Hydrogen isotopic fractionation of methane at the formation of synthetic structure I and II gas hydrates

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Hydrogen isotopic fractionation of volatile hydrocarbons occurs during the formation of gas hydrates. For example, the hydrogen isotope ratios of the hydrate-bound methane, ethane, and propane are lower than those of the ambient gases (Hachikubo *et al.*, 2007; Nikaido *et al.*, 2018). These results are supported by the difference in equilibrium pressures of hydrates encaged guest isotopologues (Ozeki *et al.*, 2018). The crystal structure of gas hydrate depends on the size of guest gas. Methane and ethane hydrates form the structure I, composed of large ($5^{12}6^2$) and small (5^{12}) cages, whereas propane hydrate forms the structure II, composed of the different size large ($5^{12}6^4$) and small (5^{12}) cages. Ethane and propane can be encaged only in their large cages due to the large guest size. Since natural gas hydrates are mixed-gas hydrates, these guest molecules share the cages of different size. In the case of methane + ethane and methane + propane systems, methane is selectively occupied in the small cages. On the contrary, methane can be rather encaged into large cages in the system of methane + argon, because argon is smaller than methane. Therefore, we can check the effect of cage size on the hydrogen isotopic difference in methane. In this study, we investigated the hydrogen isotope fractionation of methane in the mixed-gas system of methane + ethane, methane + propane, and methane + argon systems.

A pressure cell (volume: 40 mL) was filled with 0.7 g of fine ice powder in a cold room. After vacuuming the air in the cell at the temperature of liquid nitrogen, the guest gases (methane, ethane, propane, and argon) were introduced in the cell and formed the mixed-gas hydrates. In the formation processes, the partial pressure of ethane and propane was also controlled below the liquefaction pressure of propane. After the formation of mixed-gas hydrate, residual gas that was not encaged in the hydrate phase was collected. Hydrate crystals were sampled at the temperature of liquid nitrogen. The composition of the hydrate-bound and residual gases were determined by a gas chromatograph (GC-2014, Shimadzu). The hydrogen isotope ratio of methane was determined by a stable isotope ratio mass spectrometer (CF-IRMS, DeltaV, Thermo Fisher Scientific). Stable isotope compositions are reported as δ values (‰), and δD is given with reference to the V-SMOW standards.

The difference in hydrogen isotope ratios of methane (δD of residual gas – δD of hydrate-bound gas) is defined as $\Delta\delta$D. The $\Delta\delta$D values in the system of methane + ethane and methane + propane was smaller than that of pure methane reported by the previous works (Hachikubo *et al.*, 2007). Therefore, $\Delta\delta$D became small in the case that methane was encaged into small cages. On the contrary, the $\Delta\delta$D values in the system of methane + argon was not changed with their gas composition. The crystallographic structure depended on the gas composition and methane was rather encaged into large cages. We confirmed that $\Delta\delta$D values in large cages was larger than those in small cages.

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