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VARIATIONS OF THE CO_2, CH_4 AND N_2O CONCENTRATIONS AND $\delta^{13}C$ OF CO_2 IN THE GLACIAL PERIOD DEDUCED FROM AN ANTARCTIC ICE CORE, SOUTH YAMATO

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Abstract: To reconstruct variations of atmospheric greenhouse gases in the glacial period, air in an ice core recovered from a bare ice field in the southern part of the Yamato Mountains, Antarctica was extracted and then the CO_2, CH_4 and N_2O concentrations and $\delta^{13}C$ of CO_2 were analyzed. The CO_2, CH_4 and N_2O concentrations were obviously lower than the pre-industrial Holocene values, suggesting that this ice core was formed in the glacial period. The variations of the CO_2, CH_4 and N_2O concentrations during the glacial period showed a good correlation with that of $\delta^{18}O$ of ice from the core. The CO_2 concentrations varied almost opposite in phase with $\delta^{13}C$, which implies that CO_2 with isotopically light carbon was added to or subtracted from the atmosphere in the glacial period.

1. Introduction

For better understanding of the relationship between atmospheric greenhouse gases and global climatic change, it is crucial to know how the concentrations of these gases varied in the glacial and interglacial periods. In the early 1980s, DELMAS *et al.* (1980) reported from the Antarctic ice cores D57 and D10 that the CO_2 concentrations decreased in the glacial period to approximately half of those in the Holocene interglacial stage, correlating with their $\delta^{18}O$ variations, which reflect air temperature when snow accumulated. Thereafter, NEFTEL *et al.* (1982) showed, using more precise analytical techniques, that the CO_2 concentration was lower by about 30% in the last glacial maximum than in the Holocene. By analyzing the Vostok ice core for CO_2 and δD, BARNOLA *et al.* (1987) also found that the decrease of the CO_2 concentration clearly lagged behind that of air temperature during the period from the interglacial to the glacial epoch, while the CO_2 and air temperature increased almost simultaneously in the transition from the glacial to the interglacial period. On the other hand, NEFTEL *et al.* (1988) showed, by analyzing about 500 ice samples from Byrd Station for CO_2 and $\delta^{18}O$, that the increase of air temperature preceded the CO_2 concentration by 200–1200 years during the period from the last glacial maximum to the Holocene.

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The CH_4 concentrations in the glacial period were first measured in the late 1980s using Antarctic and Arctic ice cores. The results revealed that the concentration levels were only half of those in the Holocene (STAUFFER *et al.*, 1988; RAYNAUD *et al.*, 1988). CHAPPELLAZ *et al.* (1990) reported by analyzing the Vostok core that the CH_4 concentrations varied in phase with air temperatures estimated from measured values of δD. A similar correlation was also found for CO_2 from the same core.

The N_2O concentrations in the glacial period were also lower than the Holocene levels. ZARDINI *et al.* (1989) reported that N_2O concentrations during the transition period from the last glacial maximum to the early Holocene were lowered by 5–10% compared with those in the Holocene. By analyzing the Byrd core, LEUENBERGER and SIEGENTHALER (1992) found that the atmospheric N_2O concentration was lower by about 30% in the last glacial maximum than in the Holocene.

A deep ice core, which covers the whole glacial-postglacial transition, is not available yet in Japan. However, an ice core collected in a bare ice field in the southern part of the Yamato Mountains, Antarctica is expected to originate from the last glaciation, because the ice-flow vector inclines upward around the drilling site and continuous evaporation of bare ice is compensated for by such vertical movement (AZUMA *et al.*, 1985). In this paper, we will give the results obtained by analyzing this ice core and discuss variations of the CO_2, CH_4 and N_2O concentrations and $\delta^{13}C$ of CO_2 in the glacial period.

2. Experimental Procedures

A 101.4 m long ice core with a diameter of 120 mm was recovered from a bare ice field in the southern part of the Yamato Mountains, Antarctica (72°05'S, 35°11'E). The drilling was carried out using a mechanical drill by the 24th Japanese Antarctic Research Expedition in December 1983. The core was segmented every 0.5 m at the drilling site and then transported to Japan. The core was kept at temperatures of –10° to –20 °C during the transportation and stored in a cold room with –20°C of Hokkaido University until our analyses in 1992. Melt layers were hardly observed in the entire core. Many vertical cracks have been observed in the upper part of the core but no cracks any more in a depth below 7 m. No clathrate/hydrate could be confirmed by careful inspection with a microscope (NAKAWO *et al.*, 1988). Therefore, all air occluded during ice formation was thought to be included in air bubbles of the core.

Due to the complex ice flow at the drilling site, it is difficult to date the South Yamato core absolutely. However, NAKAWO *et al.* (1988) estimated the vertical velocity of ice flow in the bare ice field from the vertical distribution of bubble pressure in the South Yamato core. In this study, the age of the South Yamato core was calculated on the basis of estimated vertical velocity of ice flow given in Fig. 4 of NAKAWO *et al.* (1988), relative to the age of surface ice.

Details of our experimental procedures have been described elsewhere (NAKAZAWA *et al.*, 1993a, b, c; MACHIDA *et al.*, 1995). Ice samples of 500–700 g were used for air extraction. Each sample was placed in the stainless-steel chamber, and then, the chamber was evacuated for at least 2 hours to sublimate the ice surfaces for cleaning of the sample, maintaining the temperature at –20°C. After the evacuation, the ice sample was melted for analyses of the CH_4 concentration or milled by an ice cutter into fine powder

for analyses of the CO_2 and N_2O concentrations and $\delta^{13}C$ of CO_2. The air released from the ice sample was collected into a sample tube cooled by liquid helium after removing water vapor from the air by a glass trap held at −100°C. The CO_2, CH_4 and N_2O concentrations of the extracted air were determined against our air-based standard gases with concentrations of 200.0, 250.1 and 300.0 ppmv for CO_2, 552, 943 and 1115 ppbv for CH_4 and 199.9, 257.7, 306.2 and 351.6 ppbv for N_2O by using gas chromatography.

After the concentration analyses, CO_2 was extracted cryogenically from the remaining air in the sample tubes to measure the carbon isotopic ratios in CO_2. The mass spectrometer used in this study was a Finnigan MAT-δS installed in our laboratory. Since the amount of CO_2 available for the mass spectrometer analysis was rather limited, we used a cold finger inlet to introduce CO_2 samples into the mass spectrometer. Internal and external reproducibilities of our mass spectrometer analysis for carbon isotope were estimated to be within 0.01 and 0.02‰ (one standard deviation), respectively. N_2O contained in the air samples cannot be removed from CO_2 by the cryogenic procedure. Since the mass numbers of N_2O are the same as those of CO_2, the contribution of N_2O has to be corrected. The correction factor for the mass spectrometer we used is expressed by

$$\Delta\delta^{13}C = 250\rho, \tag{1}$$

where ρ is the concentration ratio of N_2O to CO_2 (NAKAZAWA *et al.*, 1993c).

The overall precision of our ice core analyses was estimated to be better than ±1.0 ppmv for CO_2, ±10 ppbv for CH_4, ±2 ppbv for N_2O and 0.05‰ for $\delta^{13}C$ (NAKAZAWA *et al.*, 1993a, b; MACHIDA *et al.*, 1995).

3. Results and Discussion

3.1. Concentration variations of CO_2, CH_4 and N_2O in the glacial period

Variations of the CO_2, CH_4 and N_2O concentrations obtained from the South Yamato core are shown in Figs. 1, 2 and 3, respectively. Also shown are the concentrations obtained from an ice core at Mizuho Station, Antarctica (our unpublished data) and *in situ* measurements at Syowa Station, Antarctica or the South Pole (NAKAZAWA *et al.*, 1991; LANG *et al.*, 1990; MONTZKA *et al.*, 1992), which represent the concentration variations during the Holocene. The values obtained from the South Yamato core are plotted against ice age relative to surface ice, whereas the results from the Mizuho core are plotted against absolute air age. Average values of the CO_2, CH_4 and N_2O concentrations from the South Yamato core are 213.3±8.7 ppmv, 484±44 ppbv and 243±10 ppbv, respectively. These concentrations are apparently lower than average values from the Mizuho core for the pre-industrial Holocene, *i.e.*, 281.9±4.4 ppmv for CO_2, 729±30 ppbv for CH_4 and 265±6 ppbv for N_2O. It has previously been reported that in the last glacial epoch, the CO_2 concentrations were in the range of 180–240 ppmv (NEFTEL *et al.*, 1982, 1988; BARNOLA *et al.*, 1987), the CH_4 concentrations in the range of 350–600 ppbv (STAUFFER *et al.*, 1988; RAYNAUD *et al.*, 1988; CHAPPELLAZ *et al.*, 1990) and the N_2O concentrations in the range of 180–250 ppbv (LEUENBERGER and SIEGENTHALER, 1992). Taking account of the fact that the results obtained in this study ranged within the previous estimates, the South Yamato core is thought to have possibly been formed in the glacial

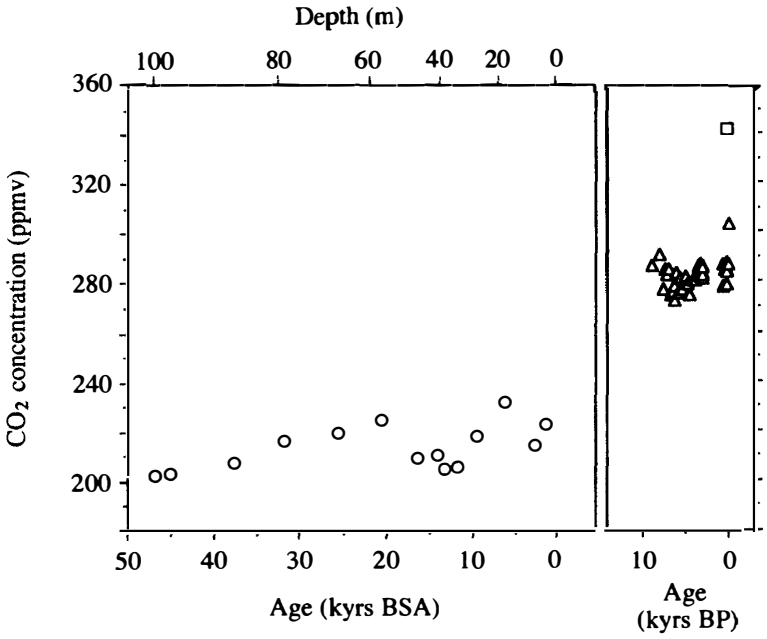

Fig. 1. *CO_2 concentrations derived from the South Yamato core. Measured values are plotted with open circles against the ice age relative to the surface ice. The results from the Mizuho core are also shown with open triangles against the absolute air age and annual mean CO_2 concentration at Syowa Station in 1984 with an open square.*

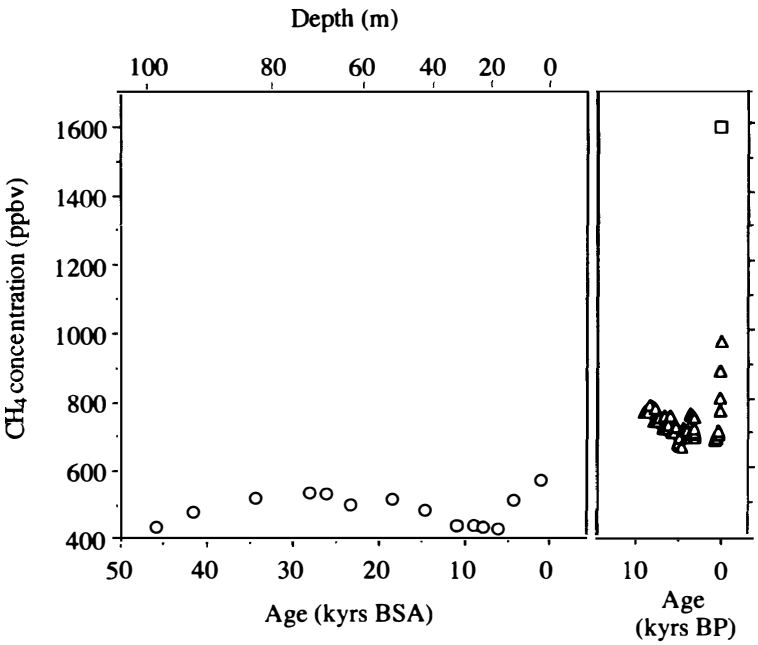

Fig. 2. *The same as in Fig. 1, but for the CH_4 concentration. The open square represents annual mean CH_4 concentration at the South Pole in 1984.*

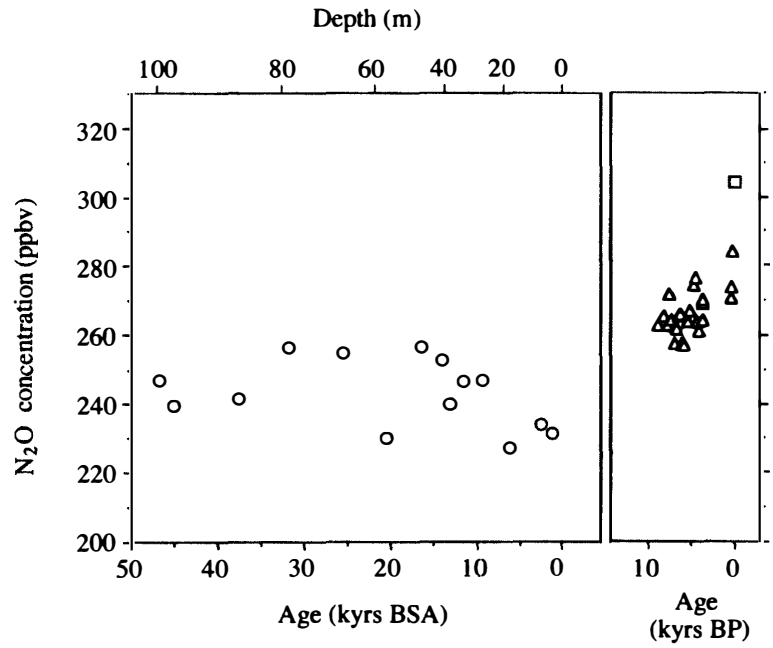

Fig. 3. The same as in Fig. 1, but for the N_2O concentration. The open square represents annual mean N_2O concentration at the South Pole in 1984.

period. In this regard, NAKAWO *et al.* (1988) pointed out that the South Yamato ice may have been deposited during the last glacial period, since the terrestrial age of meteorites found in the bare ice field near the Yamato Mountains has been estimated to be younger than 40–70 k years.

Since land biomass is expected to have been reduced in the glacial period (BIRD *et al.*, 1994), the low concentrations of atmospheric CO_2 in this period may be ascribed to changes in chemical and/or biological CO_2 processes in the oceans. BROECKER and PENG (1989) suggested that lower temperature of sea surface water in the glacial period accounts for only 17 ppmv decrease in the atmospheric CO_2 concentration. Therefore, other causes are probably responsible for such low CO_2 concentrations. One convincing candidate is an enhancement of a biological pump by which a large amount of carbon is transported from the mixed layer to the deep ocean as a form of organic particles (SARMIENT and TOGGWEILER, 1984; SIEGENTHALER and WENK, 1984); stronger biological pump might have led to lowering the atmospheric CO_2 concentration through the depletion of total CO_2 (ΣCO_2) in surface water. Another candidate is changes in alkalinity of ocean water. BROECKER and PENG (1989) estimated about 80 ppmv decrease in atmospheric CO_2 by an increase in alkalinity of polar surface waters.

To explain the reason why the concentration of atmospheric CH_4 decreased in the glacial period, the causes should be considered in terms of changes in both sources and sinks of CH_4. CH_4 emission from wetlands through bacterial processes is highly dependent upon the temperature (HAMEED and CESS, 1983). Based on the CH_4 emission rate given by HAMEED and CESS (1983), the source strength would be lowered in the glacial period by a factor of 0.59 than in the Holocene (RAYNAUD *et al.*, 1988). Wetlands at high latitudes should have been reduced during the glacial period, due to drier climate and

more extended ice-covered area (RAYNAUD *et al.*, 1988). This is also effective for reducing CH_4 emissions. On the other hand, by examining the temperature dependence of the CH_4-OH reaction rate coefficient and the production of OH from H_2O, it was estimated that the CH_4 sink was deactivated during the glacial period, which leads to an increase of 25% in the CH_4 concentration (RAYNAUD *et al.*, 1988). However, from the above-mentioned observational facts, it is thought that the former effect dominated over the latter in the glacial period. In this connection, CHAPPELLAZ *et al.* (1990) found, from marine pollen profiles (VAN CAMPO *et al.*, 1982; PRELL and VAN CAMPO, 1986) and sapropels in the eastern Mediterranean Sea (ROSSIGNOL-STRICK, 1983), that the appearance of a strong monsoon correlated well with the higher CH_4 events seen in the Vostok record. This fact probably suggests that area of wetlands at low latitudes may also have been changed by changes in the monsoon circulation which controls hydrological cycles there.

Natural sources of N_2O are primarily due to microbial processes in soils and oceans (PRATHER *et al.*, 1995). Therefore, the release rates of N_2O by denitrification and nitrification are strongly dependent on environmental parameters, particularly on the temperature (ZARDINI *et al.*, 1989) and the extent of vegetation and soils (LEUENBERGER and SIEGENTHALER, 1992). In addition, the release rate of N_2O from the oceans could be different at different temperatures, because the solubility of N_2O depends on water temperature. On the other hand, N_2O is destroyed only in the stratosphere through reaction with $O(^1D)$ as well as photolysis. Taking account of these facts, it is suggested that N_2O emissions from natural sources were reduced in the glacial period and its concentration in the atmosphere was lowered.

Variations of the CO_2, CH_4 and N_2O concentrations obtained from the South Yamato core for arbitrary 50000 years (50 kyrs) in the glacial period are given in Fig. 4. For detailed discussion of their concentration variations, oxygen isotopic ratio ($\delta^{18}O$) of ice was also analyzed every 1 m of the core, which can be used as an index of air temperature when snow accumulated. The curve of measured $\delta^{18}O$ values smoothed with a Reinsch-type cubic spline are also shown in Fig. 4. The CO_2 and CH_4 concentrations vary similarly to each other between 46 and 13 kyrs relative to the age of surface ice (before the surface age: BSA); the concentrations increase slowly from 201.9 ppmv and 433 ppbv in 46 kyrs BSA to 224.1 ppmv in 20 kyrs BSA for CO_2 and 533 ppbv in 28 kyrs BSA for CH_4, and then the respective values decrease rapidly to 204.7 ppmv and 439 ppbv around 13 kyrs BSA. However, the CO_2 concentration shows a high value of 231.9 ppmv at 6 kyrs BSA, whereas a minimum value of 427 ppbv is found for CH_4 in almost the same year. The N_2O concentration shows high values of about 256 ppbv around 30 and 16 kyrs BSA and decreases from 16 kyrs BSA to 1 kyr BSA and from 32 kyrs BSA to 47 kyrs BSA. A low value of about 230 ppbv is also found in 20 kyrs BSA. It is seen in Fig. 4 that the value of $\delta^{18}O$ shows variations similar to the CO_2 concentration during 46–10 kyrs BSA and to the CH_4 concentration during 46–6 kyrs BSA. A similar correlation with $\delta^{18}O$ is found for the N_2O concentration except for 30–25 kyrs BSA and around 45 and 6–1 kyrs BSA when the concentrations are high and low, respectively. Good correlations of $\delta^{18}O$ with the CO_2 and CH_4 concentrations during the glacial period were also reported by BARNOLA *et al.* (1987) and CHAPPELLAZ *et al.* (1990) from the Vostok core. The high values of the CO_2, CH_4 and N_2O concentrations around 30–20 kyrs BSA are probably related to high air temperatures; release of CO_2, CH_4 and N_2O from the

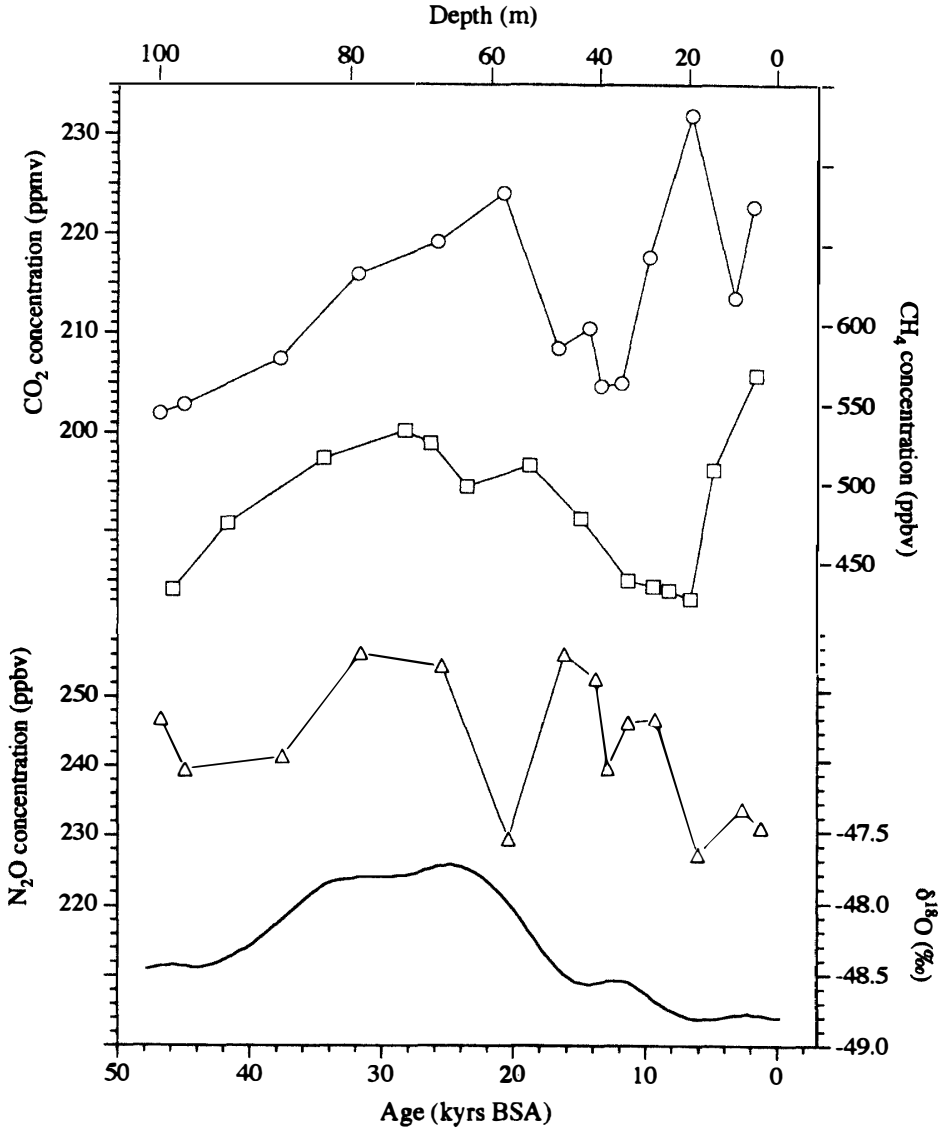

Fig. 4. Comparison of the CO_2 (open circles), CH_4 (open squares) and N_2O (open triangles) concentrations with $\delta^{18}O$ of ice (thick line) for the South Yamato core. The thick line was obtained by fitting a Reinsch-type spline with a cutoff period of 1.5 kyrs to the measured data.

oceans into the atmosphere was enhanced by lowering their solubilities in sea water and/or their emissions from land surfaces by microbial processes were intensified. The variations of the CO_2 concentration will be discussed in more detail in the following section.

3.2. Variations of $\delta^{13}C$ in CO_2 during the glacial period

To understand the causes of the CO_2 variations in more detail, the carbon isotopic ratio ($\delta^{13}C$) in CO_2 involved in the South Yamato core was also analyzed. The results obtained are shown in Fig. 5, together with the CO_2 concentrations. The measured values of $\delta^{13}C$ range from –9.5 to –6.8‰, an average value being –7.7‰. Our values are clearly lower than the pre-industrial Holocene levels of –6.8 to –6.2‰ (FRIEDLI *et al.*,

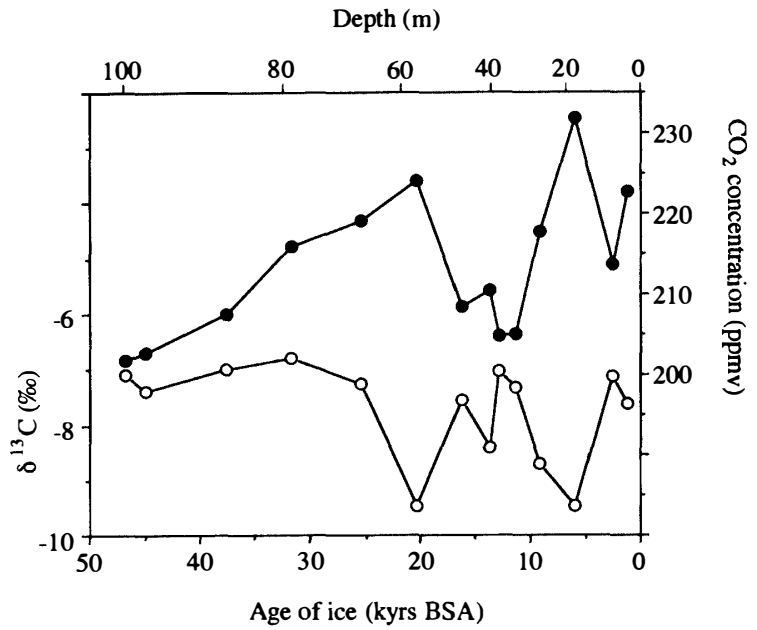

Fig. 5. Comparison of the CO_2 concentration (solid circles) with its $\delta^{13}C$ values (open circles) for the South Yamato core. Measured values of both components are plotted against the ice age relative to surface ice

1984, 1986; SIEGENTHALER *et al.*, 1988; LEUENBERGER *et al.*, 1992). LEUENBERGER *et al.* (1992) also reported the relatively low $\delta^{13}C$ value of -6.84 ± 0.12‰ for the glacial period (40–20 kyrs BP). Their value is, however, higher by about 1.0‰ than those in this study. Such a discrepancy is probably due to differences in the analytical procedures and the quality and the age of ice cores used by the two groups.

As mentioned above, the low CO_2 concentrations in the glacial period may be mainly ascribed to changes in biological/chemical CO_2 processes in the oceans. If this is the case, the atmospheric $\delta^{13}C$ would also be affected by the same effect. It is expected that by lowering sea surface temperature by about 2°C, the atmospheric $\delta^{13}C$ is decreased by about 0.2‰, due to enhanced $^{13}C/^{12}C$ fractionation of CO_2 exchanged between the atmosphere and the oceans (MOOK, 1986). According to MARINO *et al.* (1992) and DUPLESSY *et al.* (1988), the atmospheric $\delta^{13}C$ is expected to have been decreased by 0.32‰ in the glacial period, since $\delta^{13}C$ of ΣCO_2 in the whole ocean was lowered by absorbing CO_2 with light carbon released by the reduction of terrestrial biomass. LEUENBERGER *et al.* (1992) suggested that the positive shift of $\delta^{13}C$ found from early to late Holocene was due to preferential withdrawal of isotopically light CO_2 from the atmosphere during biomass buildup on land. It was also pointed out that the average oceanic surface-to-depth gradient in $\delta^{13}C$ was smaller in the glacial period than in the Holocene (JASPER and HAYES, 1990). The atmospheric $\delta^{13}C$ was estimated to be reduced by 0.2‰ by this effect. On the other hand, the carbon cycle model that invokes only changes in the biological pump predicts an increase of about 0.9‰ in the atmospheric $\delta^{13}C$ for a CO_2 concentration decrease of 90 ppmv in the glacial period (WENK and SIEGENTHALER, 1985). However, the results of more recent model studies showed changes of $\delta^{13}C$ smaller than the above prediction (KEIR, 1988). Even if the increase of the atmospheric $\delta^{13}C$ due to

enhanced biological pump is assumed to be negligible, the isotopic depression estimated from the above-mentioned three effects is still smaller than our finding. This may imply that other processes were also important during the glacial period or the above-mentioned three effects were underestimated.

As seen in Fig. 5, the CO_2 concentration varies almost opposite in phase with $\delta^{13}C$ during the glacial period, especially after 20 kyrs BSA. Such a correlation implies that isotopically light CO_2 was added to or subtracted from the atmosphere. Assuming that CO_2 is exchanged between the atmosphere and another single carbon reservoir, a balance equation for $^{13}CO_2$ in the atmosphere is given by

$$C\delta^{13}=C_0\delta^{13}{}_0+\delta^{13}{}_I(C-C_0), \tag{2}$$

where C_0 and C denote the atmospheric CO_2 concentrations (in ppmv) before and after CO_2 is exchanged, respectively, $\delta^{13}{}_0$ and δ^{13} are corresponding values of $\delta^{13}C$ (in ‰) and $\delta^{13}{}_I$ is $\delta^{13}C$ of CO_2 in the carbon reservoir considered (MOOK *et al.*, 1983; KEELING *et al.*, 1984; NAKAZAWA *et al.*, 1993c). By solving eq. (2) for δ^{13}, we obtained the following linear relation between the isotopic ratio and the reciprocal of CO_2 concentration:

$$\delta^{13}=\delta^{13}{}_I+M/C, \tag{3}$$

where M denotes a constant equal to $C_0(\delta^{13}{}_0-\delta^{13}{}_I)$. By applying eq. (3) to the CO_2 concentrations and their $\delta^{13}C$ values during the 26–1 kyrs BSA period using a least-squares-fitting technique, $\delta^{13}{}_I$ was determined to be -24.0 ± 5.9‰. The $\delta^{13}C$ value of the land biosphere at the last glacial maximum was estimated to range between −19 and −29‰ (BIRD *et al.*, 1994). Taking this fact into account, it is thought that the variations of the atmospheric CO_2 concentration during the glacial period arose mainly from CO_2 exchange with the land biosphere. Biological activities in the surface ocean may also be partly responsible for such CO_2 variations. On the other hand, the CO_2 concentrations and $\delta^{13}C$ values during the period 47–32 kyrs BSA showed no clear correlation. Such behavior suggests that imbalance of CO_2 exchange between the atmosphere and the oceans due to changes in alkalinity and/or surface ocean temperature is responsible for the CO_2 concentration variations during this period. In this regard, the exchange of CO_2 between the atmosphere and the oceans has a little effect on the atmospheric $\delta^{13}C$ (NAKAZAWA *et al.*, 1993c).

4. Conclusions

The CO_2, CH_4 and N_2O concentrations deduced from the South Yamato core were obviously lower than the pre-industrial Holocene levels, average values of the respective components being 213.3±8.7 ppmv, 484±44 ppbv and 243±10 ppbv, respectively. These low concentrations suggest that the ice core was formed in the glacial period. The variations of the CO_2, CH_4 and N_2O concentrations during the glacial period were almost similar to that of $\delta^{18}O$ of ice, reflecting the fact that source activities of the respective components are strongly dependent on temperature. During the period between 26 and 1 kyrs BSA, the CO_2 concentrations varied almost opposite in phase with $\delta^{13}C$. Such a

correlation implies that isotopically light CO_2 was added to or subtracted from the atmosphere, due mainly to terrestrial biological activities.

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