

Effect of crystallographic structure on hydrogen isotopic fractionation of ethane

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Mixed-gas hydrate composed of methane and ethane forms the cubic structure II in appropriate gas composition. We found "double structure gas hydrate" composed of the structure I and II in a same sediment core at the central and southern Baikal Basin. The structure II gas hydrate contained 13-15% of ethane, on the contrary, the structure I has only several % of 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. These results might be explained by the difference in hydrogen isotope fractionation between formation processes of the structure I and II. In this study, we synthesize methane and ethane mixed-gas hydrates and checked the isotopic difference between gas and hydrate phases.

We put 0.7g of fine ice powder into a pressure cell (volume: 30mL), introduced methane and ethane mixed-gas, and formed a gas hydrate at 273.4K. Before the retrieval of gas hydrate sample, residual gas was sampled, and then gas hydrate was cooled at the temperature of liquid nitrogen and retrieved the hydrate-bound gas. We controlled the ethane composition of hydrate-bound gas from 2% to 98%, covering the area of methane-rich structure I, ethane-rich structure I, and their intermediate structure II. We measured compositions of methane and ethane by a gas chromatograph, and hydrogen isotopic composition (δD) of 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 provides information of the crystallographic structure.

δD of hydrate-bound ethane was about 1-2‰ smaller than that of residual ethane in the case of the structure I, agreed with the previous report for pure methane and pure ethane hydrates by Hachikubo *et al.* (2007). On the contrary, these isotopic difference increased to 9-12‰ in the case of the structure II, those ethane compositions distributed around 15-34%. These results support the idea that the structure II hydrate at Lake Baikal formed by the dissociation of the structure I hydrate.

Reference

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