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—研究ノート—
Scientific Note

High precision measurements of carbon isotopic ratio of atmospheric methane using a continuous flow mass spectrometer

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連続フロー式質量分析計を用いた大気中メタンの炭素同位体比の高精度測定

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要旨：メタン（CH_4）濃縮装置とガスクロマトグラフ－燃焼炉－同位体比質量分析計を用いた大気中メタンの炭素同位体比（$\delta^{13}CH_4$）分析システムを開発した．本システムは，100 m*l* の大気試料（標準状態で 0.18 μl の CH_4）を用いて 0.07‰の再現性で $\delta^{13}CH_4$ を分析することが可能である．2002 年から 2008 年にかけて，空気ベース CH_4 標準ガスの $\delta^{13}CH_4$ を繰り返し分析することにより，$\delta^{13}CH_4$ 分析値の信頼性を確認した．国立極地研究所において大気中の CH_4 濃度と $\delta^{13}CH_4$ の日変化を観測し，両者の関係から CH_4 濃度の変動原因について情報が得られることを確認した．

Abstract: A high-precision measurement system for the carbon isotope ratio of atmospheric CH_4 ($\delta^{13}CH_4$) was developed using a pre-concentration device for CH_4 and a gas chromatograph–combustion-isotope ratio mass spectrometer (GC-C-IRMS). The measurement system required 100 ml_{STP} of an atmospheric air sample, corresponding to approximately 0.18 μl_{STP} of CH_4, to determine the $\delta^{13}CH_4$ value with a reproducibility of 0.07‰. Replicated analyses of a CH_4-in-air standard gas during the period from 2002 to 2008 indicated that the value of $\delta^{13}CH_4$ measured by this system was consistent within the measurement reproducibility. To evaluate the $\delta^{13}CH_4$ measurement system, thus developed, diurnal variations of the atmospheric CH_4 concentration and $\delta^{13}CH_4$ were observed in the northern part of the Tokyo metropolitan area. From the relationship between the CH_4 concentration and $\delta^{13}CH_4$, dominant sources of the observed CH_4 fluctuations were identified.

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1. Introduction

Methane (CH_4) is one of the most important greenhouse gases, and its increase in the atmosphere over the past 250 years has been clarified by ice core studies and direct atmospheric observations (Etheridge *et al.,* 1998; Steele *et al.,* 1987). Since the 1980s, systematic observations of the atmospheric CH_4 concentration have been expanded around the world at ground stations and using ships and aircrafts (Aoki *et al.,* 1992; Dlugokencky *et al.,* 1994; Matsueda and Inoue, 1996). These observations have shown a rapid increase of CH_4 in the 1980s, followed by a gradual decrease of the increase rate through the 1990s; the causes of such long-term variability are under discussion (Dlugokencky *et al.,* 2003). The carbon isotope ratio of CH_4, $\delta^{13}CH_4$ (‰), defined as

$$\delta^{13}CH_4 = ((^{13}CH_4/^{12}CH_4)_{sample} / (^{13}C/^{12}C)_{V\text{-}PDB} - 1) \times 10^3, \quad (1)$$

where V-PDB denotes the international standard of $\delta^{13}C$ (Coplen *et al.,* 1983), provides information on sources and sinks of CH_4. CH_4 released from biomass burning, fossil fuel and microbial sources have characteristic $\delta^{13}CH_4$ values of approximately −25, −40 and −60‰, respectively, and the $\delta^{13}CH_4$ value of CH_4 destroyed by reaction with OH radicals is −53‰ (Quay *et al.,* 1999). Precise measurements of $\delta^{13}CH_4$ together with the CH_4 concentration therefore give us additional information on the CH_4 cycling. Monitoring stations for $\delta^{13}CH_4$, however, are still sparse.

We have developed a high-precision measurement system for $\delta^{13}CH_4$ in the atmospheric CH_4 using a pre-concentration device for CH_4 and a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-C-IRMS). With this measurement system, the $\delta^{13}CH_4$ value of the atmospheric CH_4 can be precisely determined by using 100 m*l* of air sample, which is approximately one-fiftieth or one-hundredth of the sample amount required for traditional $\delta^{13}CH_4$ analysis (Quay *et al.,* 1999; Lowe *et al.,* 1999). Because of the reduced sample amount required to determine $\delta^{13}CH_4$ precisely, frequent $\delta^{13}CH_4$ observations become possible even at Arctic and Antarctic stations and air samples extracted from air bubbles in ice cores can be analyzed. We have continued systematic $\delta^{13}CH_4$ observations of atmospheric CH_4 at Ny-Ålesund, Svalbard (79°N, 12°E) (Morimoto *et al.,* 2006) and Syowa Station, Antarctica (69°S, 40°E) using the system since 1996 and 2000, respectively. This paper describes the technical details of our $\delta^{13}CH_4$ measurement system.

2. Measurement system for $\delta^{13}CH_4$

The measurement system for $\delta^{13}CH_4$ consists of a CH_4 extraction and purification unit, a gas chromatograph (GC), a combustion furnace and a continuous flow isotope ratio mass spectrometer (IRMS).

To extract and purify CH_4 from the air sample, we used a commercially available pre-concentration unit (Thermo-Fischer, PreCON unit) with several modifications. Fig. 1 shows a schematic diagram of the PreCON unit used for the system. A similar configuration of the CH_4 extraction line was also reported by Merritt *et al.* (1995), Rice *et al.* (2001) and Miller *et al.* (2002). As shown in Fig. 1, the unit has four traps for H_2O/CO_2 removal from the air sample (chemical trap and T1), CH_4 extraction (T2) and CH_4 cryo-focusing (T3). The air sample stored in a 100 m*l* Pyrex glass flask with O-ring seal stop cocks at both ends is introduced by pure helium gas (Japan Air Gases, N-60) into the front end of the chemical trap. The chemical trap is a Pyrex glass tube, 6 mm o.d. and 250 mm long, containing magnesium percolate and Ascarite to adsorb H_2O and CO_2 in the air sample. The H_2O and CO_2 still remaining in the air sample are further removed at T1, which is a stainless steel tube, 1/16 inch *o.d.* and

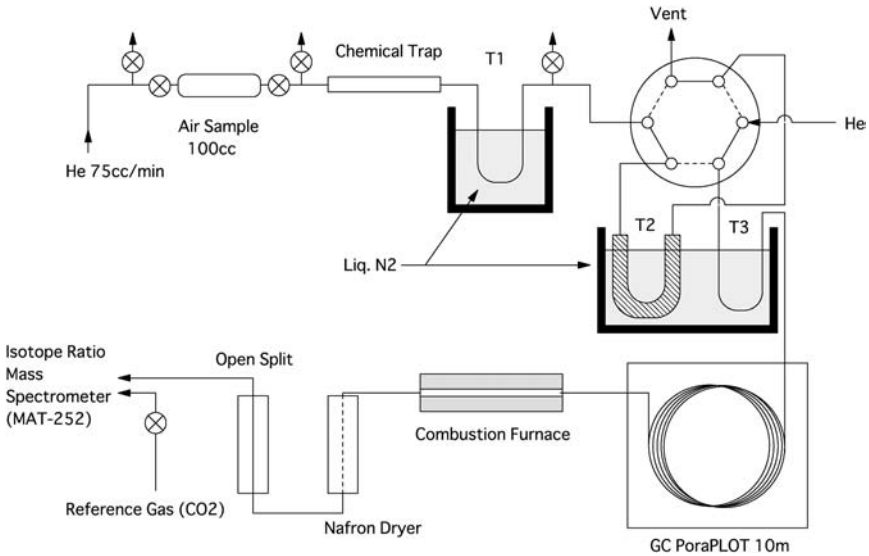

Fig. 1. Schematic representation of the modified pre-concentration (PreCON) unit and gas-chromatograph-combustion unit.

300 mm long, immersed in liquid nitrogen (LN_2, −197°C). The air sample then flows into the CH_4 extraction trap (T2), which is kept at −123°C. The T2 trap is a stainless steel tube, 1/8 inch *o.d.* and 300 mm long, containing 100/120-mesh HayeSep-D (Hayes Separation).

To maintain the temperature of the T2 trap at −123°C, heating and cooling are applied: heated with a silicon-coated wire heater coil (Nihon Dennetsu Keiki, AC100V/45W) on the T2 trap, and cooled with LN_2. The heater is controlled by a temperature controller (OMRON, E5CK); the temperature of the T2 trap is measured with a sheathed thermocouple. The T2 trap with the heater coil and the thermocouple are placed in a U-shaped copper tube (1/2 inch *o.d.*) to prevent LN_2 from penetrating into the trap. The CH_4 molecules in the air sample remains in the T2 trap at −123°C and other major components (such as N_2 and O_2) flow out from the vent port. The extracted CH_4 is then released from the T2 trap by taking the T2 trap out of the LN_2 bath, and transferred by helium gas flow into the cryo-focusing trap (T3). The T3 trap is a glass capillary column (CP-PoraBOND), diameter and length of 0.32 mm and 300 mm, respectively, and cooled to −197°C.

The concentrated CH_4 at the modified PreCON unit is further purified by using a gas chromatograph (GC; Agilent Technologies, 5890N) with a PoraPLOT-Q capillary column at a temperature of 30°C. A combustion furnace containing NiO, CuO and Pt wires at 940°C is placed at the outlet of the GC column to oxidize the CH_4 into CO_2 and H_2O. The H_2O molecules generated in the furnace are removed by a Naflon drier (semipermeable membrane tube) connected downstream of the furnace. The CH_4-derived CO_2 enters a continuous flow mass spectrometer (Thermo-Fischer, MAT-252) via an open split for carbon isotope ratio analysis.

To calculate the carbon isotope ratio of CH_4, a reference gas with known values of $\delta^{13}C$ and $\delta^{18}O$ in the V-PDB scale was also introduced into the mass spectrometer after the CH_4-derived CO_2 was analyzed. Our reference gases are pure CO_2 gas filled in a 10 *l* aluminum cylinder at a pressure of approximately 4.0 MPa. Their $\delta^{13}C$ and $\delta^{18}O$ values were determined against primary standard CO_2

gases produced from NBS-18 and NBS-19 at Tohoku University (Nakazawa *et al.,* 1993,1997). The isotope ratios of the reference gases were confirmed to have been stable within the measurement precisions of 0.02 and 0.05‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively, by comparing them with working standard gases maintained by Tohoku University using a mass spectrometer, MAT-deltaS (Nakazawa *et al.,* 1993).

3. Reproducibility and consistency of the $\delta^{13}CH_4$ analysis

To examine the analytical reproducibility and long-term stability of the $\delta^{13}CH_4$ measurement system, CH_4-in-air standard gases (Taiyo-Nissan Co.; hereafter denoted as test gases) stored in 47 *l* high-pressure cylinders, of which CH_4 concentrations are close to those in the atmosphere (*c.a.* 1.8 ppmv), were analyzed for $\delta^{13}CH_4$. Histograms and time-series of deviations of each measured value of $\delta^{13}CH_4$ from their averages from 2002 to 2008 are shown in Figs. 2 and 3, respectively. The total number of the analyses shown in the figures was 645. The standard deviation of the $\delta^{13}CH_4$ analyses was calculated to be 0.07‰, which is similar to the values reported by Miller *et al.* (2002) and Rice *et al.* (2001). Since we analyzed an air sample for $\delta^{13}CH_4$ at least twice, the standard error of the mean value becomes less than 0.05‰. As shown in Fig. 3, the $\delta^{13}CH_4$ values of the test gas analyzed by our system distribute about their mean value without any long-term trend. This fact suggests that the measurement system for $\delta^{13}CH_4$ and the isotope ratios of the reference gas had been stable within our measurement reproducibility for the period 2002 to 2008.

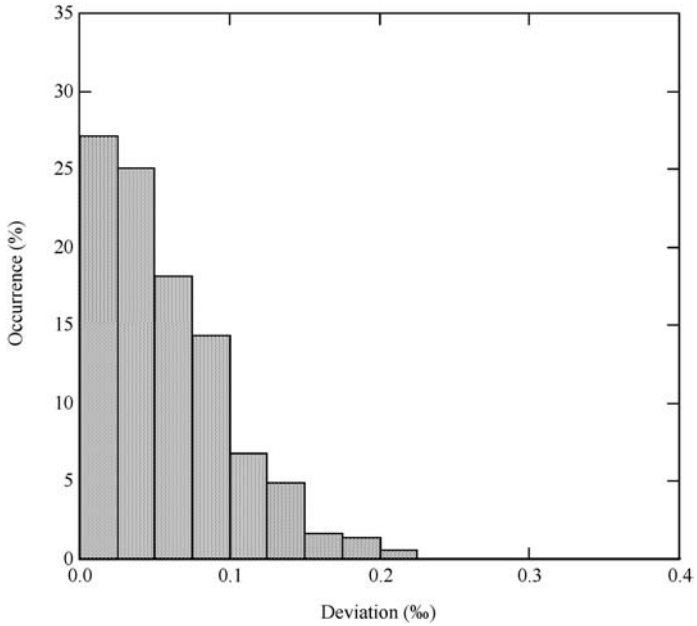

Fig. 2. Histogram of the $\delta^{13}CH_4$ values obtained by replicate analyses of a test gas with a CH_4 concentration of 1.8 ppmv. The $\delta^{13}CH_4$ values are shown as deviations from their average during the period 2002–2008.

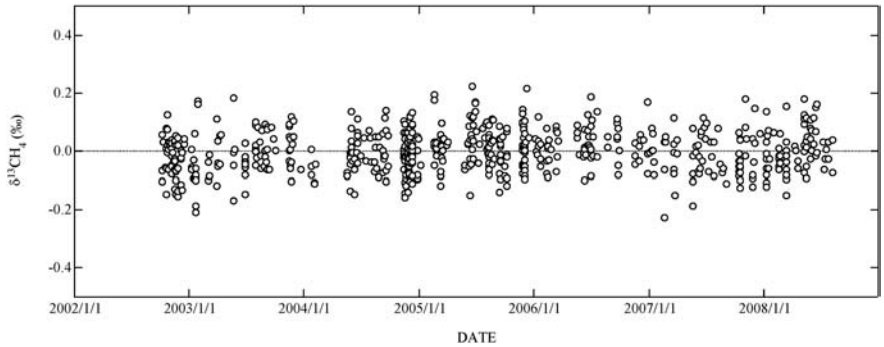

Fig. 3. Temporal variations of the $\delta^{13}CH_4$ values obtained by analyzing a test gas. The $\delta^{13}CH_4$ values are shown as deviations from their average during the period 2002–2008.

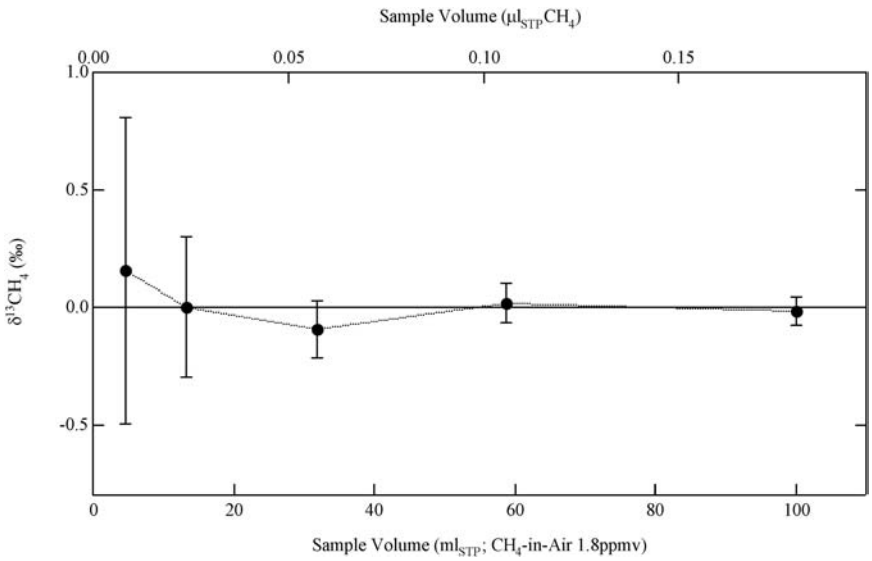

Fig. 4. Relationship between the sample amount and measured $\delta^{13}CH_4$ values, together with their standard deviations (1 σ). The $\delta^{13}CH_4$ values are shown as deviations from an average of values obtained by analyzing 100 ml air samples.

To examine the dependence of the $\delta^{13}CH_4$ measurements on the sample size, we replicated the analyses of the test gas, decreasing the amount from 100 ml_{STP} to 5 ml_{STP}, corresponding to the CH_4 amount from 0.18 μ l_{STP} to 0.01 μ l_{STP}. Fig. 4 shows the relationship between the sample volume used for the $\delta^{13}CH_4$ analysis and the measured value of $\delta^{13}CH_4$, together with their standard deviations. As seen in the figure, there is no significant trend in the $\delta^{13}CH_4$ values; however, the standard deviation increases remarkably with decrease of sample volume, especially in a range of less than 60 ml_{STP}.

Inter-comparison of the $\delta^{13}CH_4$ scales with the National Institute of Water and Atmospheric Research (NIWA), New Zealand (Lowe *et al.,* 2004) was carried out in 2004 using four air samples,

with $\delta^{13}CH_4$ values ranging from −38 to −57‰. The results showed that our scale is 0.37 ± 0.04‰ heavier than the NIWA scale at atmospheric $\delta^{13}CH_4$ levels. The source of the difference is still not clear; however, our $\delta^{13}CH_4$ data are confirmed to be internally consistent by the "test gases" analyses as shown in Fig. 4.

4. Diurnal variations of $\delta^{13}CH_4$ observed in Tokyo, Japan

To examine the measurement system, air samples collected on the roof of our institute (National Institute of Polar Research) located in the northern part of the Tokyo metropolitan area were analyzed for $\delta^{13}CH_4$ during the period September 20–21, 2000. The air sample was obtained every 1–3 hours into an 800 m*l* stainless steel flask at a pressure of about 0.9 MPa. The CH_4 concentrations of the air samples were also determined by using a gas chromatograph equipped with a flame ionization detector (Shimadzu, GC-8A) at a reproducibility of 1.0 ppbv (Aoki *et al.,* 1992).

Fig. 5 shows the temporal variations of the CH_4 concentration and $\delta^{13}CH_4$ obtained during the two days. Consistent with other observations at urban sites (*e.g.,* Lowry *et al.,* 2001), the CH_4 concentration showed maximum and minimum values in the early morning and after noon, respectively. Short-term variations of the CH_4 concentration and $\delta^{13}CH_4$ correlate positively for the period from 1500 local time (LT) on September 20 to 0000 LT on September 21, and negatively for the remaining hours. The rate of change of $\delta^{13}CH_4$ with respect to the CH_4 concentration was calculated to be +5.5 ± 2.0‰/ppmv for the period 1500–0000 LT, and −3.8 ± 0.3‰/ppmv for the remaining hours. If CH_4 is added into the atmosphere from microbial sources, fossil fuel sources, biomass burning, or atmospheric CH_4 is destroyed by reaction with OH radials, the respective change rates of $\delta^{13}CH_4$ relative to the CH_4 concentration are expected to be −6.6, +3.9, +11.8 and −2.9‰/ppmv. These factors can be derived

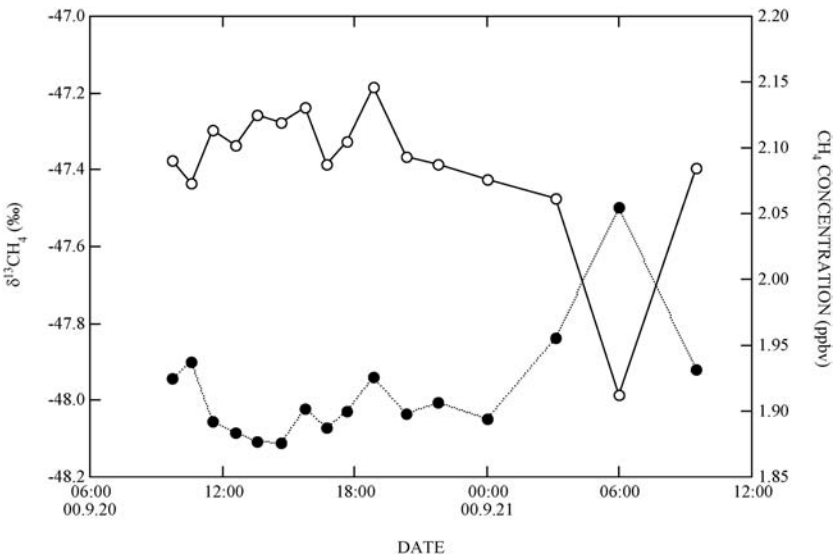

Fig. 5. Diurnal variations of the CH_4 concentration (closed circles; right axis) and $\delta^{13}CH_4$ (open circles; left axis) observed in the northern Tokyo metropolitan area on September 20-21, 2000.

from the single mixing relation (Keeling *et al.,* 1989) using the CH_4 concentration of 1.9 ppmv and $\delta^{13}CH_4$ of −47.4‰ as background values, as well as the respective characteristic isotope ratios of −60, −40, −25 and −53‰ for microbial, biomass burning, fossil fuel sources and OH sink. Taking the sensitivity factors into account, dominant causes of the observed CH_4 fluctuations could be ascribed to the fossil fuel source and OH sink for the 1500–0000 LT period, and microbial sources and OH sink for the remaining hours. Also found from Fig. 5 is that there are notable positive peak of the CH_4 concentration and negative peak of $\delta^{13}CH_4$ from 0300 to 0900 LT on September 21. The change rate of $\delta^{13}CH_4$ relative to the CH_4 concentration was calculated to be -4.9 ± 0.3‰/ppmv for that period, suggesting that the peaks are caused mainly by microbial CH_4 emissions. It is possible that CH_4 released from local rivers and/or sewage wastewater accumulated in the stable lower atmosphere before sunrise.

5. Concluding remarks

We have developed a high-precision measurement system for the carbon isotope ratio of atmospheric CH_4 ($\delta^{13}CH_4$). This system is capable of analyzing $\delta^{13}CH_4$ at a reproducibility of 0.07‰ using a 100 m*l* air sample. It was confirmed from the diurnal cycle of $\delta^{13}CH_4$ observed in Tokyo that this system enables us to investigate the sources of the observed CH_4 fluctuations. Since the system only requires a small amount of air sample to determine the $\delta^{13}CH_4$ value precisely, frequent observations of atmospheric $\delta^{13}CH_4$ are possible by a grab-sampling method, even at remote sites such as Arctic or Antarctic stations.

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