Structure Determination of Natural Gas Hydrates Recovered from Nankai Trough via Raman Spectroscopy

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Gas hydrates are crystalline compound that has several types of crystal structure (e.g. structure I or II), depending on gas composition and so on. The crystal structures affect gas content per unit hydrate and heat of dissociation. From the viewpoint of resource development, such physical parameters are directly related to the amount of natural gas resource and gas production rate. Therefore, they are important factors for the estimation of gas productivity and the determination of the location of well site.

In this study, structure determination of natural gas hydrate bearing sediments, which were recovered from Nankai trough in 2002, was carried out using Raman spectroscopy. Generally, X-ray diffraction and NMR as well as Raman spectroscopy are used for structure determination. The advantage of using Raman spectroscopy for hydrate bearing sediments can be recognized as a high spatial resolution and accuracy of estimation of hydration number, compared with them. Samples recovered from Kumano-nada were massive hydrates occurring in clay layer. And samples recovered from offshore Tokai were hydrates occurring in pore spaces of sand grains. Additionally, artificial hydrates, which were synthesized into two different crystal structures in laboratory by using some kind of gas compositions, were also measured as references. In the case of Kumano-nada sample, it was clear that distinguish between hydrate area and muddy sediment area. Ar^{+} laser that spot diameter was 10 micrometer was radiated to hydrate area and two prominent spectra were obtained at 2904 cm^{-1} and 2915 cm^{-1}. The spectrum at 2904 cm^{-1}, which was identified with methane gas in large cage of hydrate, was approximately three times larger than that of 2915 cm^{-1} which was identified with methane gas in small cage of hydrate. That result clearly suggested that the hydrate had sI structure. In the case of offshore Tokai sample, it was difficult to distinguish between sandy matrix and small portion of hydrate that existed in a pore space of sand grain by optical microscope. Comparing with SEM image, the hydrate area was estimated and Ar^{+} laser that spot diameter was 10 micrometer was radiated to that. The prominent spectrum was clearly obtained at 2904 cm^{-1}, but the spectrum at 2915 cm^{-1} was not detected because of weak S/N ratio. However, this result could strongly suggest that the hydrate had sI structure by comparison with reference spectra that was obtained by artificial samples analysis.

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