CARBON ISOTOPIC RELATIONSHIP BETWEEN METHANE AND ARCHAEAL LIPIDS: IMPLICATION FOR BIOMARKER RECORDS OF AOM AT A COLD SEEP

S. Sakata[1], U. Tsunogai[2], N. Oba[3]

[1]National Institute of Advanced Industrial Science and Technology, Japan
[2]Department of Earth and Environmental Sciences, Nagoya University, Japan
[3]Graduate School of Environmental Studies, Tohoku University, Japan

Introduction

Many previous studies have shown that archaeal lipids distinctly depleted in ^{13}C occur in methane-rich marine sediments, e.g., at cold seeps and mud-volcanoes, which are considered evidence for anaerobic oxidation of methane (AOM) conducted by syntrophic consortia of methanotrophic archaea and sulfate-reducing bacteria. This implies that methanotrophic archaea consume $^{12}CH_4$ faster than $^{13}CH_4$, making the remaining methane more enriched in ^{13}C. It is also known that the $\delta^{13}C$ values of archaeal lipids differ widely between samples, which may be partly due to difference in the isotopic composition of methane on which the methanotrophic archaea grow. In order to investigate such carbon isotopic relationship, we have undertaken to measure methane-seep sediments from the Nankai Trough for carbon isotopic compositions of methane (dissolve in porewaters) and archaeal lipids.

A near-surface core sediment sample was collected from the Nankai Trough off Tokai (34° 04.4100' N; 137° 47.5110' E; water depth 610 m) in 2001 (Oba et al., 2006). At this site, a large-scale colony (larger than 100 meters square) of *Calyptogena* (most were dead) and emission of gas bubbles had been observed on previous submersible dives. Free gas trapped under the shells had been collected on the dive in 1998, and 99.8% of the gas had been found to consist of methane with a $\delta^{13}C$ value of -57.4 ‰. The occurrence of gas hydrates below the seafloor was inferred from previous seismic surveys.

The core was 1.2 m long with low water content, high viscosity, and distinct smell of H_2S. It was sliced into about 10 cm segments for geochemical analyses as follows. Porewaters were extracted with a hydraulic piston squeezer, and analyzed for concentrations of sulphate and chloride ions with an ion chromatograph. Gases dissolved in the porewaters were released by heating sediment in a vial at 60 °C for 30 minutes, and analyzed for both the concentration and carbon isotopic composition of methane with an online GCCMS system (Tsunogai et al., 2000). Total lipids were extracted with organic solvents, separated by silica gel column chromatography into 10 fractions of different polarity, converted to less polar derivatives, and measured for the concentrations and carbon isotopic compositions of specific hydrocarbons and ether lipids with GC and GCCMS, respectively. Detail procedures for the detection of polar ether lipids are described in Oba et al. (2006).

Results and Discussion

Concentrations of methane range from 2.6 to 29 μmol kg^{-1}, maximizing at around 0.9 mbsf. They are higher than those of porewaters in common marine sediments, but far lower than those of porewaters from which methane hydrate forms. The $\delta^{13}C$ values of methane range from -75.4 to -25.9 ‰, fluctuating widely within the small depth range. This suggests that

methane, originally depleted in ^{13}C (characteristic of microbial methane), was partially consumed by ANME, giving a very wide distribution of ^{13}C due to difference in the extent of methane consumption. It seems unlikely that this isotopic profile reflects marked change in the origins of methane, i.e., the mixing ratios of ^{13}C-depleted microbial methane and ^{13}C-enirched thermogenic methane.

The δ values of hydroxyarchaeols and archaeol are much less variable, ranging from -121 to -109 ‰, and from -118 to -104 ‰, respectively. Very low δ values clearly indicate AOM signatures. It is clear that these diethers are derived mostly from ANME.

The δ values of 2,6,10,15,19-pentamethylicosane (PMI) range from -112 to -87 ‰, indicating a clear signature of AOM. There is a trend that the higher the concentrations, the lower the δ values, resulting in depth profiles of the two parameters to mirror each other. Relatively high δ values of the deeper samples suggest that this compound is derived not only from ANME but also from methanogen.

The ^{13}C depletions of diethers (archaeol and hydroxyarchaeols) relative to methane in the same sample range up to 85 ‰. This value is larger than those previously reported from different AOM sites (Bradley et al., 2009).

We find no clear correlation between the δ values of archaeal lipids and methane. Because of this point, and because δ values of archaeal diethers are low and least variable, we infer that the major fraction of these lipids are fossil, derived from ANME living in the past, when methane flux were high enough to create the large colony of *Calyptogena* at this site.

Conclusion

The δ values of porewater methane in near-surface core sediments at a methane-seep site are found to fluctuate as large as 50 ‰ within the small depth range of 1.2 m, which is likely due to different extent of methane consumption by ANME. As expected, archaeal lipids (ether lipids and hydrocarbons) with low δ values are detected in the sediments. However, no clear relationship is found between the δ values of archaeal lipids and methane. Most of the lipids may be fossil, derived from ANME living when methane flux was higher. This study demonstrates that the difference in δ between methane and lipids from ANME could become as large as 85 ‰, being larger than previously reported.

References

Oba, M., Sakata, S., Tsunogai, U. (2006) Org. Geochem. 37, 1643-1654.

Tsunogai, U., Yoshida, N., Ishibashi, J., Gamo, T. (2000) Geochim. Cosmochim. Acta 64, 2439-2452.

Bradley, A., S. ,Hayes, J. M., Summons, R. E. (2009) Geochim. Cosmochim. Acta 73, 102-118.