結晶構造II型のメタン・エタン混合ガスハイドレート生成時におけるエタン安定同位体分別
Isotopic fractionation of ethane at the formation of sII gas hydrate composed of methane and ethane

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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 delta D of hydrate-bound ethane in the structure II is smaller than that in the structure I, whereas delta 13C of methane and ethane, and delta D of methane are the same between the structure I and II. It has been unknown how the structure II concentrates light ethane in delta D (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 (13C 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. Delta D of hydrate-bound ethane was several permil smaller than that of residual ethane, similar to the behavior of methane delta D 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).
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