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Isotopic difference between hydrate-bound and sediment gases retrieved at Lake Baikal

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ABSTRACT. The objective of our study is to clarify the formation process of natural gas hydrates in the sublacustrine sediments of Lake Baikal, and we are now compiling data on stable isotope ratios of hydrocarbons in hydrate-bound and sediment gases, which have been collected in the framework of collaboration between Russia, Belgium and Japan for 15 years. The results obtained in the VER19-03 cruise at the southern and central Baikal basins were summarized in this report. Comparison of stable isotope ratios of hydrate-bound and sediment gases at the same core and depth was performed. The methane carbon isotope ratio of the hydrate-bound gas was 1 to 2‰ smaller than the sediment gas. The methane hydrogen isotope ratio was similarly about 5‰ smaller. These results can be explained generally by the isotopic fractionation of methane. In contrast, some sediment cores from pockmarks in the center of the mud volcano showed small or reversed differences in methane carbon isotope ratios, as well as small differences in methane hydrogen isotope ratios, suggesting that dissociation of gas hydrate is occurring at that point.

Keywords: gas hydrate, methane, isotopic fractionation, mud volcano

1. Introduction

Lake Baikal is the unique place in the world where natural gas hydrates are found in a freshwater environment. Gas hydrates have already been recovered at 60 sites in Lake Baikal, and we have conducted MHP project for more than ten years. Natural gas hydrates are mainly composed of methane, which consists of carbon and hydrogen. There are several isotopologues depending on the combination of stable isotopes (¹²C, ¹³C, H, and D). For example, the natural abundance ratio of ¹²CH₄, ¹³CH₄, and CH₃D is about 99%, 1%, and 0.01%, respectively. It has been reported that the hydrogen isotope fractionation of synthetic methane hydrate exists about 5‰ between hydrate-bound and residual gases, while the carbon isotope fractionation is under the detection limit (Hachikubo et al., 2007). The difference in methane stable isotope ratios between hydrate-bound and sediment gases can provide information on the formation / decomposition process of natural gas hydrates. In this study, we present the results of gas analysis for the samples obtained in 2019, and find the place where the gas supply has stopped and the gas hydrates are decomposing.

2. Material and methods

Twelve hydrate-bearing sediment cores were obtained from southern and central Baikal basins using a gravity corer on the VER19-03 cruise (August 2019) by the R/V "G.Yu. Vereshchagin". Hydrate-bound gas was collected in vials by the water displacement method on board using a funnel and plastic bucket filled with water, and a benzalkonium chloride solution (BKC, 50 wt%) was added as a preservative (Waseda and Iwano, 2007). The sediment gas (mainly dissolved gas in pore water) was obtained by the headspace-gas method by collecting the sediment every 0.4 m along the depth from the cross-section of the sediment cores, and sealing it in a vial with a saturated NaCl aqueous solution.

The molecular compositions of the hydrate-bound and sediment gases were determined using a gas chromatograph (GC2014, Shimadzu) equipped with a packed column (Shimadzu Sunpak-S), along with a thermal conductivity detector and flame ionization detector for detecting high and low concentrations of hydrocarbons, respectively. The two detectors were connected in series. The stable carbon and hydrogen

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isotopic ratios of methane were measured using a CF-IRMS (Delta V, Thermo Fisher Scientific) coupled with a gas chromatograph (Trace GC Ultra, Thermo Fisher Scientific). The gas chromatograph was equipped with a Carboxen-1006 PLOT capillary column. In the case of headspace gas samples with low concentration of methane, a Sigma-Aldrich Carboxen-1010 PLOT capillary column was also used to separate air components from methane. Stable isotope compositions are reported as δ values (‰), and $\delta^{13}\text{C}$ and δD are given with reference to the V-PDB and V-SMOW standards, respectively.

3. Results and discussion

$\Delta\delta^{13}\text{C}$ and $\Delta\delta\text{D}$ were defined as the isotopic compositions of the sediment gas minus those of the hydrate gas. For example, in the case of $\Delta\delta^{13}\text{C} = 0$, there is no fractionation in ^{13}C between hydrate-bound and sediment gases. As for the carbon isotope ratios, $\Delta\delta^{13}\text{C}$ was distributed in the range from 0‰ to +3‰ and was positive overall, indicating a concentration of lighter methane ($^{12}\text{CH}_4$) in the hydrate-bound gas than in the sediment gas.

Since the previous work (Hachikubo et al., 2007) reported that there is no fractionation in ^{13}C during the formation of methane hydrate, these results suggest that the gas hydrate in sediment is not in equilibrium. On the other hand, it has been reported that heavy methane ($^{13}\text{CH}_4$) is preferentially enclathrated when methane hydrate is synthesized by mixing diatoms as a porous medium (Oota et al., 2016), which is in contradiction to the results of the present study. Therefore, the carbon isotope fractionation of methane at the formation of natural gas hydrate is still unknown at this stage, but there may be other factors affecting the carbon isotope fractionation.

As for the hydrogen isotope ratios, $\Delta\delta\text{D}$ is distributed in the range from -3‰ to +11‰ and is positive overall, indicating a relative abundance of lighter methane (CH_4) in the hydrate-bound gas than in the sediment gas. The average $\Delta\delta\text{D}$ is 5.4‰, which agrees fairly well with the previous report that approximately 5‰ light methane in δD is preferentially enclathrated at the formation of synthetic methane hydrate (Hachikubo et al., 2007). It has been reported that diatoms do not have a significant effect on hydrogen isotope fractionation in methane during the formation of methane hydrate (Oota et al., 2016).

On the other hand, there are some characteristic sediment cores; for example, 2019St66GC4 core showed $\Delta\delta^{13}\text{C}$ of +0.4‰ and $\Delta\delta\text{D}$ of -3.3‰. This core was recovered from the center of the Kedr mud volcano at the southern Baikal basin. This coring point has been suggested that decomposition of the structure I hydrate and regeneration of the structure II ethane-rich hydrate occur simultaneously, due to the stop of gas supply from the deeper sediment layer. Thus, it is likely that the $\Delta\delta^{13}\text{C}$ and $\Delta\delta\text{D}$ values may not be predicted by the stable isotope fractionation at the site where the crystals are decomposing.

4. Conclusions

Differences in methane stable isotope ratios between hydrate-bound and sediment gases were examined. The hydrate gas is generally lighter in ^{13}C than the sediment gas, and the reason for the isotopic fractionation in ^{13}C is still unknown. On the other hand, the hydrogen isotope fractionation was in good agreement with the predictions from the experimental results of synthetic methane hydrate. Therefore, it can be inferred that hydrate-bound and sediment gases were almost in equilibrium in the Lake Baikal gas hydrate, but some exceptional sediment cores were also recovered.

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