

## Hydrogen isotopic fractionation of ethane encaged in different crystallographic structure

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Methane and ethane mixed-gas hydrate forms the cubic structure II in appropriate gas composition. Hachikubo *et al.* (2009) measured isotopic compositions of Lake Baikal gas hydrates and showed that  $\delta D$  of hydrate-bound ethane in the structure II is smaller than that in the structure I. These results might be explained by the difference in hydrogen isotope fractionation between formation processes of the structure I and II. In the last JpGU meeting we reported that the isotopic difference between gas and hydrate phases increased to 9-12‰ in the case of the structure II, whereas the difference was 1-2‰ in the case of the structure I. However, the effect of methane on the isotopic fractionation of ethane is unknown. In this study, we choose argon instead of methane and synthesize argon and ethane mixed-gas hydrates to check the isotopic difference in ethane between gas and hydrate phases.

0.7 g of fine ice powder was introduced in a pressure cell (volume: 30 mL). Argon 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 the temperature of liquid nitrogen and retrieved the hydrate-bound gas. We controlled the ethane composition of initial gas from 3% to 25%. We measured compositions of argon and ethane by a gas chromatograph, and hydrogen isotopic composition ( $\delta D$ ) of ethane by a CF-IRMS. Crystallographic structure of gas hydrate was determined using a Raman spectrometer, because the Raman spectra (around 1000  $\text{cm}^{-1}$ ) of C-C stretching mode of ethane in hydrate phase provide information of the crystallographic structure.

Because ethane was concentrated into hydrate phase rather than argon, ethane compositions of hydrate-bound gas distributed from 30% to 71%. In the case of low concentration of ethane, crystallographic structure II forms due to the effect of argon (the structure II former).  $\delta D$  of hydrate-bound ethane was about 4-7‰ smaller than that of residual ethane in the case of structure II, where ethane composition was 30-36% in the hydrate phase. On the other hand, in the case of high concentration of ethane (around 70% in the hydrate phase)  $\delta D$  of hydrate-bound ethane was around 2‰ larger than that of residual ethane. In the transition zone between the structures I and II the isotopic difference between hydrate and residual gas phases seemed to be an intermediate value (1-4‰). From these results we can conclude that light ethane ( $\text{C}_2\text{H}_6$ ) prefers to be encaged into the structure II clathrate hydrate, compared to heavy ethane ( $\text{C}_2\text{H}_5\text{D}$ ).

### Reference

Hachikubo A, Khlystov O, Manakov A, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H, Kalmychkov G, Poort J (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

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