Characteristics of gas hydrate crystals and their hydrate-bound gases retrieved at the seepage field off Tokachi (the Pacific Ocean)

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We report the first recovery of natural gas hydrate off Tokachi, the Pacific Ocean. In the framework of practical education of Kitami Institute of Technology, we conducted research cruises off Tokachi since 2014, to investigate gas hydrate fields around Hokkaido. There are many gas seeps ascend from the sea floor and their height exceeded 700 m at the study area off Tokachi.
Using TS Oshoro-maru of Hokkaido University, 17 sediment cores were retrieved by gravity and hydrostatic corers during five cruises. The last C095 cruise was conducted on November 2020, and we obtained massive gas hydrate crystals. In this report we focus on the results of crystallographic properties of gas hydrate and their gas characteristics.
In the cruise of C095, we obtained six sediment cores, including a hydrate-bound core. Gas hydrate crystals were preserved at the temperature of liquid nitrogen, and sediment gases were obtained by a headspace gas method. Raman spectroscopic analysis was conducted to know crystallographic structure, hydration number and cage occupancies. Molecular and isotopic compositions of hydrate-bound and sediment gas samples were measured using a gas chromatograph (GC2014, Shimadzu) and an CF-IRMS (Delta V, Thermo Fisher Scientific), respectively.
Crystallographic structure of gas hydrate samples belonged to the structure I, and hydration number was estimated as 6.07±0.04 from the Raman peaks of hydrate-bound methane. Hydrate-bound H_2S and N_2 molecules were also detected in the Raman spectra, however, that of CO_2 was not detected.
Hydrate-bound gas was mainly methane, and C_1 / (C_2 + C_3) distributed between 3,300 and 6,800. $\delta^{13}C$ and δD of methane were -66‰ and -188‰. These molecular and isotopic compositions of hydrate-bound hydrocarbons suggested microbial origin, and methane was derived by CO_2 reduction. $\delta^{13}C$ of ethane was -52‰, therefore such light ethane seemed to be also microbial.
The depth of sulfate-methane interface (SMI) in C095-GC2002 (hydrate-bound core) was 45 cm, and those in other C095 sediment cores were less less than 1 m, indicating high methane flux from deep layer. Concentrations of H_2S in the headspace gas samples were in the same order (around 1 mM), suggesting that the process of anaerobic oxidation of methane was active. C_1 / (C_2 + C_3) of headspace gases in the hydrate-bound and gas-rich cores distributed between 970 and 2,090 below their SMI depths.
Hydrate-bound and gas-rich sediment cores contained carbonates; their $\delta^{13}C$ ranged from -43‰ to -39‰. Since $\delta^{13}C$ of CO_2 in headspace gases in these cores ranged from -58‰ to -34‰, the site of gas hydrate is characterized as depletion in ^{13}C of carbon dioxide and light carbon dioxide was derived from oxidation of light methane.

Keywords: gas hydrate, methane, the Pacific Ocean

