

## Characteristics of gas hydrate crystal retrieved at the gas seepage area off Hidaka, the Pacific Ocean

\*Yuki Moriya<sup>1</sup>, Daisuke Yahagi<sup>1</sup>, Akihiro Hachikubo<sup>1</sup>, Hirotohi Sakagami<sup>1</sup>, Masato Kida<sup>1</sup>, Masaaki Konishi<sup>1</sup>, Hirotsugu Minami<sup>1</sup>, Satoshi Yamashita<sup>1</sup>

1. Kitami Institute of Technology

We report the first recovery of natural gas hydrate off Hidaka, the Pacific Ocean. In the framework of practical education of Kitami Institute of Technology, we conducted research cruises off Hokkaido since 2012 using TS Oshoro-maru of Hokkaido University. We have retrieved samples of natural gas hydrate off Abashiri and Tokachi, where many gas seeps ascend from the sea floor. In 2020, we conducted K2-2020 cruise off Hidaka using Kaiyo-Marun No. 2 and found gas plumes during a multibeam survey. In the C114 cruise using TS Oshoro-maru conducted on November 2021, we obtained six sub-bottom sediment cores, including hydrate-bound and gas-rich cores, using a gravity corer at the gas seepage sites. Plate-like gas hydrate crystals were found in the core of C114-GC2104, located around 160 cm beneath the sea floor. Gas hydrate crystals were stored in the temperature of liquid nitrogen and Raman spectroscopic analysis was conducted. Sediment gases were obtained by a headspace gas method and their molecular and isotopic compositions were measured using a gas chromatograph and an isotope ratio mass spectrometer, respectively.

Raman spectroscopy revealed that crystallographic structure of gas hydrate samples belonged to the structure I, and hydration number, cage occupancies of large and small cages were estimated as 6.00,  $0.97 \pm 0.00$ , and  $0.93 \pm 0.01$ , respectively. Hydrate-bound gas was mainly composed of methane, and  $C_1 / (C_2 + C_3)$  was around 2,800.  $\delta^{13}C$  and  $\delta D$  of methane were -68‰ and -176‰. These molecular and isotopic compositions of hydrate-bound methane suggested microbial origin via  $CO_2$  reduction.  $\delta^{13}C$  of ethane was -49‰, indicating that ethane is also microbial. Molecular and isotopic compositions of sediment gas were almost the same as those of hydrate-bound gas.  $\delta^{13}C$  of propane in the sediment gas samples was around -30‰, and  $\delta^{13}C$  of  $CO_2$  in the sediment gas samples was less than -60‰ in the C114-GC2104 core. Therefore, light hydrocarbons and  $CO_2$  are depleted in  $^{13}C$ . The depth of sulfate-methane interface (SMI) in the C114 sediment cores distributed from 35 cm to 225 cm, and such shallow SMI indicated high methane flux from deep sediment layer.  $C_1 / (C_2 + C_3)$  of the headspace gases distributed between 2,000 and 10,500 below their SMI depths. Almost all sediment cores contained a lot of carbonate derived from oxidation of light methane.

Keywords: gas hydrate, the Pacific Ocean, microbial origin