

## Western Pacific Air-Sea Interaction Study

year	2014
URL	<a href="http://hdl.handle.net/2261/58891">http://hdl.handle.net/2261/58891</a>

# Study of the Production Processes of Marine Biogenic Methane and Carbonyl Sulfide Using Stable Isotope Analysis

S. Toyoda<sup>1\*</sup>, K. Yamada<sup>1</sup>, Y. Ueno<sup>2</sup>, K. Koba<sup>3</sup> and O. Yoshida<sup>4</sup>

<sup>1</sup>Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

<sup>2</sup>Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan

<sup>3</sup>Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

<sup>4</sup>Department of Environmental and Symbiotic Science, College of Agriculture, Food and Environment Sciences, Rakuno Gakuen University, 582 Bunkyo-dai-Midorimachi, Ebetsu 069-8501, Japan

\*E-mail: toyoda.s.aa@m.titech.ac.jp

Keywords: Methane; Carbonyl Sulfide; Stable Isotope Ratio

## Introduction

Methane (CH<sub>4</sub>) and carbonyl sulfide (COS) directly, or indirectly, contribute to the radiative energy budget of the Earth. They are known to be produced in the ocean surface and lower atmosphere mainly by biological activities. However, their production processes and global budget are still not fully understood.

Methane is one of the greenhouse gases and its identified major sources are anaerobic bacterial processes and non-biogenic thermal processes (IPCC 2007). In the open ocean, CH<sub>4</sub> shows a concentration maximum in the subsurface water. The origin of the supersaturated CH<sub>4</sub> is not clear, although production by CH<sub>4</sub>-producing bacteria in zooplanktons or faecal pellets has been proposed (Tilbrook and Karl 1994).

Carbonyl sulfide indirectly contributes to the Earth's radiative budget as a source of atmospheric sulfate aerosol. Its sources include the photochemical reaction of or-

ganic sulfur compounds produced by marine organisms, the gas phase oxidation of biogenic CS<sub>2</sub> and dimethylsulfide (DMS) (Watts 2000). However, it has been suggested that the ocean can also be a sink of COS in a certain period of the year, because it can be hydrolyzed (Kettle *et al.* 2002). The material budget of COS between the ocean and the atmosphere has a large uncertainty due to the lack of observations.

Stable isotope ratios have been used to elucidate the material cycle of environmental substances since they reflect the origin of the substance, and the physical and chemical processes. The purpose of this study is (1) to reveal the production and consumption processes of CH<sub>4</sub> by analyzing hydrogen and carbon isotope ratios in natural seawater, and water samples in laboratory simulation experiments, and (2) to develop a method for high-sensitive and high-precision sulfur isotope analysis of COS to know its signature in the atmosphere and ocean.

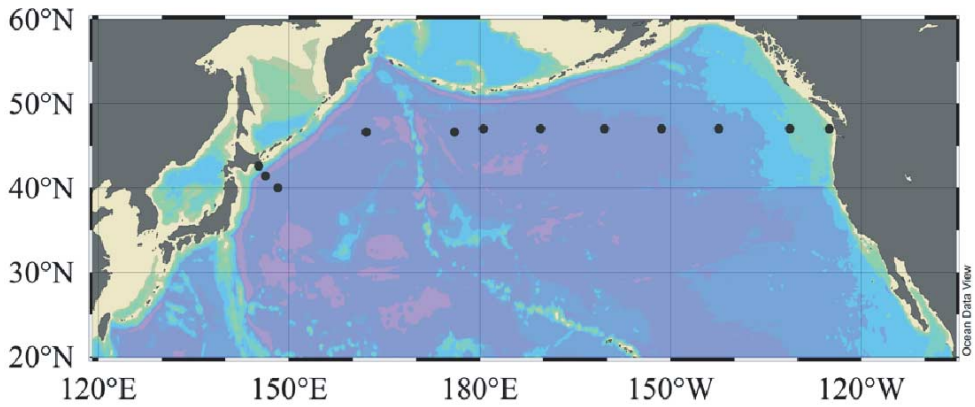


Fig. 1. Map of seawater sampling for  $\text{CH}_4$  analysis.

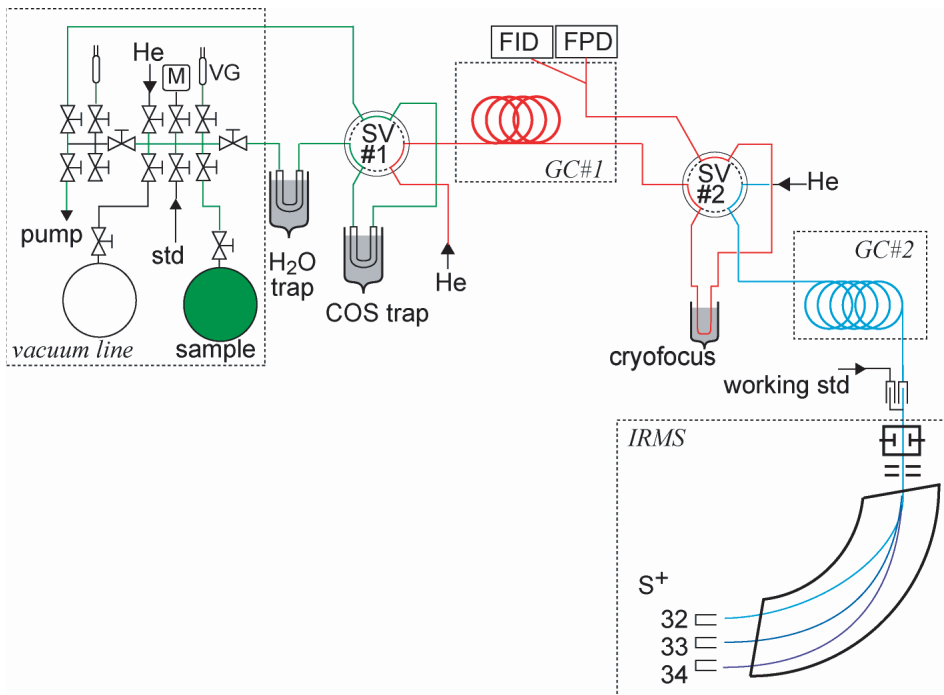
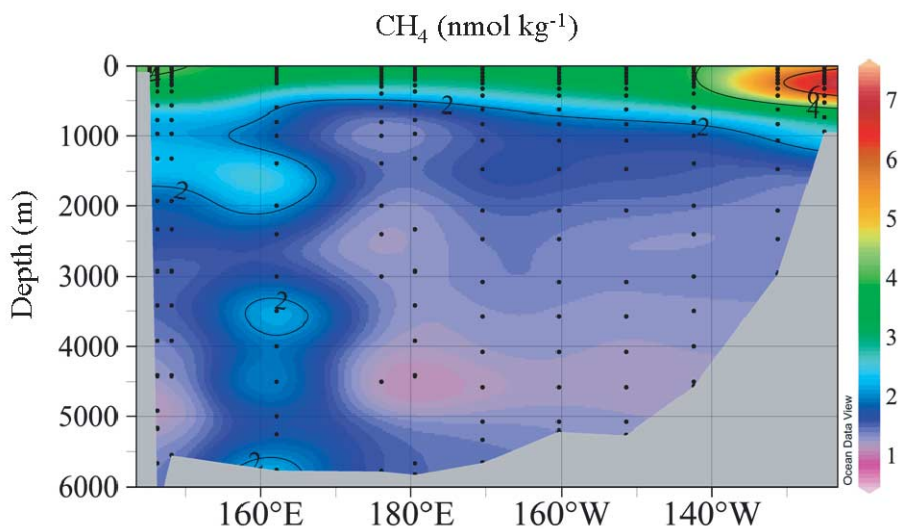


Fig. 2. Schematic of analytical system for sulfur isotope ratio in COS.

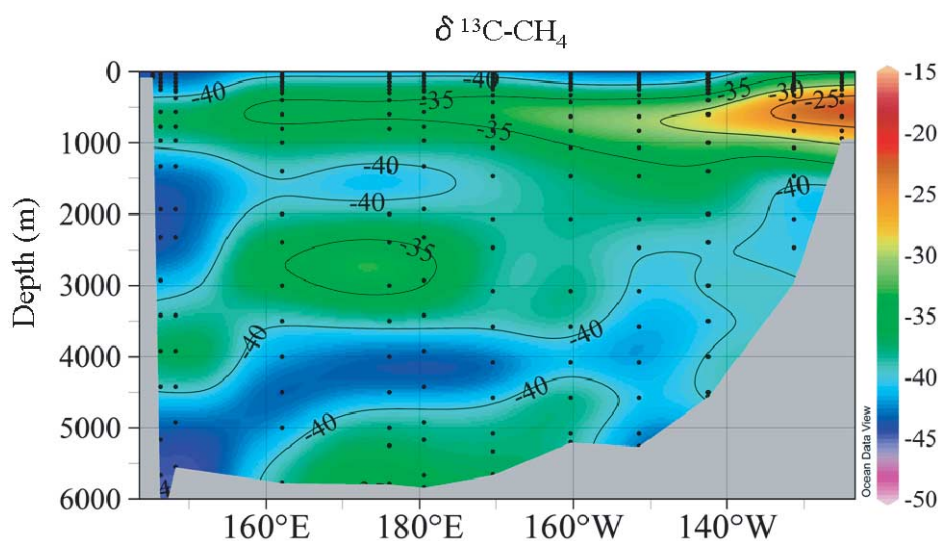
## Methods

Seawater samples for  $\text{CH}_4$  analysis were collected along the  $47^\circ\text{N}$  line (WOCE P01) in the North Pacific during the re-

search cruise of R/V Mirai (MR07-04) in July–September, 2007 (Fig. 1). Samples for concentration, carbon isotope ratio, and hydrogen isotope ratio were collected from a Niskin bottle into 30, 125, 600 mL vials,



**Fig. 3.** Depth-longitude distribution of dissolved CH<sub>4</sub> concentration in the North Pacific (47°N).

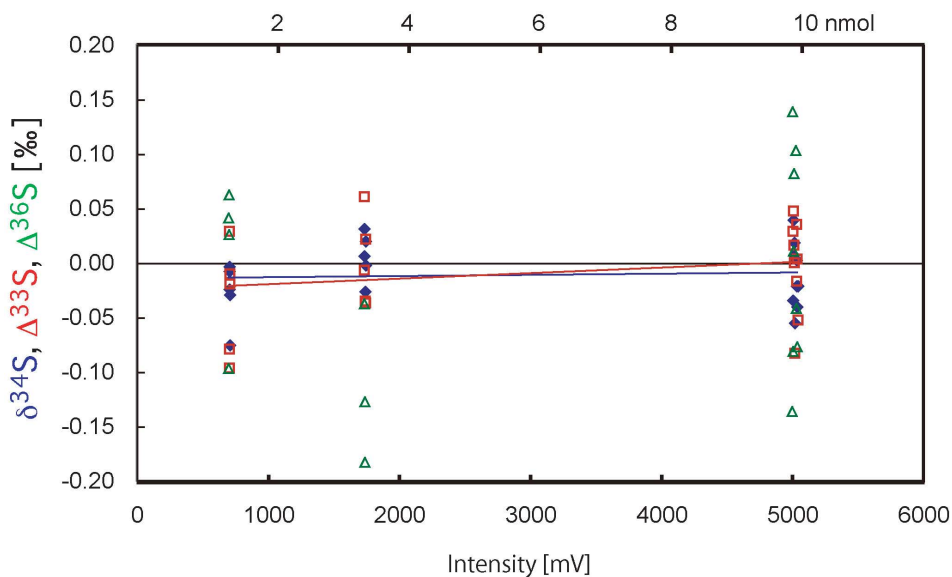


**Fig. 4.** Depth-longitude distribution of carbon isotope ratio of dissolved CH<sub>4</sub> in the North Pacific (47°N).

respectively, and preserved after adding saturated HgCl<sub>2</sub> solution. The concentration of CH<sub>4</sub> was measured by GC-FID, and its carbon and hydrogen isotope ratios were

determined by GC-C-IRMS and GC-TC-IRMS, respectively.

In order to measure sulfur isotope ratios in trace COS (nmol level), we have



**Fig. 5.** Precision and sample-size dependence of sulfur isotope ratios (diamonds,  $\delta^{34}\text{S}$ ; squares,  $\Delta^{33}\text{S}$ ; triangles,  $\Delta^{36}\text{S}$ ) in  $\text{SF}_6$  on a GC-IRMS.

made a preparation system that concentrates the COS in a large volume of air (~50 L), and we examined two approaches by GC-IRMS: (a) the mass analysis of an  $\text{S}^+$  fragment produced by the ionization of COS (Fig. 2) and (b) the chemical conversion of COS to  $\text{SF}_6$  and on-line injection to IRMS. Isotopic calibration of laboratory COS standard was conducted using a conventional off-line method for converting COS to  $\text{SF}_6$ . Maritime air samples were collected into glass and silica-lined stainless steel containers during the cruises, including the above-mentioned one.

## Results and Discussion

### $\text{CH}_4$

Figures 3 and 4 show depth-longitude profiles of the concentration and carbon isotope ratio of dissolved  $\text{CH}_4$  observed along the 47°N line in the North Pacific. A common feature in the studied area is that the concentration shows a maximum of about 4.5 nmol  $\text{kg}^{-1}$  at a depth shallower

than 300 m, and rapidly decreases below that depth (Fig. 3). The carbon isotope ratio,  $\delta^{13}\text{C}-\text{CH}_4$ , at around 400 m was higher than  $-35\text{‰}$ , indicating that the oxidative layer exists immediately below the  $\text{CH}_4$  concentration maximum (Fig. 4). The depth of the  $\text{CH}_4$  concentration maximum coincided with pycnocline, which suggests the origin of  $\text{CH}_4$  is not the vertically transported  $\text{CH}_4$  from the bottom or deep layer but  $\text{CH}_4$  produced in situ. Since  $\delta^{13}\text{C}-\text{CH}_4$  at the  $\text{CH}_4$  concentration maximum was higher than  $-40\text{‰}$ , it is not probable that it is produced in the zooplankton (Sasakawa *et al.* 2008). It would be produced by  $\text{CH}_4$ -producing bacteria in the reducing environment in the micro particles. The hydrogen isotope ratio in  $\text{CH}_4$  was also measured, but it was found that the amount of the sample was insufficient for a high precision analysis.

### COS

As for approach (a), the precision of  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  with 14 nmol COS in stand-

ard gas (11 ppm in He) was about 1.7‰ and 0.9‰, respectively. However, the delta values showed an increase with decreasing sample size, which requires adjustment of the amount of introduction of sample and standard. As for approach (b), the precision of  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  with 5 nmol of SF<sub>6</sub> introduced into GC-IRMS was both better than 0.1‰, and showed only a slight dependence on the sample size (Fig. 5). The preparation line for converting COS into SF<sub>6</sub> has been constructed and its operating condition is being optimized.

### Conclusions

We observed supersaturated CH<sub>4</sub> in the subsurface water along the 47°N line in the North Pacific, and deduced its origin as production by CH<sub>4</sub>-producing bacteria in the reducing environment in the micro particles. Measurements of hydrogen isotope

ratios will supply additional information to that obtained with the carbon isotope ratio. In order to evaluate the possibility of CH<sub>4</sub> production by phytoplankton, incubated subsurface seawater, or phytoplankton, should be analyzed for carbon and hydrogen isotope ratios.

Sulfur isotope ratio analysis with a small amount of COS has been found to be possible. After improvement of the precision and accuracy by optimization of the analytical conditions, atmospheric and oceanic samples will be analyzed.

### Acknowledgements

We are grateful to the directors, researchers, captains, and the crews of the R/V Mirai for their help. We also thank N. Yoshida for providing experimental facilities, K. Kawano and T. Miyafukuro for the sampling and analysis of dissolved CH<sub>4</sub>, and T. Watanabe and S. Hattori for developing the analytical method for COS.

### References

- IPCC (2007) *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, U.K. and New York.
- Kettle AJ, Kuhn U, von Hobe M, Kesselmeier J, Andreae MO (2002) Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *J. Geophys. Res.* **107**: 4658, doi:10.1029/2002JD002187.
- Sasakawa M, Tsunogai U, Kameyama S, Nakagawa F, Nojiri Y, Tsuda A (2008) Carbon isotopic characterization for the origin of excess methane in subsurface seawater. *J. Geophys. Res.* **113**: C03012, doi:10.1029/2007JC004217.
- Tilbrook BD, Karl DM (1994) Dissolved methane distributions, sources, and sinks in the western Bransfield Strait, Antarctica. *J. Geophys. Res.* **99**: 16383–16393.