## The Methane Concentrations of Sea Water above the Methane Plume

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Methane hydrate is an ice-like crystalline solid that consists of hydrogen-bonded water cage and methane molecules, with its stable conditions of low temperature and high pressure. Methane hydrate is found under the seabed around Japan, and have been developing as unconventional natural gas resources. Two types of methane hydrate are confirmed to exist in the sea areas around Japan. "Shallow-type" exists hundreds of meters below seabed in gaps between sandstones and tuffs, and "sand-layer-type" exists at a relatively shallow sub bottom. Methane gas seeping from seabed, called "methane seep", has been reported at methane bearing areas of shallow-type methane hydrate. Gas seepage can be observed as

"methane plume" by using acoustic instruments, such as quantitative echosounder and multi beam echosounder. On the other hand, the greenhouse effect of methane gas is approximately 25 times more effective than that of carbon dioxide. Therefore, if naturally seeping methane gas reach to the atmosphere, global warming may be enhanced. Methane seeps have recently been researched to be used as natural gas resources, and the effects on global warming is being studied. However, there are many unknown elements. It is crucial to understand methane seepage point and its amount. In the present study, methane concentrations above methane plume are determined, measuring dissociated methane concentrations of sampled sea water above methane plumes.

Water samples were collected above the targeted methane plume, approximately every 25 m from 850 m depth to sea surface using Rosette sampling arrays in the sea area of 900 m depth. Collected water samples were translocated and sealed into sample bottles. These sample bottles were heated and sonicated to extract dissociated methane gas from sample sea water. Extracted gas phase composition was measured by gas chromatography, and the author determined methane concentration by measuring the composition and sea water mass.

Significantly high methane concentrations were measured at the depths of about 850 m, 700 m, and shallower than 300 m. At 850 m depth near the seafloor, high methane concentration is caused by seeping methane from seafloor. Methane gas bubbles, directly observed by a remotely operated vehicle (ROV), and methane dissolved water are discharged from the seafloor. This is why, the methane concentration around seafloor is high. In addition, the condition is favorable for methane hydrate near the seafloor with low temperature and high pressure. The author observed the methane hydrate membrane covered the surface of seeped methane gas. Surrounding temperature and pressure increase and decrease respectively when methane hydrate coated bubbles rise with their buoyancy. When these bubbles reach around 300 m depth, the temperature-pressure condition becomes methane hydrate equilibrium. Coated methane hydrate begins to dissociate, and methane gas supplies increase by dissociated gas. It is considered that this is the origin of high methane concentration shallower than 300 m depth. However, methane concentration around 700 m is high, despite the low concentrations at depth deeper and shallower than 700 m depth. This is most likely caused by the change in methane hydrate membrane on rising morphology. Laboratory experiments on morphological change were conducted.

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