

Isotopic fractionation of methane during the formation of hydrate crystals near the ice point

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Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperature, high partial pressure of each gas component, and high gas concentration. Isotopic fractionation of carbon and hydrogen in methane during the formation of clathrate hydrate was reported by Hachikubo *et al.* (2007) that δD of hydrate-bound methane is $4.8 \pm 0.4\%$ and $9.0 \pm 0.9\%$ lower than that of residual methane for samples prepared from liquid water and ice powder, respectively. In this report, we discussed about the temperature effect on the isotopic difference between residual and hydrate-bound methane.

The methane hydrate samples were experimentally prepared in a pressure cell, and the temperature was controlled by a liquid bath. Isotopic compositions of both residual and hydrate-bound methane were measured by an IRMS. Samples were formed in the temperature range from 274.2K to 283.2K, corresponded to the temperature of natural near-surface gas hydrates in the world. The hydrogen isotopic difference between hydrate-bound and residual methane were 3.5-5.5%, agreed with the previous report above the ice point. Kikuchi *et al.* (2018) reported that the equilibrium pressure of CH_3D hydrate is about 0.07MPa larger than that of CH_4 hydrate in the temperature range from 273.2K to 277.2K. Therefore, we can explain that the difference in equilibrium pressure between CH_3D and CH_4 hydrates causes such isotopic difference in δD . Hachikubo *et al.* (2007) reported that the difference in δD between hydrate-bound and residual methane is around 9‰ below the ice point, suggesting that the difference in equilibrium pressure below 273.2K becomes larger than above 273.2K.

Reference

Hachikubo A, Kosaka T, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H (2007) Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases. *Geophys Res Lett* 34: L21502. doi:10.1029/2007GL030557

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Keywords: gas hydrate, stable isotope, methane, isotopic fractionation