

Temperature effect on isotopic fractionation of methane hydrate between gas and hydrate phases

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Methane hydrates are stable under high pressure and low temperature conditions, and exist in the sea/lake bottom sediments and permafrost layers. Stable isotope ratio of methane hydrate provides information to know their gas sources. Although isotopic fractionation of guest molecules at the formation of methane hydrate has been reported by Hachikubo *et al.* (2007), little is known about the mechanism of this isotopic fractionation. To understand a controlling factor of the fractionation process, we would like to show a temperature effect (from 223K to 278K) on the isotopic fractionation of methane between gas and hydrate phases for synthetic methane hydrates.

Liquid water or ice powder was set into a batch-type reactor (small pressure chamber), and pressurized by methane above the equilibrium pressure. Temperature was kept for several days. Both phases of gas and hydrate were sampled and isotopic compositions ($\delta^{13}\text{C}$ and δD) of gas molecules were measured by using a mass spectrometer (DELTA plus XP; Thermo Finnigan).

Data of methane δD in hydrate phase were 3.5 permil and 8.4-9.4 permil smaller than those of gas phase at 278K and 265-243K, respectively. The difference between them reached to 33 permil at 223K. While the difference of methane $\delta^{13}\text{C}$ between gas and hydrate phases was less than 1 permil at 243-278K as observed by Hachikubo *et al.* (2007), it increased with the decrease in temperature. Methane $\delta^{13}\text{C}$ of hydrate phase was 3.3-3.9 permil larger than that of gas phase. Therefore, we can conclude that the hydrate phase concentrates methane molecules composed of light hydrogen and/or heavy carbon at low temperature. This study is the first report that an isotopic fractionation of carbon exists at the formation of methane hydrate.