



Crystallographic study on natural gas hydrates recovered from the eastern Nankai Trough

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Natural gas hydrates are crystalline clathrate compounds, which encage a large amount of natural gas. The crystallographic structure of natural gas hydrates depends on the encaged natural gas components. In addition, the amount of hydrate-bound natural gas is attributed to the crystallographic structure. Massive and pore-space natural gas hydrates were obtained from the eastern Nankai Trough area during Japan's Methane Hydrate R&D Program conducted by the Ministry of Economy, Trade and Industry (METI) of Japan, aboard the RV JOIDES Resolution. In this study, hydrate-bound gas, crystal structure, and cage occupancies, and hydration number of the natural gas hydrates were characterized.

The pore-space natural gas hydrates recovered from the eastern Nankai Trough area existed in pore-spaces of sandy sediments with median diameters of approximately 80-180 μm . The PXRD profiles of the massive and pore-space natural gas hydrates revealed that the crystallographic structures of the all natural gas hydrates studied were structure I. The lattice constants of the pore-space natural gas hydrates were ranging from 1.183-1.207 nm, depending on the content of fine sediment particles less than 40 μm in the sandy samples.

All samples contained CH_4 as a main hydrocarbon component, indicating that the natural gas in marine sediment at the study areas is mainly CH_4 . The hydrocarbon compositions agreed well with those reported for microbial (CO_2 reduction) natural gas in gas hydrate-bearing sediments recovered previously from the eastern Nankai Trough area. In this study, on the other hand, although almost all samples contained small amounts of C_2H_6 (less than 200 ppm), C_3H_8 (less than 50 ppm), and $i\text{-C}_4\text{H}_{10}$ (less than 20 ppm), large concentrations of heavier hydrocarbons such as C_3H_8 or $i\text{-C}_4\text{H}_{10}$ were found in three of 15 samples.

^{13}C NMR and Raman spectroscopic techniques were used to obtain molecular information on the encaged hydrocarbon molecules. The ^{13}C NMR chemical shifts and Raman shifts of guest molecules showed that the primary component of guest molecule is CH_4 and their crystallographic structure is structure I, supporting the PXRD data.

The occupancies of small and large cages were evaluated from the ^{13}C NMR and Raman spectra, which the pore-space gas hydrates had 0.83 small cage occupancy of CH_4 and 0.97 large cage occupancy of CH_4 , indicating the large cages were almost fully occupied by CH_4 molecules. The hydration number estimated from the obtained cage occupancies was 6.1–6.2, which resembled those of the massive NGHs studied. The obtained cage occupancies and hydration numbers are important parameters for estimation of amount of hydrocarbons in hydrate-bound natural gases in the eastern Nankai Trough area.

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