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Determination of Methane Concentration in Air Extracted from Antarctic Ice Core Samples

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Synopsis. A convenient method was developed for detrmination of methane concentration in old air trapped in Antarctic ice core samples. The air was extracted with a stainless steel bellows pump after quick refreezing of melted ice samples and the methane was measured with a gas chromatograph with an FID. The averaged methane concentration in the Mizuho ice core at a depth of 330 m (ca. 3600 BP, 11 samples) was 750±20 ppbv.

Great concern has been expressed about the increasing concentrations of trace gases in the atmosphere and their effects on the global environment. The atmospheric concentrations in ancient times give us information on their natural background concentrations and the contribution of human activities.

In polar regions, snow is consolidated to firn, which contains permeable pore space for the air. When the firn turns into ice through densification and recrystallization over the course of 100 to 3000 years, the air in the ice pores becomes isolated from the atmosphere and enclosed in the ice as bubbles. A typical ice sample contains about 100 ml air (STP) per kg ice. Analyses of the air trapped in ice bubbles have revealed the historical changes of carbon dioxide[1-4] and methane concentrations.[5-10]

For extraction of the air in ice core samples, the ice block placed in a flask must be either crushed in a vacuum at temperatures below 0 °C (dry extraction method) or thawed (melt extraction method). The melt extraction method has advantages over the dry extraction method because the air in the sample is recovered quantitatively with a very simple apparatus. The dry extraction method requires a sophisticated apparatus with an inevitably large dead volume to extract only the air in bubbles. Moreover, the extracted air was reported to become contaminated by methane when ice was ground by a milling cutter.[7,8]

We, therefore, developed a new melt extraction method in which an ice sample was thawed and quickly refrozen. To transfer the extracted air we used an all-stainless-steel bellows pump instead of a mercury Toepler pump or liquid helium condensation, which may cause contamination and is expensive.

Experimental

Analytical Procedure for Ice Samples. The setup for the extraction and analysis of air is shown in Fig. 1. An ice core sample was cut into several pieces and weighed after removal of the surface layer (1 cm) at −20 °C in the cold room of the National Institute of Polar Research (NIPR). Ice blocks (about 100 g) were placed in a thick-walled, cylindrical glass flask (230 ml) sealed with a Viton O-ring and equipped with a glass-Teflon valve at the top. The flask was first evacuated for one hour at Dry Ice temperature; then the valve was closed and the ice was thawed in a water bath at 80 °C. When about 80% of the ice was thawed, the water bath was removed and the melt water was stirred with a magnetic spinner placed inside to bring the air in gas phase into equilibrium with that in liquid phase. Then it was quickly frozen at liquid nitrogen temperature so as to trap the dissolved gases. It took about 45 min to refreeze 100 g of melt water. The air in the gas phase was extracted, dried by being passed through a cold trap at −100 °C, and transferred into a preevacuated stainless steel sample loop (20 ml) or a small flask by an all-stainless steel bellows pump (specially made by GL Science, Co., using the excellent stainless-steel bellows material AM350) with no polymer parts inside. The gas was eventually analyzed with a gas chromatograph (Shimadzu GC-8A) equipped with a Polapak Q column (3 mm i.d., 4 ml length) and a flame ionization detector (FID).

The methane peak area in the chromatogram was compared with that of the clean air sample in a stainless steel flask calibrated in our laboratory.

Selection of Extraction Conditions. Each component of

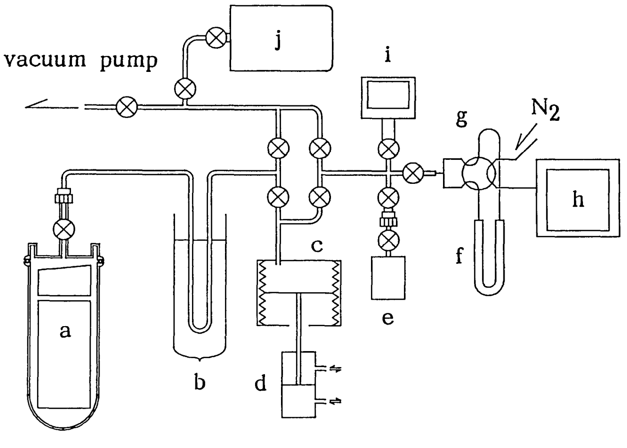

Fig. 1. Schematic diagram of air extraction from ice core sample and methane measurement system. a: sample flask; b: water vapor trap (−100 °C); c: all-stainless-steel bellows pump; d: actuator for pump; e: small flask; f: sampling loop (20 ml); g: 6-way valve; h: gas chromatograph (Shimadzu GC8A): i: pressure gauge (Datametrics Barocel Pressure Sensor); j: secondary standard.

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the air released from the melted sample is distributed differently between liquid and gas phases depending on its particular solubility in water. Since the water solubility of methane is greater than that of nitrogen or oxygen, the methane mixing ratio is depleted in the gas phase. If we could refreeze the melt water again extremely slowly from the bottom of the flask, most air dissolved in the water might be purged due to its negligible solubility in ice crystals, and the original air composition might be closely reproduced in the head space. However, it would take many hours to free the ice completely of air, or it is almost impossible to do so.

In quick freezing, the air purged from the growing ice crystals condenses at the ice–water interface. When the air at the interface cannot be dissolved in the water, nucleation of air bubbles occurs, and the air bubbles are trapped in the growing ice. Hence, if the growth of ice is faster than the air diffusion in the water, the ice incorporates the initially dissolved air almost completely. In this work, the ice grew at the rate of about 3×10^{-3} cm s^{-1}, which was much larger than the rate of diffusion of air in water (the diffusion coefficient: about 10^{-5} cm^2 s^{-1}), and in practice the ice contained many bubbles. Accordingly, we assume that the dissolved air can be preserved in the quickly refrozen ice and that the air in the gas phase has the same composition with that in equilibrium with the melted water.

It was reported that the air in the bubbles of Camp Century ice from Greenland had almost the same composition as to nitrogen, oxygen and argon as that in the present air.[11] Assuming that the main components are of the same composition as that in the present air and follow Henry's law, we can calculate the methane concentration in the head space air. The methane concentration (C) in the head space of the sample flask is given by

$$C=\frac{(V_a/V_w+\alpha_{\mathrm{air}}T/T_0)}{(V_a/V_w+\alpha_{\mathrm{CH_4}}T/T_0)}\times C_0$$

where C_0 is the initial methane concentration in ice bubbles; α_{air} and $\alpha_{\mathrm{CH_4}}$ are Bunsen solubility coefficients of air and methane, respectively; T is the temperature at which the thawed water was equilibrated; T_0 is 273 K; V_a is the volume of head space of sample flask; and V_w is water volume. Figure 2 shows the ratio of C to C_0 calculated at several equilibrium temperatures as a function of the volume ratio of V_a to V_w. If the volume ratio is <1, methane concentration decreases sharply with the decrease in the volume ratio. If the volume ratio is >1, methane concentration approaches the original concentration in ice bubbles (C_0). In this work, we kept the volume of the sample vessel constant so that V_a/V_w remained at about 1, or the methane concentration was depleted by about 2%.

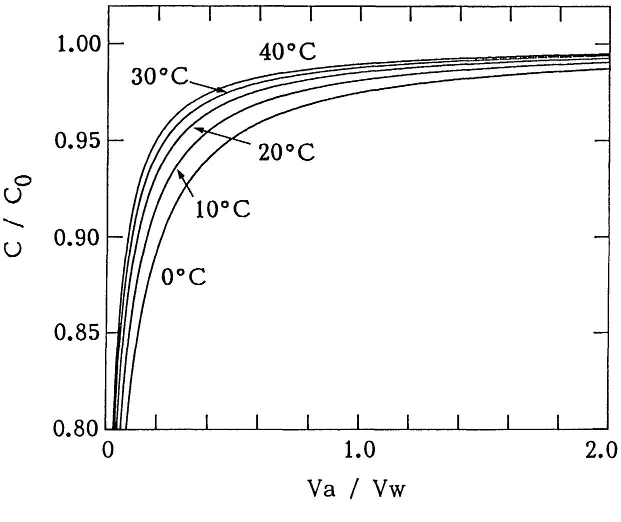

Fig. 2. Relation between the ratio of methane concentration in the air equilibrated with sample water (C) to that in ice bubbles (C_0) and the ratio of volume of headspace (V_a) to that of the water (V_w). The curves correspond to samples equilibrated at indicated temperatures.

Results and Discussion

Contamination and Correction of Methane Concentration. When the air was transferred with a bellows pump, the methane concentration was found to increase with a pumpling motion. In order to estimate the amount of methane emitted from the bellows pump, methane-free nitrogen was introduced into the pump and analyzed after some pumping motions. The amount of methane released from the stainless steel bellows increased linearly with the pumping time. Since this pump had been carefully baked and evacuated before its use, the methane released could not be explained by the desorption of the adsorbed methane from the metal surface. Since the frictional contact between metals is known to produce trace amounts of methane,[7,8] deformation of even the most excellent metal bellows (AM 350) may have produced the methane.

However, in practice, sufficient air can be obtained by one or two strokes of pumping motion to measure methane concentration, and contamination can be kept below 20 ppbv. For correction of the methane contamination during the analysis of ice samples, blank tests were carried out as follows:

(1) Ice prepared under air-free conditions was placed in the sample flask and evacuated. Methane-free nitrogen was then introduced into the sample flask at the same pressure as that for the air released from ice core samples. Following the same thaw-and-freeze procedure, methane concentration was determined.

(2) The same procedure as described above in (1) was used, but in the absence of ice. Blank values obtained were 40±20 ppbv and 20±5 ppbv, respectively. The former was slightly larger than the contamination arising from the bellows pump: even if the ice contained no air bubbles visually, a small amount of methane may have been included in the ice lattice. The latter value was consistent with the contamination from the bellows pump. As has been reported by Rasmussen and Khalil on snow samples from Mt. Hood,[12] we can assume that no methane is contained in falling snow in the Antarctica. Thus it is likely that almost all the contamination was caused by the bellows metal; correction was made for such unavoidable and reproducible contamination. In addition, methane concentration was corrected for change in concentration due to the gas–liquid distribution.

Application to Antarctic Core Samples. Methane concentration in the ice core drilled at Mizuho Station in 1984 was determined by the melt extraction method. The core sample for analysis (30 cm in length) was obtained at 330 m depth and was estimated to be about 3600 years old;[13] a 30 cm span at the depth of 330 m

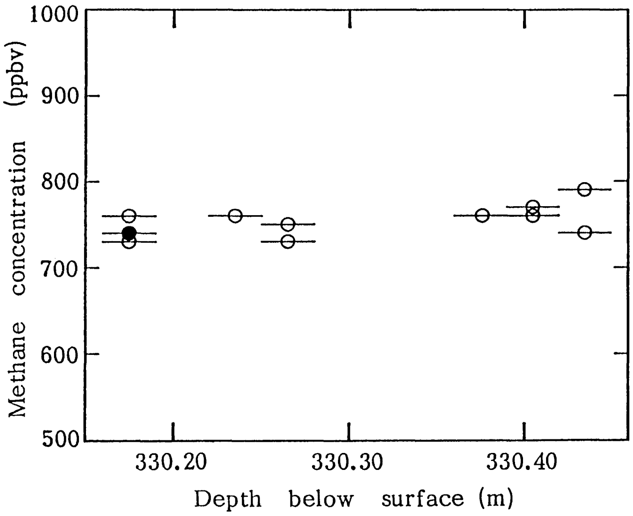

Fig. 3. Observed methane concentrations in the Mizuho core sample drilled in 1984 at 330-m depth below the surface. The solid circle shows the sample from the surface of the core.

corresponds to about 4 years. The core sample (13 cm in diameter) was first sliced horizontally into 3 cm thick disks, which were then divided into two halves after their rims, about 1 cm below the surface, had been removed. We took eleven sections of ice blocks from the core sample; one of them was the surface ice of the sample. The result of the analysis is shown in Fig. 3; the solid circle shows the concentration in the surface ice. The methane concentrations were observed to be uniform over the period studied, and the concentration at the surface was not necessarily higher than the others. The averaged methane concentration of the eleven samples was found to be 750±20 ppbv, a slightly higher value than those previously reported for similar ages.[5,6,10] After the presentation of our results,[14] Nakazawa et al. reported that the methane concentrations of several Mizuho core samples near the depth of 330 m were 690 to 750 ppbv.[15] Since the preesent core sample had many horizontal cracks probably produced during thermal core boring, we cannot exclude the possibility that the air in the ice core sample was contaminated by modern air.

We have developed a technique for extrication of air in polar ice. The precision of the methane analysis with 100 g core samples was about 20 ppbv. Although the bellows pump released negligible amounts of methane during operation, the current analytical system and procedures are simple and convenient; with improvements in the pump, or for analysis of te other components, this method will be quite useful.

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