

## Crystallographic Studies on Natural Gas Hydrates Recovered from Offshore Tokai and Kumano-nada, Japan

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During the drilling program of METI 'Tokai-oki to Kumano-nada' in 2002, natural gas hydrate-bearing sediment cores were recovered from offshore Tokai and Kumano-nada. At offshore Tokai, a core was recovered with hydrates occurring in pore spaces of sand grains. At Kumano-nada, a core was recovered with massive hydrates occurring in clay layer. The present study attempted to determine the crystal structure and hydration number of the natural gas hydrates using X-ray diffraction (XRD) and  $^{13}\text{C}$  NMR. Additionally, the dissociated gas compositions of the hydrate samples were measured by TCD gas chromatograph.

The crystallographic structure of gas hydrate is known to depend on the gas component or gas composition. The crystallographic structure of natural gas hydrates is important to estimate the amount of natural gas, since the gas capacity in the hydrate crystal depends on the structure.

The XRD patterns of the hydrate samples recovered from offshore Tokai and Kumano-nada indicated that the both samples include structure I hydrate. The  $^{13}\text{C}$  NMR spectrum of the sample recovered from Kumano-nada showed peaks from methane encaged in structure I hydrate crystal. No other  $^{13}\text{C}$  NMR signals from higher hydrocarbons were observed. The hydration number estimated by the  $^{13}\text{C}$  NMR data and the statistical thermodynamic model was 6.2. The gas analyses by gas chromatography revealed that both samples contain more than 99% methane and trace amount of ethane.

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