Characteristics of structure I natural gas hydrate encaged thermogenic methane

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Crystallographic structures of natural gas hydrate are usually either structure I or structure II. The latter can encage larger hydrocarbons, for example, propane, isobutane, n-butane, and neopentane. Because the origin of these molecules is thermogenic, methane ascending with them from deeper sediment layer is also thermogenic. Hydrate-bound thermogenic methane has been reported in the world (Gulf of Mexico, offshore Vancouver Island, Caspian Sea, etc.). C1/C2+ of guest gas in these sites are less than 10, indicating that compositions of ethane and propane in hydrate-bound hydrocarbons are in an order of several percent. Therefore, crystallographic structure of gas hydrate composed of thermogenic gas is primarily the cubic structure II.
On the other hand, the structure I gas hydrates retrieved off Joetsu contained thermogenic methane (delta 13C > -50 permil, e.g. Lu et al., 2011). C1/C2+ of hydrate-bound hydrocarbons was more than 2,000, whereas the maximum value of methane delta 13C was -35permil (Hachikubo et al., 2015). It is still unknown how higher hydrocarbons reduced in the sediment. Gas hydrates have been discovered at the southwestern Sakhalin Island in the cruises of LV59 (2012), LV62 (2013), LV67 (2014), and LV70 (2015) on board R/V Akademik M. A. Lavrentyev in the framework of Sakhalin Slope Gas Hydrate (SSGH) project. We reported in the last JpGU meeting that hydrate-bound gas contained 13C-rich methane, suggesting thermogenic origin. In this study, we focus on the gas hydrates of the cubic structure I containing thermogenic methane retrieved from the Tatar Trough, off Sakhalin Island, and compare with those retrieved off Joetsu.
We obtained hydrate crystals from sediment cores, and stored them in liquid nitrogen. Raman spectra of the crystal showed two peaks of C-H stretching mode, correspond to methane molecules in large and small cages of the structure I, and small peaks of hydrogen sulfide were also detected. We also obtained hydrate-bound gas on board and measured their molecular and stable isotope compositions. C1/C2+ of hydrate-bound hydrocarbons ranged between 200 and 800, suggesting that contribution of thermogenic C2+ was low. However, delta 13C and delta D of hydrate-bound methane distributed from -48permil to -42permil and from -200 permil to -170 permil, respectively. According to an empirical classification of the methane stable isotopes (delta 13C and delta D; Whiticar, 1999), hydrate-bound methane obtained at the Tatarsky Trough was mainly thermogenic origin. Characteristics of hydrate-bound methane is similar to those obtained off Joetsu. delta 13C of CO_2 in sediment gases was high (+20 permil), suggesting interaction between methane and CO_2 through microbial activity.
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