Isotopic fractionation of methane gas with clathrate hydrate formation under the condition of ice crust / internal ocean boundary in icy satellite

*Kushi Kudo[1], Atsushi Tani[1], Keita Yamada[2], Naohiro Yoshida[2,3]

1. Department of Human Environmental Science, Graduate School of Human Development and Environment, Kobe University, 2. Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 3. Earth-Life Science Institute, Tokyo Institute of Technology

Icy satellites have capability of having extra biota due to eruption of plume, which is consisted by sea ice particles including organic matter. The observation using Cassini clarified that this plume included hydrogen molecule (H_2), CO_2, methane (CH_4) and organic matter (e.g. Porco et al. 2006; Waite et al. 2006, 2009, 2017). Especially in plume gas species, methane (CH_4) is regarded as one of the candidate of signature of biological activity due to CH_4 formation reaction by methanogen. However CH_4 gas in plume is consisted of not only microbial origin but also primitive and/or hydrothermal origin and this fact does not let CH_4 detection is sufficient for conclusion for existence of biological activity by microbe. Therefore, we consider that evaluation of the elementary process of CH_4 isotopic fractionation ($\delta^{13}C$ and δD of CH_4) via room experiment is important for isotopic observation of icy satellite in nearly future.

In this study, we focus on CH_4 hydrate which is reservoir to produce the plume (Kieffer et al. 2006) and plan to evaluate isotopic fractionation with its formation. Isotopic fractionation with hydrate formation has been found at only δD of CH_4 (~10‰) at the Earth condition (P: ~6 MPa) (e.g. Hachikubo et al. 2007, 2015; Lapham et al. 2012). In the case of condition of icy satellites and icy planets, the pressure range is wider than of the Earth, and therefore we need to estimate isotopic fractionation (P: 5–50 MPa).

We formed clathrate hydrate samples using hydrate formation equipment under the extreme environments, which can hold until 50 MPa. We lowered cell temperature from room temperature to 276 K, and then stirred CH_4 gas and pure water at 85 or 400 RPM stirring rotation speed to form hydrate sample. We inserted CH_4 gas at slightly higher pressure than the previous studies (5, 10 MPa). We collected gas samples of primitive gas from CH_4 gas cylinder and remained gas samples from the high pressure cell after hydrate formation, and then we measured stable isotopic ratio ($\delta^{13}C$ and δD of CH_4) using GC-IRMS equipment at Tokyo Tech.
Results in isotopic measurements show that the $\delta^{13}C$ value of remained gas phase was slight lower (less than 1‰) than of primitive gas phases and became lower at higher pressure. This suggest that 1) $^{13}CH_4$ and $^{12}CH_4$ easily condensed into gas phase in hydrate and remained gas phase (plume) with clathrate hydrate formation, respectively, and 2) this condensation became stronger at higher pressure. Furthermore, the $\delta^{13}C$ value of remained gas phase became lower at faster stirring rotation speed. Since Wijayanti (2018) reported that hydrate formation rate, stability and storage capacity became higher at higher stirring rotation speed, the above tendency of stronger isotopic fractionation at higher stirring rotation speed is acceptable. We found slight isotopic fractionation unlike in the previous reports. As the isotopic fractionation easily occurs by pressure, we plan to proceed the experiment at higher pressure. These tendencies indicate that isotopic fractionation of CH_4 with clathrate hydrate formation in icy satellites may depend on pressure and stirring rotation speed in internal ocean water-CH_4 gas mixing.

Keywords: methane gas, icy satellite, clathrate hydrate, isotopic fractionation, pressure dependence, stirring rotation speed

