

Hydrogen isotopic fractionation of methane and propane at the formation of their mixed-gas hydrate

*RYOYA KAMATA¹, Yunosuke Hase¹, Akihiro Hachikubo¹, Satoshi Takeya²

1. Kitami Institute Of Technology, 2. National Institute of Advanced Industrial Science and Technology (AIST)

During the formation of methane hydrate, hydrogen isotope fractionation for methane occurs between gas and hydrate phases (Hachikubo *et al.*, 2007); δD of hydrate-bound methane is $4.8 \pm 0.4\%$ lower than that of residual methane at 274.2 K. In the case of ethane, the isotopic difference between them is $1.1 \pm 0.7\%$ and smaller than methane. In the case of propane, the difference is reported as $4.6 \pm 1.0\%$ (Nikaido *et al.*, 2018). We suppose that the relation between the sizes of guest molecules and cage size of crystallographic structure affects the isotopic fractionation. Methane is enclathrated in both large (tetrakaidecahedral, $5^{12}6^2$) and small (dodecahedral, 5^{12}) cages of the cubic structure I. On the other hand, in the case of methane and propane mixed-gas hydrate, methane prefers to be enclathrated in small cages, because propane is enclathrated only in the large cages (hexakaidecahedral, $5^{12}6^4$) of the cubic structure II. Therefore, we can evaluate the effect of cage size on the isotopic fractionation for methane using the above mixed-gas hydrate. In this report, we checked hydrogen isotopic differences for methane and propane between gas and hydrate phases. 0.7 g of fine ice powder was introduced in a pressure cell (volume: 30 mL). Methane and ethane mixed-gas were introduced in the cell and gas hydrate sample formed at 274.2 K. Before the retrieval of gas hydrate sample, residual gas was sampled, and then gas hydrate was cooled at 77 K and retrieved the hydrate-bound gas. We measured compositions of methane and ethane by a gas chromatograph (GC2014, Shimadzu) and hydrogen isotopic composition (δD) of methane and propane by a CF-IRMS (Delta V, Thermo Fisher Scientific). The hydrogen isotopic differences between hydrate-bound and residual propane was $4.9 \pm 0.6\%$, agreed well with the previous work, whereas those of methane was $3.7 \pm 0.9\%$, slightly smaller than the value reported by Hachikubo *et al.* (2007). These results indicate that isotopic difference in methane δD for 5^{12} cages is smaller than those for $5^{12}6^2$ cages.

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

Nikaido T, Matsuda J, Hachikubo A, Takeya S (2018) Hydrogen isotope fractionation of propane and isobutane hydrates between gas and hydrate phases. *JSSI & JSSE Joint Conference -2018 in Sapporo*, doi:10.14851/jcsir.2018.0_158

Keywords: gas hydrate, methane, propane, hydrogen isotope ratio