

## Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases

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Stable isotope ratio of natural gas hydrates are useful to know their gas sources. Large and small  $\delta^{13}\text{C}$  of methane indicates thermogenic and microbial origins, respectively, and  $\delta\text{D}$  of methane provides information of methyl-type fermentation or  $\text{CO}_2$  reduction in the microbial region (Whiticar, 1999). Although isotopic fractionation of host molecules at the formation of methane hydrate has been reported by Maekawa (2004), little is known about those of guest molecules. In this study, we would like to report the isotopic fractionation of gas molecules between gas and hydrate phases for synthetic methane and ethane hydrates.

Liquid water or ice powder was set into a batch-type reactor (small pressure chamber), and pressurized by methane or ethane above their equilibrium pressures. The temperature was kept for several days at 274K or 255K, respectively. Both phases of gas and hydrate were sampled and isotopic composition ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of gas molecules were measured. The effect of gas consumption on the isotopic composition was also investigated by changing the amount of liquid water or ice powder.

$\delta\text{D}$  of methane and ethane in hydrate phase were approximately 8-11 permil and 3 permil smaller than those of gas phase, respectively. Besides this,  $\delta^{13}\text{C}$  of them in hydrate phase seemed a little bit smaller than those of gas phase, but their differences were less than 0.3 permil. Although the  $\delta\text{D}$  of residual gas was almost same as that of the original gas when the amount of liquid water or ice powder was small, it became heavier and  $\delta\text{D}$  of guest gas in hydrate phase closed to that of the original gas in case of much water or ice. We also confirmed by changing the isotopic composition of water that  $\delta\text{D}$  of host molecules was not effective on the above results of isotopic differences, hence the isotopic fractionation seems to occur in the formation process of gas hydrate, not in the isotopic exchange process between the host and guest molecules.

Consequently,  $\delta\text{D}$  of guest molecules of methane and ethane hydrates was smaller than that of molecules in gas phase at their formation processes. However, their differences seemed small and not effective to discuss the gas source of natural gas hydrates.