

## Temperature effect on the isotopic fractionation of methane at a formation of synthetic methane hydrates

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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 in a hydrate phase 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 isotopic fractionation. To understand a controlling factor of the fractionation process, we revealed a temperature effect (from 223K to 278K) on the isotopic fractionation of methane between gas and hydrate phases at a formation of synthetic methane hydrates.

Liquid water or ice powder was set into a batch-type reactor (small pressure chamber), and pressurized by methane at a pressure of +2MPa above the equilibrium pressure of methane hydrate. Temperature was kept for several days. Both phases of gas and hydrate were then sampled and isotopic compositions ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of gas molecules were measured by using a mass spectrometer (DELTA plus XP; Thermo Finnigan).

$\delta\text{D}$  of methane in a hydrate phase was 3.5 permil and 10.7-5.8 permil smaller than those of gas phase at 278K and 243-265K, respectively. The difference between them reached to 7.2-13.2 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 0.6-3.3 permil larger than that of gas phase at 223K. Therefore, we can conclude that the hydrate phase concentrates methane molecules composed of light hydrogen and/or heavy carbon at low temperature.