Similarities between hot spring gas at the northern Hokkaido area and hydrate-bound gas retrieved at the Tatar Trough (Japan Sea)

*Takahiro Ozeki[1], Akihiro Hachikubo[1], Hirotoshi Sakagami[1], Hirotsugu Minami[1], Satoshi Yamashita[1], Kenji Nishina[2]

1. Kitami Institute of Technology, 2. Geological Survey of Hokkaido, Hokkaido Research Organization

Composition of hydrocarbon gases primarily decides the crystallographic structure of gas hydrate; pure methane hydrate belongs to the structure I, while propane, butane, and appropriate composition of methane and ethane mixed-gas hydrate form the structure II. Origin of higher hydrocarbons (ethane, propane, butane, etc.) is generally thermogenic, and their carbon isotopic composition are larger than those of microbial. Therefore, we can say that thermogenic gas forms the cubic structure II gas hydrate. However, there are only two exceptions in the world; natural gas hydrates retrieved off Joetsu (Hachikubo *et al.*, 2015) and Tatar Trough (Hachikubo, 2017), Japan Sea, contain thermogenic methane and belong to the structure I, because of small amount of higher hydrocarbons. In this study, we obtained hot spring gases in Hokkaido along with the eastern margin of Japan Sea, measured their molecular and isotopic compositions of hydrocarbons, and discussed the similarity between these hot spring gases and hydrate-bound gases in Japan Sea, to understand decreasing process of higher hydrocarbons from thermogenic gas.

We obtained hot spring gases from (1) Kamihoronobe mud volcano and (2) Asahi hot spring, both located at northern Hokkaido in March 2017. We also obtained a natural gas trapped under the lake ice from Lake Nukabira for comparison. Gas samples were collected in 5mL glass vials and small amount of benzalkonium chloride was put as a preservative. Molecular and isotopic compositions of these samples were measured using a gas chromatograph and CF-IRMS.

In the Bernard plot, one of the classification of natural gas, microbial gas field is expressed as lower methane $\delta^{13}C$ (light methane) and higher C_1/C_2, whereas thermogenic gas field is expressed as higher methane $\delta^{13}C$ (heavy methane) and lower C_1/C_2. Gas samples at the Kamihoronobe mud volcano and Asahi hot spring are plotted in the field of higher methane $\delta^{13}C$ and higher C_1/C_2, agree with those of hydrate-bound gas retrieved off Joetsu and Tatar Trough. Isotopes of methane showed that methane of Kamihoronobe mud volcano, Asahi hot spring, gas hydrates from off Joetsu and Tatar Trough are plotted in the field of thermogenic in the Whiticar plot (relation between methane $\delta^{13}C$ and δD), while methane in the Lake Nukabira is plotted in the field of microbial via methyl-type fermentation. CO_2 $\delta^{13}C$ of Kamihoronobe mud volcano was large (+20.3‰), indicating that higher hydrocarbons (ethane, propane, etc.) in the thermogenic gas are consumed by a microbial process, heavy CO_2 is generated, and heavy methane is produced via CO_2 reduction.

As for other gas compositions, concentrations of helium were 80ppm and 160ppm for Kamihoronobe mud volcano and Asahi hot spring, respectively, while those of hydrogen were around 5ppm for both sites. Because R/R_A of helium is less than 1.0 in the area of northern Hokkaido (Kusano *et al.*, 2012), the source of natural gas is not the origin of mantle.

Reference

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