

Consideration of factors on the isotopic fractionation of guest gas molecules at the formation of gas hydrate

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Gas hydrates are stable under the conditions of low temperature and high partial pressure of guest gases, as they 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, however, isotopic fractionation of guest molecules at the formation of methane hydrate affects their isotope ratio (Hachikubo et al., 2007). In this study, we discussed a possible process on the isotopic fractionation to understand a controlling factor of the fractionation process. Besides this, isotopic fractionation between gas and dissolved gas in water and a possibility of proton exchange between the guest and host molecules was examined in the case of methane hydrate.

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. After the formation of hydrate, both phases of gas and hydrate were then 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). We first revealed a temperature effect (from 223K to 278K) on the isotopic fractionation of methane between gas and hydrate phases at the formation of synthetic methane hydrates; we confirmed that the hydrate phase concentrates methane molecules composed of light hydrogen and /or heavy carbon at low temperature. Our hypothesis is as follows: because the size of CH_3D molecules seems to be relatively larger than CH_4 , CH_3D is hardly encaged. The molecular size of $^{13}\text{CH}_4$ is almost the same as that of $^{12}\text{CH}_4$, and the hydrate phase gets enriched with a heavier isotope in carbon as a guest molecule, as well as the host molecule reported by Maekawa (2004). In addition, methane dD values provided almost the same isotopic difference even in the case of D_2O as the host molecules. Therefore, the host molecules did not cause the above mentioned isotopic differences in dD . On the other hand, we confirmed that there were no isotopic differences in both carbon and hydrogen between gas and dissolved gas in water. It is reasonable to conclude that the process of methane solution into water does not affect the above isotopic difference.

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