GEOCHEMISTRY OF PORE WATERS IN METHANE RICH SEDIMENTS, EASTERN MARGIN OF THE JAPAN SEA

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ABSTRACT
The Umitaka Spur and Joetsu Knoll in the eastern margin of the Japan Sea have been characterized with a large-scaled continuous methane venting system, associated bio-geochemical processes, e.g. gas hydrate formation, carbonate precipitation, development of bacterial/benthos community, have also been observed near the seafloor. A total of 39 piston coring operations were carried out in this region with R/V Marion Dufresne in 2010, integrated geophysical, bio-geochemical, and geological research program was conducted to understand entire methane production-migration-discharge system and its behavior during the development of the Japan Sea. Here we show the results of geochemical analyses of pore waters, an important medium for bio-geochemical reactions occurring in the shallow sediments. Chloride concentration decreases generally downward as well as spiky decreases due to local gas hydrate dissociation, indicating fresh water input from depths. Contrary, chloride enriches in pore waters nearby the massive gas hydrate deposition, reflecting rapid hydrate formation exceeding ion diffusion. Rapid increase in alkalinity and decrease in sulfate in pore water due to anaerobic oxidation of methane are observed widely in the research area, indicating high methane flux along the eastern margin of the Japan Sea. Calcium concentration decreases gradually downward, correlating with alkalinity increase, which results in precipitation of carbonates. Detailed analyses between sulfate decrease and alkalinity increase modulated with carbonate formation suggest that the ordinary oxidation of marine organic matter dominates just below the seafloor and anaerobic oxidation of methane is thereafter common down to the sulfate methane interface. Pore water geochemistry describes well the history of bio-geochemical processes induced by active methane delivery.

Keywords: pore water, Japan Sea, SMI, AOM

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INTRODUCTION
Marine pore waters on the continental margins are often enriched in methane, which enhances a series of organic/inorganic reactions in an envelope of fluid, mineral, and microbes. Oxidation of methane and/or organic matter is one of the key reactions that take place in shallow marine sediments, pore water geochemistry provides fundamental information for the material transport in such environments.
An intensive coring program was conducted along the eastern margin of the Japan Sea by R/V Marion Dufresne in June 2010 (MD179 Japan Sea Gas Hydrates) under the cooperation with MH21 Research Consortium Japan to explore gas venting and shallow gas hydrate depositional system on the Umitaka Spur-Joetsu Knoll area (Fig. 1) and to investigate its behavior since the formation and development of the Japan Sea. Here we report the basic geochemistry of pore waters collected from various locations along the eastern margin of the Japan Sea during the MD179 cruise to examine bio-geochemical processes controlling near seafloor environment and potential linkage of massive methane generation offshore the Umitaka Spur and Joetsu Knoll area and the history of the formation of the Japan Sea.

GEOLOGICAL SETTINGS
The Japan Sea was formed by the crustal extension

Figure 1 Red dots indicate coring sites. (A) Geological setting of the eastern margin of the Japan Sea and locations of research area during MD179 cruise. Boxes denote the area of detailed map in (B) and (C). (B) Detailed bathymetry of the Umitaka Spur and Joetsu Knoll area. (C) Detailed bathymetry of western Okushiri Ridge, off Hokkaido.
in the northeastern Asian continent and the following back-arc spreading during the Early to early Middle Miocene. The eastern margin of the Japan Sea is characterized by N-S to NE-SW trending thrust and fold system that has been developed since an incipient subduction between the North American Plate and Amurian Plate since the Neogene [1]. Organic matter-rich, laminated and bioturbated marine sediment as thick as >4,000 m accumulated during this period, these sediments have been responsible potentially for the accumulation of oil and gas deposits in this area [2].

The Umitaka Spur and Joetsu Knoll region, off Niigata, the largest hydrocarbon filed of Japan, has been characterized by a large-scaled continuous gas (methane) emission on the seafloor on the echo sounder images [3]. The NNE-SSW and NE-SW trending large depression (pockmark) and mound structures of >500 m in diameter are also typical on the spur and knoll, respectively (Fig. 1). The seismic studies have demonstrated chaotic sediment structure probably reflecting gas-charged sediments under these topographies [4]. Gas hydrate accumulation was observed by the submersible dives near the mound and pock mark structures, and large chunks of gas hydrate were recovered by piston coring, dredge sampling, and submersible sampling since 2004 [4].

SAMPLING AND ANALYTICAL METHODS

Sediment core was sectioned and split soon after core recovery. Pore water was extracted from a 5 to 15 cm sediment using hydraulic squeezing system onboard through 0.2 \( \mu \text{m} \) disc filter and stored in plastic bottle at 4 °C [5]. Alkalinity of pore water was measured on board by spectrophotometric method using Bromo-Phenol Blue with a precision better than 0.8% [6]. Concentrations of major ions (\( \text{SO}_4^{2-}, \text{Cl}^-, \text{Ca}^{2+} \)) in this research were measured using ion chromatography at the University of Tokyo with precisions better than 2.5%. Isotopic composition of dissolved inorganic carbon (\( \delta^{13}\text{C}_{\text{DIC}} \)) was determined by extracting DIC with amide sulfuric acid using gas chromatography and mass spectrometer at Kitami Institute of Technology.

RESULTS AND DISCUSSION

Depth profile of dissolved ions

Figure 2 shows depth profiles of dissolved ion concentrations at selected deeply-penetrated sites. Because \( \text{Cl}^- \) is conservative in normal marine environments, concentration of \( \text{Cl}^- \) in pore water can be changed by the input or uptake of \( \text{H}_2\text{O} \) [7]. There are gentle decreases in \( \text{Cl}^- \) concentration, resulting from the input of fresh water from clay mineral dehydration at depth. On the other hand, downward increases in \( \text{Cl}^- \) are observed near the pockmark, Site 3317, reflecting uptake of \( \text{H}_2\text{O} \) and exclusion of ions from gas hydrate crystal during the formation near the core bottom. Anomalously high \( \text{Cl}^- \) concentrations up to 1100 mM are found at Site 3306 where massive gas hydrate chunks were recovered. Although sediment core was disturbed due to gas hydrate sampling, pore waters are generally enriched in any ions, which reflects massive and rapid gas hydrate formation exceeding the rate of ion diffusion in pore water [7]. Spiky decreases in \( \text{Cl}^- \) and other profiles are evidence of gas hydrate dissociation during core recovery and consequent dilution of pore water, which corresponds to the distribution of low temperature anomalies on the core surface measured by infrared camera just after core recovery.

Pore water alkalinity increases rapidly in the upper 10 to 15 meters below the seafloor (mbsf) and reaches stable value of 40 to 120 mM because the alkalinity is constrained mainly by \( \text{HCO}_3^- \) concentration in pore water, that is produced as:

\[
\begin{align*}
\text{CH}_4 + \text{SO}_4^{2-} & \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \quad (1) \\
2\text{CH}_2\text{O} + \text{SO}_4^{2-} & \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S} + \text{H}_2\text{O} \quad (2) \\
2\text{CH}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{CH}_4 + \text{HCO}_3^- + \text{H}^+ \quad (3)
\end{align*}
\]

These processes are essentially mediated by microbial activities, representing (1) anaerobic oxidation of ascending methane with sulfate from seawater, (2) decomposition of marine organic matter in sediment by sulfate from seawater, and (3) decomposition of marine organic matter in \( \text{SO}_4^{2-} \)-depleted environment, respectively. The gradient of alkalinity increase is significantly high around the summit of the Umitaka Spur and Joetsu Knoll, indicating close association of microbial activities with methane delivery in shallow sediments.

Depth pattern of \( \text{SO}_4^{2-} \) is an indicative of ascending methane flux from deep sediment, \( \text{SO}_4^{2-} \) concentration decreases to ~0 mM at the Sulfate-Methane Interface (SMI) where the anaerobic oxidation of methane takes place as described in Eq. (1). The SMI locates generally at 0 to 3 mbsf around the summit of the Umitaka Spur and Joetsu
Knoll, indicating ascending methane reaches near the seafloor. Depths of the SMI (~10 mbsf) are generally shallow at all sites compared to other large gas hydrate fields, e.g. >10 mbsf in the Nankai Trough and Hydrate Ridge, methane flux is likely high over the research area [8,9]. The $\delta^{13}$C value of CH$_4$ in Eq. (1) is generally below -50‰ [4], obviously lower than seawater value of ~0‰ in marine environment. The HCO$_3^-$ produced in Eq. (1) thus has low $\delta^{13}$C,
corresponding to the minimum value of $\delta^{13}$C$_{DIC}$ ranging between -10 and -40‰ around the SMI. The minimum $\delta^{13}$C$_{DIC}$ values vary among sites, probably reflecting the origin and source of CH$_4$. Concentration of Ca$^{2+}$ rapidly decreases in the upper 10 to 15 mbsf, and reach stable at low level. This is ascribed to the precipitation of carbonates, which is enhanced by the increase of alkalinity.

Bio-geochemical processes near the seafloor
There are two significant modes of SO$_4^{2-}$ consumption (alkalinity production) in SO$_4^{2-}$-rich environment just below the seafloor; anaerobic oxidation of methane (AOM) as described in Eq. (1) and ordinary oxidation of organic matter (OOM) as in Eq. (2). A 1 mol SO$_4^{2-}$ consumption results in a production of 1 mol HCO$_3^-$ (alkalinity) during the AOM while the OOM produces 2 mol HCO$_3^-$ from 1 mol SO$_4^{2-}$. Because pore water alkalinity is decreased by the precipitation of carbonates, initial alkalinity increase can be compensated by adding the difference of Ca$^{2+}$ and Mg$^{2+}$ concentrations between pore water and seawater [10]. The SO$_4^{2-}$ decrease and alkalinity increase during bio-geochemical processes near the seafloor are therefore estimated as;

$$\Delta SO_4^{2-} = SO_4^{2-}_{(SW)} - SO_4^{2-}_{(SA)}$$  \hspace{1cm} (4)

$\Delta$Alkalinity$=Alk_{(SA)} - Alk_{(SW)} + Ca_{(SW)} - Ca_{(SA)} + Mg_{(SW)} - Mg_{(SA)}$  \hspace{1cm} (5)

where "SW" and "SA" represent vales for seawater and sample, respectively.

Our results are plotted in $\Delta SO_4^{2-}$ vs. $\Delta$Alkalinity space (Fig. 3). Although the shallow samples with small $\Delta SO_4^{2-}$ value locate generally close to the OOM line ($\Delta SO_4^{2-}:\Delta$Alkalinity=1:2), the deep samples with large $\Delta SO_4^{2-}$ value likely have more association with the AOM line ($\Delta SO_4^{2-}:\Delta$Alkalinity=1:1). This suggests that very early diagenesis of marine organic matter occurs just below the seafloor, ~2 to 3 mbsf according to the $\Delta SO_4^{2-}$ value of ~10 mM, and the process of AOM at the SMI constrains these profiles thereafter.

SUMMARY
Pore water geochemistry characterizes occurrence of gas hydrate, methane flux, and potential bio-geochemical processes utilizing dissolved SO$_4^{2-}$. Distribution of gas hydrate in sediment core is described well both by high and low Cl$^-$ anomalies, in addition, downward increase of Cl$^-$ indicates massive formation of gas hydrate at depth. Depths of the SMI show strong methane flux from depth over the research area, in particular, around the summit of the Umitaka Spur and Joetsu Knoll,
corresponding well to the occurrence of methane venting. Alkalinity increase accompanied by \textit{SO}_4^{2-} decrease has been resulted mainly from two biogeochemical processes; oxidation of marine organic matter in shallow part and anaerobic oxidation of ascending methane in deep part (SMI).

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**REFERENCES**


