

MIS027-12

Room:201A

Time:May 22 17:15-17:30

## Analysis of volatile organic compounds in the dissociated water of gas hydrate recovered from Joetsu Basin

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Radiation-induced radicals and further radical reactions in gas hydrate were investigated by electron spin resonance (ESR) and gas chromatography-mass spectrometry (GC-MS). Although methyl radical is the most stable radical in methane hydrate, it cannot survive in the pressure and temperature condition of natural gas hydrate occurrence. Recently our studies revealed that methanol and formaldehyde were formed in methane hydrate by gamma-ray irradiation (Tani et al., 2008; Tani et al., 2010). Therefore, we conjecture that these compounds might be also formed by natural radiation and have been accumulated in natural gas hydrate after formation of gas hydrate. To test this hypothesis, we analysed volatile organic compounds (VOCs) in the dissociated water of natural gas hydrates.

Investigation of gas hydrate was carried out at Umitaka Spur and Joetsu Knoll, in Joetsu Basin, eastern margin of the Sea of Japan during MD179 cruise in 2010. Gas hydrate samples were recovered from 4 sites and kept at 77 K in liquid nitrogen. We selected one massive gas hydrate sample for this study to avoid contamination of pore water. After the sample broken, several pieces of gas hydrate were picked up and dissociated in a glass vial. The headspace gas from the dissociated water was analyzed by GC-MS. Both methanol and ethanol were detected. The successful detection of methanol from natural gas hydrate might be a positive signal for the determination of the age of hydrate formation.

This research is supported by MH21 Research Consortium JAPAN.

Keywords: gas hydrate, Joetsu Basin, volatile organic compounds, methanol, natural radiation, formation age