ORIGINS OF HIGH-TEMPERATURE FLUIDS IN THE GOSHOGAKE MUD VOLCANO FIELD, TOHOKU, NORTHERN JAPAN: CHEMICAL AND ISOTOPIC STUDIES OF GAS AND WATER.

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Introduction: Mud volcanoes occur everywhere in various geological settings on the Earth [e.g., 1] and, possibly, on other planetary bodies, such as Mars [e.g., 2] and Enceladus ocean floor. Their surface terrains are formed by mud ascending and erupting, together with water and gas, from depths. Therefore, mud volcano is one of the most suitable landforms for exploring the subsurface geology and microbiology (i.e., extremophile) because mud volcanoes allow us to access easily to deep underground materials. Recognizing the importance of astrobiological potential of mud volcanoes, we have conducted field works, laboratory chemical and microbial analyses on terrestrial mud volcano fields as an analog for future exploration missions to the planetary bodies [3, 4, 5, 6, 7].

In this study, we focus on the Goshogake mud volcano field in Tohoku, Japan. The field has hot springs fed with high-temperature fluids emerging on the eastern flank of the Quaternary Akita Yakeyama volcano. Its uniqueness is highlighted by the following reasons: (i) The geomorphological features observed in the Goshogake (salsa, gryphon, and mud pod) are similar to those commonly observed in conventional sedimentary mud volcanoes [5]. (ii) On the other hand, the physico-chemical environment in the Goshogake mud volcano field is an acidic and high-temperature system in association with magmatic volcanism, which is totally different from conventional sedimentary mud volcanoes characterized by relatively low temperatures [5]. In-depth understanding of this unique example will tell us about the environmental and biological diversities and formation conditions of mud volcanoes on the Earth and beyond. We present in this study the results of in-situ measurements and laboratory analyses of gas and water at the Goshogake mud volcano field to discuss the nature of its mud fluids and their origins, which are essential for understanding habitability and ecology of such systems.

Method:

In-situ methane measurement. In-situ methane gas measurement was conducted at selected gas-emitting vents using a handheld gas detector with an infrared absorption spectroscopy.

Gas sampling and laboratory analysis. Gases were collected with a custom-made sampling device for laboratory measurement of the gas species. The composition analysis of the gas samples in the chamber was conducted using Gas Chromatography (GS) in the laboratory. The GC analyses are made in two ways: qualitative and quantitative analyses. The quantitative analyses were conducted for O_2, N_2, CO, CO_2, H_2, CH_4, C_2H_6, C_3H_8 and H_2S using GC-TCD, GC-FPD, GC-BID. The qualitative analysis was carried out for gas species without standard gases for calibration of GC.

The carbon isotopic composition of the hydrocarbon gas components was also measured by an isotope ratio mass spectrometer.

Water sampling and laboratory analyses. We collected water samples from mud volcanoes and measured δD and $\delta^{18}O$ isotope compositions for the samples using an isotope ratio mass spectrometer to examine the origins of the mud water.

Result:

Methane column density above the vents. We conducted in-situ measurement of methane at 0.5 seconds intervals using the handheld gas detector. Methane column density above the mud volcano increased and decreased repeatedly. Their peak values (16-37ppm) are about 4 to 9 times higher than those in other regions (about 4 ppm on average). In the measurement at the salsa we found that the peaks of methane abundance are associated with eruption of gas bubbles on the surface of the salsa, supporting that the measured methane gas is originated from the mud volcano vents.

Chemical and isotopic compositions of gas samples. Table 1 shows the gas composition determined by the GC quantitative analyses. Table 2 shows the gas composition detected by the GC qualitative analysis. Not only various hydrocarbons and organic compounds but also CO_2 is detected. CO and H_2S were not detected. Here, we do not consider O_2 and N_2 as gas species erupted from the mud volcano vents because (i) our gas sampling device can not prevent ambient air from being mixed into the gas sample, (ii) it's highly unlikely that O_2 emerges from the deep subsurface, CO_2 and

H_2O are identified to be the main components of volcanic gases from the Akita Yakeyama volcano [8] on which the Goshogake mud volcano field is located. The $\delta^{13}C$ values for hydrocarbons from the salsa and gryphon are -44.0 ‰ and -37.2 ‰, respectively. From the relationship between $\delta^{13}C$ and $C_1/(C_2 + C_3)$ (the Bernard classification diagram [9]), we found that the isotopic composition is consistent with the thermogenic origin of hydrocarbon gases in the mud volcanoes.

Isotopic compositions of water samples. The δD values for water samples of the salsa and gryphon are -34.8 ‰ and -41.6‰, respectively. The $\delta^{18}O$ values for water samples of the salsa and gryphon are 2.53‰ and 0.057 ‰, respectively. The measured isotope values deviate substantially from (or higher than) those (δD of ~ -68 ‰ and $\delta^{18}O$ of ~ -11 ‰) of the reported local meteoric water [8], although it rained on the day we took the sample.

Discussion: In our gas analyses, it is noteworthy that reducing gases (hydrocarbons and organic compounds) coexist with oxidizing gas (CO_2). This is because reducing gases tend to be chemically unstable in the presence of oxidizing gases. We found that when the sample gas composition is in thermal equilibrium under the subsurface pressure-temperature conditions, hydrocarbons are decomposed to convert into mainly CO_2, H_2O, and graphite. Therefore, the coexistence of those gases suggests that the Goshogake mud volcano originate from a combination of fluids deriving separately from two different sources: reducing and oxidizing ones.

Since hydrocarbons are generally the dominant gas involved in sedimentary mud volcano systems [e.g., 10], our detection of hydrocarbons from both in-situ and laboratory measurements suggest a contribution of organic-rich sedimentary mud layer(s) as one of their mud sources. Actually, the presence of a clay-rich lacustrine sediment layer at some depths (possibly 500-1000m), which are now feeding the mud volcano, is proposed [5]. This is also consistent with our result of the Bernard classification diagram indicating the thermogenic origin of hydrocarbons (i.e., from organics decomposed geothermally at depths [e.g., 11]).

On the other hand, CO_2 instead may relate to high-temperature oxidizing magmatic volcanism because CO_2 is identified to be one of the main components of volcanic gases around the Akita Yakeyama volcano [8] on which the mud volcanoes is located. The identified mineralogy of the sampled Goshogake mud includes high-temperature polymorphs of quartz (tridymite and cristobalite) and an amorphous form of silica (opal) [7]. This also supports the idea that the mud volcano system likely has a fluid source involving high temperatures and/or hydrothermal alteration [5].

If the above picture is the case, the Goshogake mud volcano field is expected to be a hybrid system based on a combination of sedimentary and magmatic volcanisms. Organohalogens such as 1,1-difluoroethane detected by our study (Table 2) may reinforce our hybrid system hypothesis. This is because organohalogens come not from thermal equilibrium in a single gas source but rather from disequilibrium process involving both non-magmatic hydrocarbons and high-temperature volcanic gas mixtures including hydrogen halides [12]. Furthermore, the water isotopic compositions also imply an association with sedimentary mud and/or magmatic volcanism. The increase in δD and/or $\delta^{18}O$ of water samples in Goshogake mud volcanoes with respect to the value of current meteoritic water can be explained by some geological processes, such as dehydration of hydrous minerals (clay minerals and opal) in the mud source region [1, 11] and evaporation of surface water [11]. Incorporation of the magmatic waters and volcanic gases with enrichment in both D and ^{18}O may also affect the isotopic composition at the Goshogake influenced by magmatic volcanism [8].

Table 1 Gas composition determined by the GC quantitative analyses

Site	Molecular composition (%)				
	CO_2	CH_4	C_2H_6	C_3H_8	H_2
Salsa	65.1	15.6	0.14	0.025	19.1
Gryphon	96.8	1.7	–	–	1.5

Table 2 Gas compositions detected by the GC qualitative analyses

Chemical compound	Site	
	Salsa	Gryphon
1,1-difluoroethane ($C_2H_4F_2$)	Detect	–
Cyclobutene (C_4H_8)	Detect	–
Isobutane (C_4H_{10})	Detect	–
Acetone (C_3H_6O)	Detect	Detect
Carbon disulfide (CS_2)	Detect	Detect

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