

Measurements of CO₂ and CH₄ concentrations in air in a polar ice core

TAKAKIYO NAKAZAWA, TOSHINOBU MACHIDA, KENJI ESUMI*, MASAYUKI TANAKA,
Center for Atmospheric and Oceanic Studies, Faculty of Science, Tohoku University, Sendai 980, Japan

YOSHIYUKI FUJII, SHUJI AOKI AND OKITSUGU WATANABE
National Institute of Polar Research, 1-9-10 Kaga, Itabashi, Tokyo 173, Japan

ABSTRACT. Dry and wet air-extraction systems and precise analysis systems of the CO₂ and CH₄ concentrations for a polar ice core were developed to reconstruct their ancient levels. A dry-extraction system was capable of crushing an ice sample of 1000 g into fine powder within 2 min, and its air-extraction efficiency was found to be 98%. The CO₂ and CH₄ concentrations of extracted air were determined using gas chromatography with a flame-ionized detector. The overall precision of our measurements, including air extraction, was estimated to be better than ± 1 ppmv for CO₂ and ± 10 ppbv for CH₄. Preliminary analysis of the ice core drilled at Mizuho Station, Antarctica, showed that the CO₂ and CH₄ concentrations at 3340–3700 year BP were about 280 ppmv and 700 ppbv, respectively. The Yamato core drilled at the terminus of the glacial flow near the Yamato Mountains, Antarctica, yielded concentrations of 230–240 ppmv for CO₂ and 520–550 ppbv for CH₄, suggesting that the core had formed during the glacial period.

INTRODUCTION

The concentrations of atmospheric greenhouse gases such as CO₂, CH₄ and N₂O have been increasing steadily due to human activities (e.g. Rasmussen and Khalil, 1984; Siegenthaler and Oeschger, 1987; Blake and Rowland, 1988; Khalil and Rasmussen, 1988; Keeling and others, 1989; Fraser and Coram, 1991; Nakazawa and others, 1991; Aoki and others, 1992), and a global climate change is likely to occur in the near future. To understand the causes of such increases, the concentration history of these gases is important. This knowledge is also necessary for elucidating the relationship between the greenhouse gases and the climate. Therefore, substantial efforts have been devoted to reconstructing the concentration variations of the atmospheric greenhouse gases in the past. The analysis of air extracted from a polar ice core is the most promising method for this purpose, because air bubbles in an ice sheet preserve the atmosphere at the time of formation of their surrounding ice.

An air-extraction technique is essential to ice-core analysis. The air occluded in an ice core is easily extracted by melting it in an evacuated chamber, and this method has been applied to determine the concentration of relatively insoluble gases such as CH₄ and the total air

content in ice. It was, however, found that the air thus extracted shows remarkably high concentrations in CO₂ (Raynaud and others, 1982). In order to extract the air without melting the ice core, a metal ball crusher and needle matrix crusher were developed and used for the analysis of small ice samples of 1–40 g (Raynaud and others, 1982; Zumbunn and others, 1982). Other devices, in which the ice core is milled (Moor and Stauffer, 1984; Etheridge and others, 1988), were also developed to extract a large amount of air. Air-extraction efficiency of these devices was estimated at 60–90%. The CO₂ and CH₄ concentrations of extracted air were usually determined by using gas chromatography, laser spectrometer or manometric methods.

Based on these measurement techniques, many polar ice cores have been analyzed to reconstruct the concentration history of the atmospheric CO₂ and CH₄ (e.g. Craig and Chou, 1982; Neftel and others, 1985; Stauffer and others, 1985; Barnola and others, 1987; Chappellaz and others, 1990). The results obtained so far show that pre-industrial/agricultural levels of the CO₂ and CH₄ concentrations were 270–285 ppmv and 650–800 ppbv, respectively, and that respective concentrations decreased to as low as about 200 ppmv and 350 ppbv during the glacial maximum. However, for a better understanding of concentration variations of the atmospheric trace gases in the past, further ice-core analyses are required.

We have also developed measurement systems to determine precisely the CO₂ and CH₄ concentrations of air trapped in a polar ice core, in which both dry- and

* Present address: Japan Weather Association, 2-1-2 Ichibancho, Sendai 980, Japan.

wet-extraction techniques were employed. In this paper, descriptions of our techniques are given in detail. We also present the results of preliminary analyses of the Mizuho and Yamato cores drilled in East Antarctica.

AIR-EXTRACTION AND CONCENTRATION ANALYSIS

Figure 1 shows a schematic diagram of the air-extraction system for CH_4 . This system was installed in our laboratory. All parts used were made of stainless steel except for the water trap 1, which was made of Pyrex glass, and they were washed sufficiently in an acid solution and trichloroethane, and then dried by passing N_2 gas before they were assembled. Respective parts were welded together as far as possible, and the remaining parts were connected with metal gaskets to minimize leakage in the system. Prior to use, the system was evacuated for 1 week at temperatures above 100°C , and leakage in the system was confirmed as less than $1 \times 10^{-10} \text{ Pa m}^3 \text{ s}^{-1}$, using a mass-spectrometer leak detector.

Ice cores of up to 1200 g, of which contaminated surfaces were removed by a bandsaw and knife, were inserted into the extraction chamber in a cold room at -20°C . The chamber was then connected to the above-mentioned system and evacuated by a rotary pump, retaining the temperature at -20°C by using an electric refrigerator. The evacuation was made not only to remove residuary room air from the chamber but also to sublimate the ice surface for further cleaning of the sample. After these procedures, the chamber was gradually immersed in a warm waterbath, and air released from the ice core was collected in a sample tube cooled to -269°C by liquid He. The sample tubes with different volumes of 7–24 cm^3 were used, depending on the size of ice core to be melted. Water vapor was removed from the sample air by specially designed traps held at -100°C . A fore trap (water trap 1) had sufficient inner space to condense a large amount of water vapor, and a rear trap (water trap 2) involved many fine glass tubes to increase its trapping efficiency. The pressure in the system was monitored by a Pirani gauge, and the melting rate of the ice core was adjusted so that the

pressure did not exceed 130 Pa. After confirming the reading of the Pirani gauge that the ice core had melted and the air released had been completely collected, which usually required about 20 min for an ice sample of 1000 g, the sample tube was disconnected from the system and set aside in the laboratory for more than 2 d to ensure that the respective components of the sampled air were mixed well. Dry N_2 was introduced into the the system before the extraction chamber and sample tubes were disconnected in order to minimize the intrusion of contaminated room air.

A schematic diagram of our dry-extraction system is given in Figure 2. This system was also made of stainless steel except for the glass trap with fine glass tubes, and it was installed in a cold room at -20°C . General attention paid in the assembly of respective components was the same as had been done for the wet-extraction system. The detailed structure of the extraction chamber is illustrated in Figure 3. This chamber was designed to extract a large amount of air for measurements of CO_2 concentration as well as the carbon-isotope ratio of CO_2 . An ice sample of up to approximately 1300 g was placed on both sides of the partition and pressed down to an ice cutter by a stainless steel block with magnets. The diameter and length of the ice-core compartment were 100 and 410 mm, respectively. The ice cutter, with three stainless steel edges, was rotated horizontally from outside through a magnetic coupler with two greaseless stainless-steel ball bearings, and the partition prevented the ice core from moving with the cutter. Therefore, only very thin ice samples remained unmilled. The height of the edges was adjusted depending on the size of the bubbles in the ice core, to attain a high efficiency of air extraction. The crushed ice was stored in the bottom part of the chamber (150 mm in diameter and 280 mm in length). To minimize the deterioration risks of sample air due to selective adsorption of CO_2 on the inner wall of the chamber and the surface of crushed ice, it was necessary to extract air from the ice core as quickly as possible (Moor and Stauffer, 1984). The crushing rate of the ice core was closely related to the weight of the stainless steel block. To mill an ice sample of 1000 g within 2 min, its weight was chosen as 7000 g. This was adjustable within ± 2000 g by means of the magnetic coupler. We found

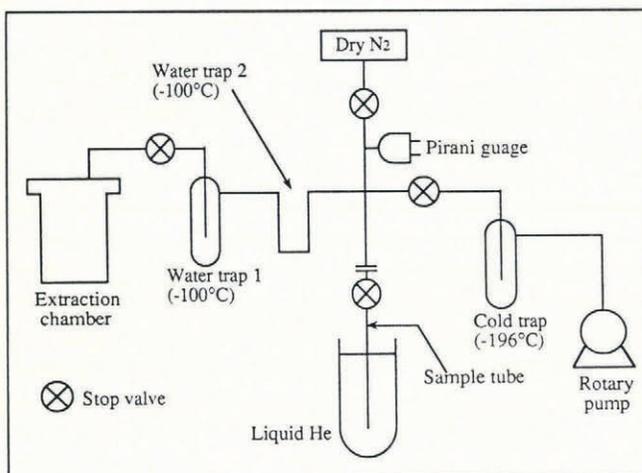


Fig. 1. Wet air-extraction system for ice-core analysis.

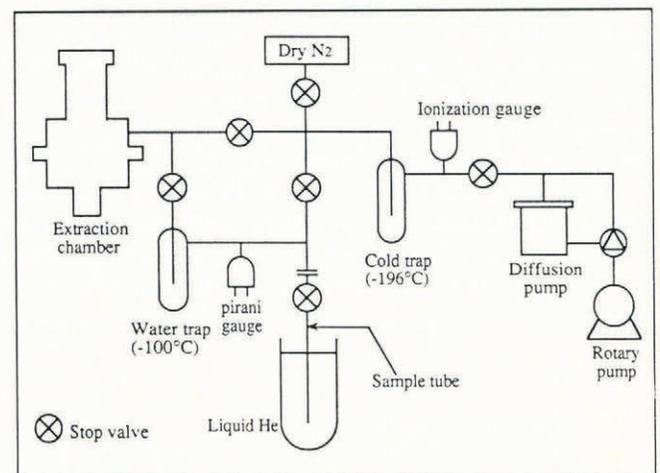


Fig. 2. Dry air-extraction system for ice-core analysis.

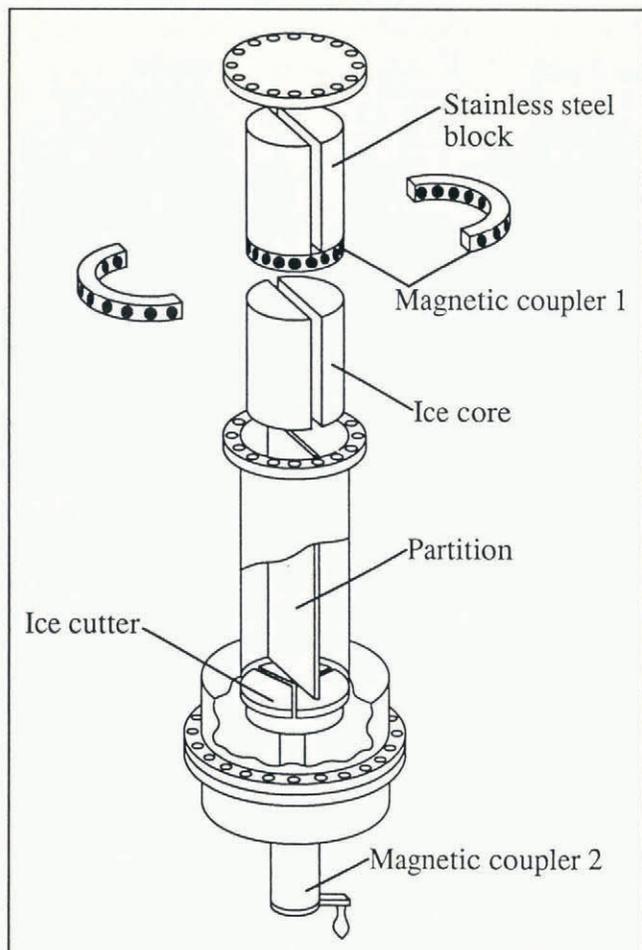


Fig. 3. Structure of the milling cutter for extracting the air from a polar ice core.

that air extracted by this system showed CH₄ concentrations were higher by 50–200 ppbv than those from the wet-extraction system, due to CH₄ produced probably by collision of the stainless steel block with the inner wall of the chamber. A similar phenomenon has also been pointed out by Stauffer and others (1985) and Pearman and others (1986).

The CO₂ and CH₄ concentrations in extracted air were determined against our air-based standard gases by using gas chromatography equipped with a flame-ionized detector (FID). A quantity of extracted air was measured using a small semi-conductor pressure sensor attached to an inlet system which was used to introduce the sampled air into sample loops of the gas-chromatography system. Sample loops with volumes of 1 and 10 cm³ were used for CO₂ and CH₄, respectively, and one end of each loop was opened to an ambient atmosphere through a fine stainless steel tube to equalize quantities of the standard gases and the sampled air. CO₂ and CH₄ were separated from the air components in columns filled with Porapak N and Molecular Sieve 5A, respectively, and then detected by FID. Here, separated CO₂ was converted into CH₄ by a Ni catalyst before the detector, because FID does not respond to CO₂. Each chromatogram was integrated by a microcomputer to calculate its dimension. The computer was also used to control the overall operation of the measurement system.

The standard gases were classified into two categories,

i.e. the primary and working standards. The working standards consisted of three gases with different concentrations of both CO₂ and CH₄, and each gas was stored in a 47 l aluminium cylinder. Their concentrations were determined against our primary standard-gas system by using gas chromatography. The primary standard gases were prepared gravimetrically by a four-stage dilution using 10 l aluminium cylinders and an extremely precise balance with a standard deviation of 1.5 mg in a wide range of 1 mg–100 kg. Uncertainties in the concentration were estimated as 0.03 and 0.2% for CO₂ and CH₄, respectively. The gravimetrically determined concentrations of the primary standard gases were 200.0, 250.1 and 300.0 ppmv for CO₂, and 552, 943 and 1115 ppbv for CH₄.

Two working standard gases, of which the concentrations were chosen so that the concentrations of sampled air fell between them, were introduced into the gas-chromatography system before and after each analysis of the sampled air. Then, dimension values of the two chromatograms for each gas were simply averaged. The CO₂ and CH₄ concentrations of sampled air were calculated from the dimension values of the standard gases and the sample, assuming a linear relationship between the chromatogram dimension and the concentration. We confirmed that the errors arising from a non-linear relationship were negligibly small, at least in a concentration range covered by these standard gases, compared with the overall precision of our measurements which will be described later.

PRECISION OF MEASUREMENTS AND AIR-EXTRACTION EFFICIENCY OF THE DRY SYSTEM

The measurement precision of our gas chromatography was examined by using three primary standard gases; the concentration of the middle gas was determined repeatedly from those of high and low gases, assuming a linear relationship between the chromatogram dimension and the concentration. Then, differences from its gravimetrically determined concentration were calculated. The results indicated that more than 85% of all differences fell within ± 0.2 ppmv for CO₂, and more than 90% within ± 2 ppbv for CH₄. These uncertainties were almost compatible with those in the concentrations of the primary standard gases.

Deterioration of the sampled air may occur because of several factors, such as selective adsorption of CO₂ and CH₄ on the inner wall of the extraction chamber, leakage of the system, incomplete collection of the sampled air and inhomogeneous mixing of each component of the air in the sample tubes. We therefore introduced standard gases of approximately 100 cm³ with known concentrations into each evacuated extraction chamber without ice, and collected them in the sample tubes. After 2–7 d, the CO₂ and CH₄ concentrations of the collected gases were analyzed using gas chromatography. The results are given in Figures 4 and 5 for CO₂ and CH₄, respectively. As seen in these figures, almost all differences between measured and original values of the concentrations are within ± 1.0 ppmv for CO₂ and ± 10 ppbv for CH₄.

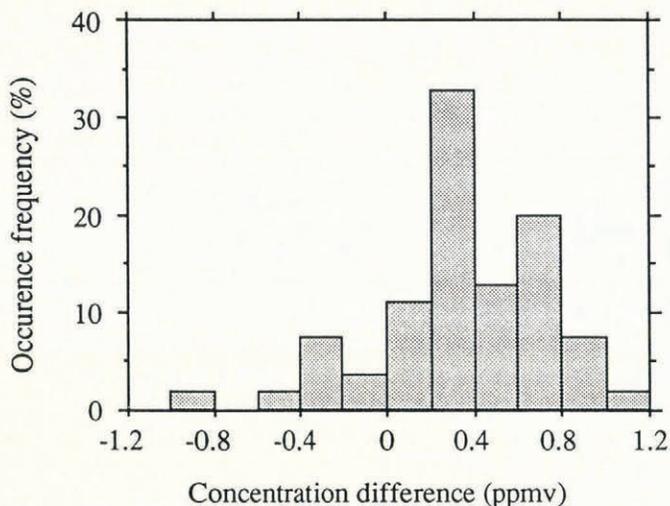


Fig. 4. Concentration changes in CO₂ standard gases injected into the air-extraction system. The total number of gas samples is 55.

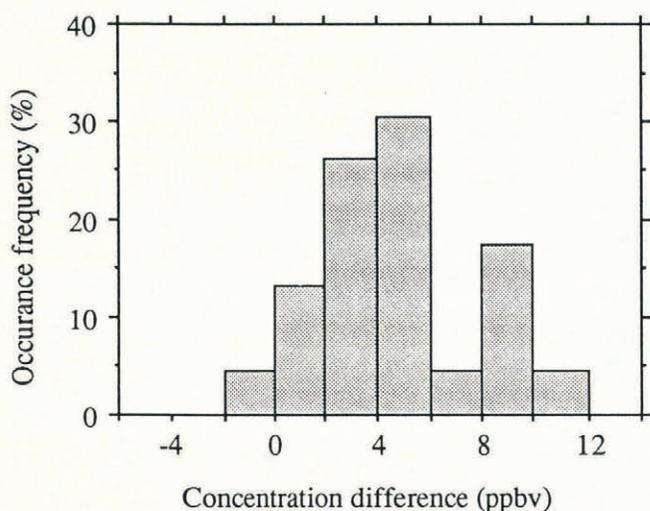


Fig. 5. The same as in Figure 4 but for CH₄ concentration. The total number of gas samples is 23.

However, differences are slightly shifted positively for both components. Similar differences were also obtained from the analysis of standard gases stored in the sample tubes. Therefore, such a positive shift in the concentration may be attributed to the sample tubes themselves.

In the actual procedure of the air extraction, we have to consider the influence of newly formed surfaces of crushed ice in the dry system and of dissolved water in the wet system. To examine these effects, the following tests were made. We evacuated the dry-extraction system for 1 h after an ice core of 800–1000 g was crushed and then introduced standard gases of 80–100 cm³ into the chamber. The standard gases were stored in the chamber for 2 min and then collected in the sample tubes, taking about 15 min, which are practically necessary to extract air from an ice core of 1000 g. In the wet system, standard gases of the same amounts as above were added to the evacuated chamber with crushed ice of 500–800 g, and collected in the sample tubes, melting the crushed ice for about 15 min. The collection of the standard gases was completed about 20 min after commencing melting of the ice. The CO₂ and CH₄ concentrations of the collected standard gases were analyzed using gas chromatography.

Table 1. Concentration changes of standard gases of 80–100 cm³ injected into air-extraction chambers with crushed ice

	CO ₂		CH ₄		
	ppmv		ppbv		
Injected air	273.2	274.0	943.0	943.0	943.0
Collected air	272.2	273.9	946.8	947.2	944.1
Concentration change	-1.0	-0.1	+3.8	+4.2	+1.1

The results thus obtained are shown in Table 1. Concentration differences are still positive for CH₄ but those for CO₂ change their sign, suggesting a possible selective adsorption of CO₂ on newly formed surfaces of crushed ice. Zumbunn and others (1982) found that a strong increase in the CO₂ concentration occurs in the stainless-steel cell due to the desorption of CO₂ from its wall, in association with the water vapor present in the cell. However, such a phenomenon was hardly observable in our dry-extraction system.

To examine reproducibilities of our analyses, several ice-core samples were divided vertically, and the CO₂ and CH₄ concentrations determined from two pieces of respective samples were compared. The results thus obtained are given in Table 2. Concentration differences are less than 1 ppmv and 1 ppbv for CO₂ and CH₄, respectively.

From the above results, the overall precision of our ice-core analyses were estimated to be better than ±1.0 ppmv for CO₂ and ±10 ppbv for CH₄; these are sufficiently precise to resolve variations in the ancient atmospheric CO₂ and CH₄ concentrations.

In the dry-extraction method, ice-core samples were crushed into small chips with finite size. Therefore, all bubbles might not have been opened completely by this method. On the other hand, almost all air occluded in bubbles was released by melting the ice core. Air-

Table 2. Concentration differences of two pieces obtained by dividing an ice-core sample vertically

	CO ₂		CH ₄		
	ppmv		ppbv		
Measured concentration	282.5	286.4	545.7	530.7	702.7
Concentration difference	0.7	0.8	0.1	0.2	0.4

extraction efficiency of our dry system was estimated by comparing quantities of air extracted by both methods. Ice-core samples drilled thermally from a 313–340 m depth at Mizuho Station (East Antarctica, 70°42' S, 44°20' E) were used here. Air extraction was made by using the dry method for 12 samples and the wet method for 11 samples. Average values of the air extracted by respective methods were 64.6 ± 2.7 and $66.0 \pm 2.6 \text{ cm}^3_{\text{STP}} \text{ kg}^{-1}$ (ice). Since this core has many cracks caused by thermal stress, the air content in the ice was rather low compared to those of ice cores with no cracks (Kameda and others, 1990). From a comparison of these two values, air-extraction efficiency was estimated to be about 98%, almost all bubbles being opened by our dry system at least for ice-core samples collected above approximately a 340 m depth at Mizuho Station. In this case, height of the edges of the ice cutter was adjusted at 0.5 mm. To maintain a high-extraction efficiency, it was necessary for deeper ice samples to lower their height.

EFFECT OF EVACUATION TIME OF AN ICE SAMPLE ON CO₂ AND CH₄ CONCENTRATIONS

As mentioned above, we evacuated the chambers with an ice core to sublimate its surface prior to air extraction. We examined the effect of the evacuation time on the CO₂ and CH₄ concentrations, using 25 ice samples collected from 313–340 m depth at Mizuho Station. The results obtained for CO₂ are shown in Figure 6. Four samples evacuated for shorter than 3 h gave CO₂ concentrations higher than 290 ppmv. The concentrations of the other ten samples with an evacuation time longer than 4 h were lower by about 10 ppmv than the above values. Since ice samples evacuated for 4–8 h showed fairly constant concentrations, no appreciable decrease in concentration could occur by further evacuation. This phenomenon was probably attributable to ice samples contaminated by the air in the cold room with extremely high CO₂ concentrations mainly due to human respiration. The ice-core sample was usually left in the cold room for 0.5–

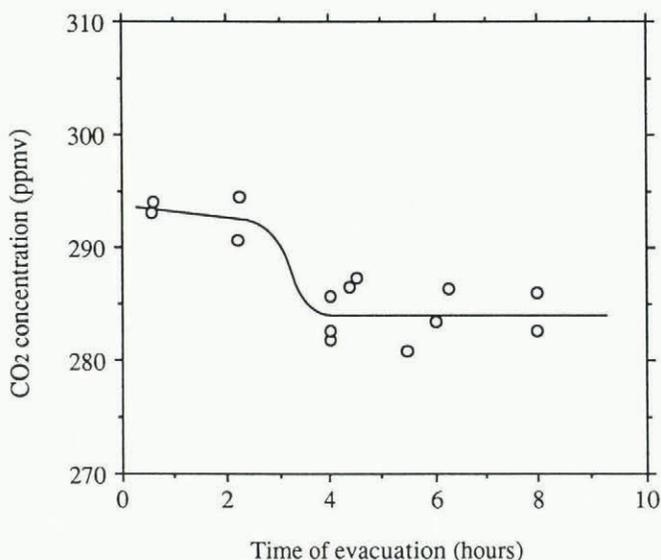


Fig. 6. Dependence of CO₂ concentration on evacuation time of the ice core.

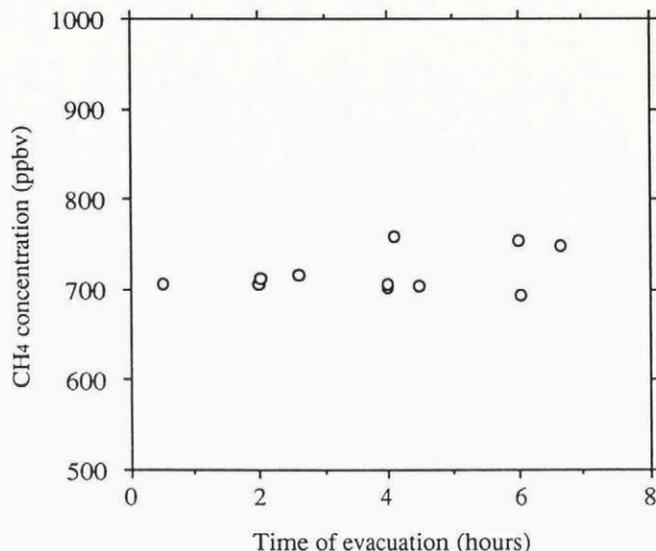


Fig. 7. The same as Figure 6 but for CH₄ concentration.

1 h until it was placed in the extraction chamber after removing its surface. During this period, CO₂ in the room air could have been adsorbed on the ice's surface or intruded into cracks opened partly by processing the surface of the ice core. To reduce such contamination, it was necessary to evacuate the chamber for at least 4 h before air extraction.

The results for CH₄ concentration are shown in Figure 7. As seen in this figure, the CH₄ concentrations range from 700 to 750 ppbv, mostly independent of the evacuation time. In this connection, it should be noted that the CO₂ concentrations in the cold room were ~70 times higher than those of the extracted air, while the CH₄ concentrations were only three times.

ANCIENT LEVELS OF ATMOSPHERIC CO₂ AND CH₄ CONCENTRATIONS

We present here the results of preliminary analysis of two Antarctic ice cores, Mizuho and Yamato. Detailed results and analysis procedures, as well as descriptions of the cores, will be given elsewhere. The CO₂ concentrations obtained by analyzing the Mizuho core are shown with open circles in Figure 8. The age of this core has been estimated by Nakawo and others (1989), and mean age difference between the ice and the occluded air was determined to be about 350 years from the measured vertical distribution of the total air content of the ice, assuming that it is nearly equal to the age of the ice at a depth where half of the final amount of air is closed off. The CO₂ concentrations range between 280 and 287 ppmv, giving an average value of 284 ppmv. These concentration differences are considerably larger than our experimental uncertainties. Natural variations in the atmospheric CO₂ concentration in the past and inhomogeneity of the ice core may be partly responsible for such differences. However, their main cause can be ascribed to the influence of modern air enclosed in the ice core. The Mizuho core used here cracked when it was thermally drilled and its melted surface was refrozen until it was pulled up to the surface. In this process, modern air

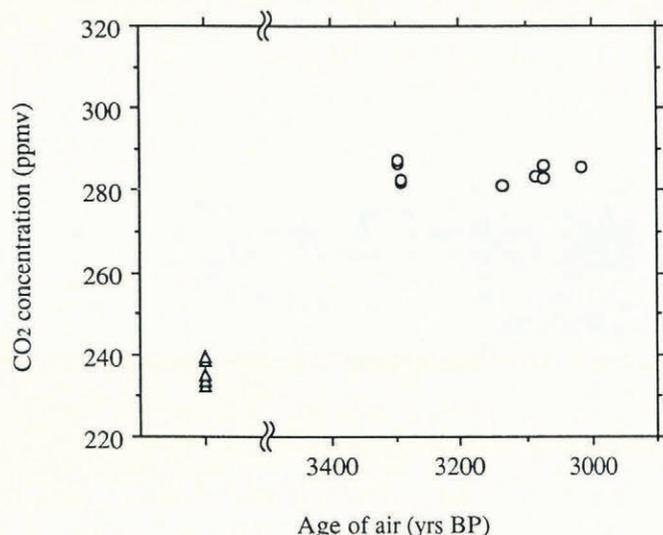


Fig. 8. Ancient CO₂ concentrations estimated by analyzing the two Antarctic ice cores. Values deduced from the Mizuho core are represented by open circles and those from the Yamato core by open triangles.

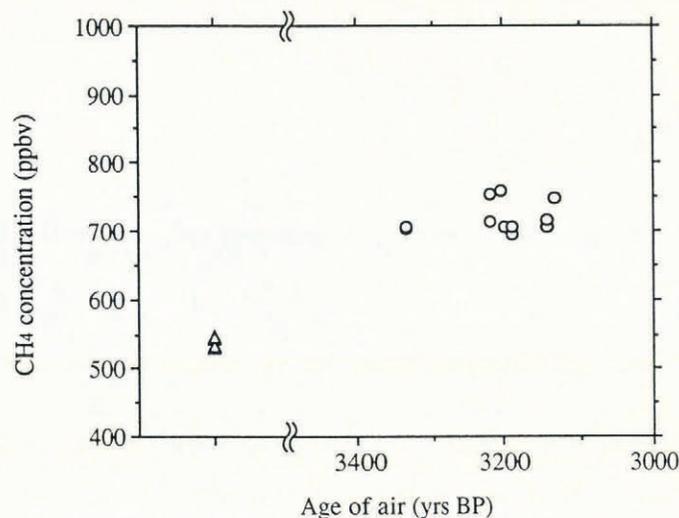


Fig. 9. The same as in Figure 8 but for CH₄ concentration.

brought into the borehole by the drill was partly enclosed in the cracks. For 6 years between the drilling and the analysis, the ice surrounding the cracks adhered to each other by sublimation and condensation, and the intruded air was isolated in the core. Such air cannot be removed from the ice core, even if the extraction chamber is evacuated for a long time. Therefore, lower values obtained in this analysis may be plausible for pre-industrial levels of the CO₂ concentration. In this connection, the analyses of shallower core samples with no cracks and deeper samples with cracks at Mizuho Station indicated CO₂ concentrations of about 280 ppmv. These values are in good agreement with the results obtained by Siegenthaler and Oeschger (1987), Siegenthaler and others (1988) and Wahlen and others (1991), and higher, by almost 10 ppmv, than those by Raynaud and Barnola (1985) and Barnola and others (1987), and they are lower by about 70 ppmv than recent values from continuous CO₂ measurements at Syowa Station, Antarctica (Nakazawa and others, 1991).

Open triangles in Figure 8 show the CO₂ concentrations obtained by analyzing the ice-core samples collected from 3–10 m depth in a bare icefield near the Yamato Mountains, East Antarctica. The age of this core is not determined, but it is expected to be very old, because the drilling was made in an upwelling area of the glacial flow. The CO₂ concentrations obtained show values of 230–240 ppmv, which are obviously lower than the pre-industrial background levels described above. Concentration differences of up to 10 ppmv could arise from different ages of different ice samples, as well as inhomogeneity of the ice samples due to complicated glacial flow. It has been reported by Neftel and others (1988) and Barnola and others (1987) that the CO₂ concentrations were lower by 80–90 ppmv during the last glacial maximum than in the Holocene. Therefore, our results suggest that the Yamato core used in this study was formed during the glacial period.

The CH₄ concentrations obtained from the Mizuho core are shown by open circles in Figure 9. The CH₄

concentrations are distributed between 700 and 760 ppbv, their average value being 719 ppbv. Higher values of the concentration are probably affected by modern air enclosed in the core, as mentioned above. Therefore, plausible background values of the CH₄ concentration around 3100–3400 year BP are thought to be about 700 ppbv, which is less than half of the recent values obtained from systematic CH₄ measurements at Syowa Station (Aoki and others, 1992). These values are close to pre-industrial/agricultural levels proposed by Craig and Chou (1982), Rasmussen and Khalil (1984) and Stauffer and others (1985).

As seen in Figure 9, the Yamato core gave values of 520–550 ppbv for the CH₄ concentration, which are lower by almost 150 ppbv than the post-glacial levels. Raynaud and others (1988) and Stauffer and others (1988) reported in their papers that the CH₄ concentration had decreased down to almost 350 ppbv during the last glacial maximum. Therefore, our results for the CH₄ concentration are consistent with the above suggestion that the Yamato core is extremely old and had formed during the glacial period.

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