Isotope fractionation between hydrate-bound and ambient gases - case study in Lake Baikal gas hydrates -

*Hiromi Kimura[1], Akihiro Hachikubo[1], Oleg Khlystov[2], Gennadiy Kalmychkov[3], Marc De Batist[4], Hirotoshi Sakagami[1], Hirotsugu Minami[1], Satoshi Yamashita[1]

1. Kitami Institute of Technology, 2. Limnological Institute, SB RAS, 3. Vinogradov Institute of Geochemistry, SB RAS, 4. Ghent University

Isotope fractionation of methane occurs between gas and hydrate phases (Hachikubo *et al.*, 2007). However, such fractionation is not applied to understand the formation process of natural gas hydrates in the sublacustrine sediments of Lake Baikal. In this study, we compiled data on stable isotope ratios of hydrocarbons in hydrate-bound and sediment gases, which have been collected in the framework of collaboration between Limnological Institute (Russia), Ghent University (Belgium), and Kitami Institute of Technology (Japan) for 15 years.
Hydrate-bearing sediment cores were collected by R/V *G. Yu. Vereshchagin* using a gravity corer. Hydrate-bound gas was collected in vials by a water displacement method on board, and sediment gas was obtained using the headspace gas method by collecting sediment at 40 cm intervals from the sediment core sections. The gas composition and stable isotope ratios of volatile hydrocarbons were measured for these samples by gas chromatograph (GC2014, Shimadzu) and CF-IRMS (Delta V, Thermo Fisher Scientific), respectively. Comparison of stable isotope ratios of hydrate-bound and sediment gases at the same core and depth was performed.
The methane carbon isotope ratio of the hydrate-bound gas was 0 to +3‰ smaller than the sediment gas. These isotopic difference in carbon was slightly positive overall, indicating a concentration of lighter methane ($^{12}CH_4$) in the hydrate-bound gas than in the sediment gas. The difference in hydrogen between hydrate-bound and sediment gases distributed from -3‰ to +11‰ and is also positive overall as well. The average difference in δD was 5.4‰, which agreed fairly well with the previous report that approximately 5‰ light methane in δD is preferentially enclathrated at the formation of synthetic methane hydrate (Hachikubo *et al.*, 2007). Although the positive difference in δ^{13}C cannot be explained yet, these results can be explained generally by the isotopic fractionation of methane. In contrast, some sediment cores retrieved at the Kedr mud volcano showed small or reversed differences in methane carbon isotope ratios, as well as small differences in methane hydrogen isotope ratios, suggesting that dissociation of gas hydrate is occurring at that point.

References

Hachikubo A, Kosaka T, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H (2007) Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases. *Geophys Res Lett* **34**: L21502. doi:10.1029/2007GL030557

Keywords: gas hydrate, isotope fractionation, methane

