

## Geochemical characteristics of natural gases from mud volcanoes in Tokamachi City, Niigata Prefecture

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### Introduction:

Mud volcanoes are widely distributed in oil and gas fields, erupting groundwater, mud, natural gas (gas) and crude oil (oil). Driving force of the fluid exhalations are thought to be abnormal pore water pressure generated in deep underground. Shinya and Tanaka (2005) reported two active mud volcanoes (Kamou mud volcano, Muro no mud volcano) and a passive mud volcano in Tokamachi City, Niigata Prefecture. It is clarified that the erupted groundwater is originated from deep underground at the depth of more than 3400m and that the mud chamber is formed about 400m in depth (Shinya and Tanaka, 2004; Tokuyasu et al., 2006). Objective of the study is to investigate the ascending process of fluid and gas by the measurement of molecular composition and carbon isotopic ratio of gases in the Kamou and the Muro no area.

### Results and Discussion:

#### 1. Molecular composition and carbon isotopic ratio of gas

In the study area, gases are mainly composed of methane (C1), a small amount of CO<sub>2</sub> and N<sub>2</sub>, and heavy hydrocarbons such as ethane (C2) and propane (C3). Seasonal fluctuation of the carbon isotopic ratio ( $\delta^{13}C$ ) of the hydrocarbons sampled in the Kamou mud volcano and the Muro no mud volcano is not recognized in 2004 (Kato et al., 2005), 2005 and 2006 (this study).

#### 2. Origin of gas

In the study area, the  $\delta^{13}C_1$  and the C<sub>1</sub>/(C<sub>2</sub>+C<sub>3</sub>) ratios fluctuate in the range of -31.9 to -36.5 permillage and 15 to 10775 respectively. According to the  $\delta^{13}C_1$ , it is assumed that gases in the study area are thermogenic (Waseda et al., 2002). However, most of C<sub>1</sub>/(C<sub>2</sub>+C<sub>3</sub>) ratios are plotted outside of the range of the thermogenic gas. It is interpreted that proportion of the C<sub>1</sub> in the hydrocarbon gas increases in the process of gas migration from deep underground to ground surface (Schoell, 1983). The C<sub>1</sub>/(C<sub>2</sub>+C<sub>3</sub>) ratio of some gas in the Muro no area is 15 that is similar to that of gases in the oil and gas reservoirs in the Katakai, Yoshii gas fields and the Mitsuke oil field in the Chuetsu region, Niigata Prefecture. Hence, it is thought they may ascend in a short time through the fractures. Also, it is thought that the gas in the area is originated from the same source in deep underground because the carbon isotope ratio of the hydrocarbon is not fluctuated for last three years (2004 to 2006).

#### 3. Influence of biodegradation

As i-C<sub>4</sub>/n-C<sub>4</sub> ratio is more than 1, C<sub>2</sub>/C<sub>3</sub> ratio is high, and  $\delta^{13}C_3$  is very heavy, it is concluded that most of the gases in the study area are biodegraded. It is estimated that the gas ascending from the deep underground stays once near the ground surface where the biodegradation occurred. The influence of the biodegradation on  $\delta^{13}C_2$  and  $\delta^{13}C_3$  is recognized in all the gases of the Kamou area. Hence, it is possible that gases stay at once in the mud chamber 400m in depth (Tokuyasu et al., 2006) and are biodegraded at that time.

#### 4. Stratigraphic formation of gas generation

The maturity of gas is estimated to be 1.1% vitrinite reflectance equivalent by the carbon isotopic ratios of gases that are plotted on the maturity line (Waseda et al., 2002). It is assumed that source rock of the gas in the study area belongs to the Upper Nanatani Formation and the Lower Teradomari Formation. The result is also supported by Hirai et al. (1995) that studied on the source rock of petroleum and concluded that source rocks with high potential of petroleum generation belongs to the Lower Teradomari Formation. Moreover, it is estimated that the gases are originated from the same horizon as that of groundwater. Hence, it is thought that the gases start to ascend at the same depth and same time as groundwater.

### Conclusion:

As mentioned above, it is concluded that the gas generated in deep underground ascends with the groundwater and they stay once in the mud chamber near the ground surface where the biodegradation occurred. Finally, they erupt to ground surface and form mud volcano.