Methane is composed of carbon and hydrogen. Because these components have isotopes, $^{12}\text{CH}_4$ (98.9%), $^{13}\text{CH}_4$ (1.1%), and CH$_3$D (0.013%) exist in nature. Since their molecular weight differs with each other, physicochemical properties of them are also different with each other. Pure methane hydrate is "mixed-gas hydrate" of their isotopologues. Equilibrium pressure of pure methane hydrate was first reported more than a half century ago; however, those of $^{13}\text{CH}_4$ and CH$_3$D hydrate have not been studied yet. Fractionation of hydrogen isotope during the formation of methane hydrate has been reported by Hachikubo et al. (2007) that δD of hydrate-bound methane becomes several ‰smaller than that of residual methane in the formation process. This result suggests that the equilibrium pressure of CH$_3$D hydrate is larger than that of CH$_4$ hydrate. In this study, we measured the equilibrium pressures of CH$_3$D hydrate and confirmed the difference between them.

Methane hydrate samples were synthesized in small pressure cells (volume: 5mL). Fine ice powder (1g) was put in a pressure cell, and introduced CH$_3$D (purity: 98%, Taiyo-Nissan). Clathrate hydrate was formed by melting the ice powder at the temperature of 273.2K under high pressure of methane. We also prepared normal methane (purity: 99.99% for methane, but 98.9% for $^{12}\text{CH}_4$, Takachiho Chemical Industry Co. Ltd.) hydrate as a reference, using the same preparation method. These pressure cells were placed in a temperature-controlled liquid bath, and measured their equilibrium pressures from 273.2K to 277.2K.

The equilibrium pressure of CH$_3$D hydrate was about 0.07MPa larger than that of CH$_4$ hydrate, and the results agreed with the previous report by Hachikubo et al. (2007).

Reference