-1} in order to estimate an upper limit of the effect. The typical values for the temperature and the amount of the melt water, the air pressure during the melting of the ice sample, the amount of the extracted air and the CO_2 concentration of the air were assumed to be 0 °C, 300 cm^3, 1.5 hPa, 25 cm$^3{}_{\mathrm{STP}}$ and 250 ppmv, respectively. The area of the water surface was set to 85 cm^2, which is the cross-sectional area of the extraction chamber. The duration of ice sample melting was assumed to be 5 min, for which the amount of the melt water increased from 0 to 300 cm^3. C_{eq} was calculated to be 3×10^{-11} mol cm^{-3} on the basis of Henry's law, and C_{w} was set to zero at the beginning of ice melting. By substituting these values into eq. (2), the average CO_2 flux from air to water during the ice melting were calculated to be 1.5×10^{-13} mol cm^{-2} s^{-1}. Based on this flux, the amount of CO_2 dissolved in the melt water was estimated to be 3.7×10^{-9} mol, which corresponds to 3.4 ppmv of the CO_2 concentration in the sample air. The result depends largely on the transfer velocity, as well as on the area of the interface between air and water in the extraction chamber. If we take 1×10^{-3} cm s^{-1} for the transfer velocity, the effect of dissolved CO_2 is reduced to about 1 ppmv. If the interfacial area is decreased to 44 cm^2, which is equal to the area at the beginning of the ice sample melting, the effect becomes less than 1 ppmv.

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