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Analysis of volatile organic compounds in the pore water from Joetsu Basin, eastern margin of the Sea of Japan

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Natural gas hydrate is a clathrate compound. Gas molecules are encaged by hydrogen-bonded water molecules. Gas hydrate is found together with deep-sea sediments that contain natural radioisotopes like uranium-series, thorium-series, and ⁴⁰K. Natural radiation from those radioisotopes will break bonds of water and guest gas molecules, and form radical species. Although the radical species are unstable in the pressure and temperature of natural gas hydrate occurrence on the Earth, radical reactions may occur in the hydrate. Our recent studies reported that methanol and formaldehyde were mainly formed in gamma-irradiated methane hydrate (Tani et al., 2008; Tani et al., 2010). The amount of these compounds will become one of the indicators for the formation age of natural gas hydrate, because they may be accumulated in gas hydrate. For age estimation, it is necessary to determine the amount of them captured from pore water when natural gas hydrate is formed. However, abundance of methanol and formaldehyde in pore water of seafloor sediments is veiled. In this study, we have investigated light volatile organic compounds such as methanol and formaldehyde in pore water of the sediments obtained during MD179 cruise in 2010.

Pore water was obtained by squeezing sediments recovered from Umitaka Spur and Joetsu Knoll, in Joetsu Basin. Each sample was taken into a glass vial (3-5 ml), sealed, and kept in a freezer. These procedures are performed on the ship. The vials were warmed at room temperature before the following analysis. Headspace gas in each vial was analyzed by gas chromatography-mass spectrometry (GC-MS). Especially for formaldehyde analysis, *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA) was used as a derivative reagent for aldehyde (Kobayashi et al., 1980).

In preliminary results, the concentration in pore water was 1-2 micro M (methanol) and 0.5-1 micro M (formaldehyde) beneath the seafloor, and 10-20 micro M (methanol) and 1-2 micro M (formaldehyde) around 30 m below the seafloor. It means that (1) both methanol and formaldehyde increases in depth and (2) the amount of the increase is about 10 times for methanol, which is 5 times larger than for formaldehyde. These results indicate that the amount of these compounds initially captured into hydrate may depend on the depth. For more detailed discussion, distribution coefficients for them into gas hydrate are necessary and will be investigated in future.

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Keywords: pore water, gas hydrate, Joetsu Basin, GC-MS, volatile organic compounds