

Isotopic fractionation of ethane at the formation of sII gas hydrate composed of methane and ethane

*Yuka Oota¹, Akihiro Hachikubo¹, Satoshi Takeya²

1.Environmental and Energy Resources Research Center, Kitami Institute of Technology, 2.National Institute of Advanced Industrial Science and Technology (AIST)

Methane and ethane mixed-gas hydrate of the cubic structure II exists at the central and southern Baikal Basin. We found "double structure gas hydrate" composed of the structure I and II in a same sediment core. The structure II gas hydrate contained 13-15% of ethane, on the contrary, the structure I has only several % of ethane. Subramanian et al. (2000a; 2000b) reported that a structure II forms in appropriate gas composition of methane and ethane. Hachikubo et al. (2009) showed that δD of hydrate-bound ethane in the structure II is smaller than that in the structure I, whereas $\delta^{13}C$ of methane and ethane, and δD of methane are the same between the structure I and II. It has been unknown how the structure II concentrates light ethane in δD (hydrogen isotope).

In this study, synthetic mixed-gas (methane and ethane) hydrates were formed and checked isotopic fractionation between phases of hydrate and residual gas. We made a hydrate sample from methane and ethane mixed-gas (85% C1; 15% C2) in a pressure chamber (volume: 120 mL). Before the retrieval of gas hydrate sample, residual gas was also sampled. We measured isotopic compositions (^{13}C and D) of methane and ethane using CF-IRMS. Crystallographic structure of gas hydrate was determined using a Raman spectrometer.

The Raman spectra of C-C stretching mode of ethane in hydrate phase indicated that the sample belonged to structure II. δD of hydrate-bound ethane was several permil smaller than that of residual ethane, similar to the behavior of methane δD in the structure I. Although the mechanism of ethane fractionation at the formation process of the structure II is not fully understood, the results agree with the observation at the Kukuy K-2 mud volcano reported by Hachikubo et al. (2009).

Hachikubo et al. (2009) Model of formation of double structure gas hydrates in Lake Baikal based on isotopic data. *Geophys Res Lett* 36: L18504. doi:10.1029/2009GL039805

Subramanian et al. (2000a) Evidence of structure II hydrate formation from methane + ethane mixtures. *Chem Eng Sci* 55: 1981-1999. doi:10.1016/S0009-2509(99)00389-9

Subramanian et al. (2000b) Structural transitions in methane + ethane gas hydrates - part I: upper transition point and applications.

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