Effect of water depth on hydration number of natural gas hydrate in Lake Baikal

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Natural gas hydrates exist under the deep sea/lake or permafrost are considered to be a potential natural gas resource. Hydration number "n" of methane hydrate (CH_4 nH_2O) decides the amount of methane in an unit volume/weight of crystal. In the case of ideal full-occupation of hydrate cages, the value of hydration number is 5.75 (Sloan and Koh, 2008). However, researchers have reported that the hydration number is around 6, because small amount of empty cages decrease the free energy and stabilize the crystal. Natural gas hydrates have been retrieved from lake-bottom sediment at Lake Baikal, where the water depths ranged from 450m to 1400m, and their main gas component is methane. Hydration number may change under various pressure condition, but it has not been examined yet. In this study, we report the pressure effect on hydration number of synthetic methane hydrate and natural gas hydrate of Lake Baikal.
Methane hydrate was synthesized under the pressure range between 3 MPa to 20 MPa. Natural hydrate samples were retrieved at the southern Baikal basin (Malenky, Bolshoy, Peschanka P-2, and Goloustnoye G-1) and central Baikal basin (Kukuy K-1, K-2, K-8, K-9, K-10, and Novosibirsk). Raman spectroscopic measurements were made to assess the hydration numbers of samples. Raman spectra were obtained at 123 K in the range 2,800-3,000 cm^{-1} for the C-H stretching peaks of methane, and fitted using a Voigt function to obtain the integrated intensities of the two peaks corresponding to methane encaged in large and small cages of the cubic structure I. The cage occupancies and the hydration numbers were estimated from these peak intensities using a statistical thermodynamic model (Sum et al., 1997). Hydration number of synthetic methane hydrate decreased with pressure, from 6.05 (2.7 MPa) to 5.97 (20.9 MPa), and those of natural gas hydrate also decreased slightly with water depth.
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