



## 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  $\mu\text{m}$ . 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  $\mu\text{m}$  in the sandy samples.

All samples contained CH<sub>4</sub> as a main hydrocarbon component, indicating that the natural gas in marine sediment at the study areas is mainly CH<sub>4</sub>. The hydrocarbon compositions agreed well with those reported for microbial (CO<sub>2</sub> 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<sub>2</sub>H<sub>6</sub> (less than 200 ppm), C<sub>3</sub>H<sub>8</sub> (less than 50 ppm), and i-C<sub>4</sub>H<sub>10</sub> (less than 20 ppm), large concentrations of heavier hydrocarbons such as C<sub>3</sub>H<sub>8</sub> or i-C<sub>4</sub>H<sub>10</sub> were found in three of 15 samples.

<sup>13</sup>C NMR and Raman spectroscopic techniques were used to obtain molecular information on the encaged hydrocarbon molecules. The <sup>13</sup>C NMR chemical shifts and Raman shifts of guest molecules showed that the primary component of guest molecule is CH<sub>4</sub> and their crystallographic structure is structure I, supporting the PXRD data.

The occupancies of small and large cages were evaluated from the <sup>13</sup>C NMR and Raman spectra, which the pore-space gas hydrates had 0.83 small cage occupancy of CH<sub>4</sub> and 0.97 large cage occupancy of CH<sub>4</sub>, indicating the large cages were almost fully occupied by CH<sub>4</sub> 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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