

Age models in two piston cores (MD179-3312 and 3304) off Joetsu in the southwestern part of the Japan Sea: based on the

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We constructed the age models of MD179-3312 and MD179-3304 off Joetsu, in the southwestern part of the Japan Sea based on AMS ¹⁴C determinations, tephra identifications, MIS events (as control points) and correlations of TL layers (as sub-control points). Bases of 11 TL layers (TL-1, TL-2, TL-3, TL-12, TL-14, TL-18, TL-19, TL-20, TL-21, TL-22 and TL-23) could be recognized the same horizons by the correlations with microfossil dates. The estimated sedimentation rates of core 3312 in average were about 0.24 m/kyr lower than those of core 3304, 0.32 m/kyr.

Keywords: Japan Sea, biostratigraphy, age model, late Quaternary, gas hydrates, TL layers

Depth distribution of trace elements in pore water collected from Japan Sea sediments associated with methane hydrate

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Methane hydrate occurs in the deep ocean floor, and also in the permafrost layers of Siberia and Alaska. In Japan, relevant gas hydrate studies have been carried out in Nankai Trough since the 1990s and in the Japan Sea since 2004.

This study focuses on the trace element concentrations, with a special reference to iodine, in pore water samples collected from Japan Sea sediments. The long-lived iodine isotope, ¹²⁹I, which is produced by the spallation of atmospheric and by spontaneous fission, was also measured in order to provide an estimation of the age of iodine.

Marine sediment samples were collected from methane hydrate areas of Umitaka Spur and Joetsu Knoll, Japan Sea, during the cruise with R/V Marion Dufresne (MD179; MH21 Research Consortium) in 2010. The depths of the sediment cores obtained with a giant piston corer reached maximum depths of about 40 mbsf, which is much deeper than previous piston core samples (down to 8 mbsf) recovered by R/V Umitaka-maru on previous cruises in the region. Pore waters were extracted from the sediment soon after recovery. The concentrations of iodine, bromine and some trace metals (such as Mn, Sr, Ba) were later determined by ICP-MS. Samples having a high iodine concentration were selected for ¹²⁹I analysis. For this, iodine from samples was extracted by solvent extraction and precipitated as AgI. ¹²⁹I/¹²⁷I ratios were determined by accelerator mass spectrometry (AMS) at MALT, the University of Tokyo.

Our results show that iodine concentrations in pore water increase constantly with depth in almost all cases. In particular, samples on the Umitaka Spur showed a markedly high increase of iodine concentrations, i.e. the concentration at 35 mbsf was 0.4 mM, which is about 800 times higher than the average iodine concentration in the ocean. Bromine concentration in pore water also increased with the depth, but not as much (only about 1.7 times seawater). On the other hand, profiles show a decreasing trend with depth in pore water chlorine concentrations. This may be explained by the dilution effect with non-saline water produced by the dissociation of methane hydrate.

Analytical results for ¹²⁹I/¹²⁷I ratio in pore waters deeper than 3 mbsf ranged from 0.20 - 0.35 x 10⁻¹². These values were much lower than the background value of ¹²⁹I/¹²⁷I ratio of 1.5 x 10⁻¹² in the ocean in the pre-atomic age. Considering the ¹²⁹I systematics, iodine age for the samples was estimated to be 30-45 Ma. This age is almost the same or older than the age when the Japan Sea was formed. The results of lower ¹²⁹I/¹²⁷I ratios and increasing iodine concentration in pore water with depth suggest that iodine did not originate from shallow marine sediments. The iodine must be derived from deeper layers, such as old sediments rich in organic matter and iodine which were deposited in the sediments at the opening of Japan Sea. Alternatively, since the iodine ratios indicate minimum ages, it may be possible that iodine was released from sediment layers which were formed before the formation of Japan Sea.

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Keywords: iodine, methane hydrate, Japan Sea, radioisotope ratio

3D observation of shallow gas hydrates in eastern margin of the Sea of Japan by X-CT

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Gas hydrate has clathrate structure of a gas molecule in a water cage, and is found naturally in deep-sea and permafrost sediments. Natural gas hydrates were recovered in eastern margin of the Sea of Japan through scientific expeditions since 2005 (Matsumoto et al., 2011) and their characterization was investigated (Lu et al., 2011). On-board observation of the hydrate samples indicated that occurrence of the gas hydrates in silt sediments was classified into roughly three groups; flake-like, laminated, and massive types. Sometimes, many hydrate pieces appeared in one depth, which gave us questions how they occurred in sediment and whether they connected each other, or not. Therefore, we here study 3D observation of shallow gas hydrates in eastern margin of the Sea of Japan by X-CT. The samples recovered during MD179 expedition were used in this study. Histograms of gray scales in slice images of all the samples show that we can distinguish between sediment and gas hydrate/water. Flake-like, laminated, and massive gas hydrates are observed. In one sample, platy gas hydrates are broken and sediment seems to intrude into platy gas hydrates. This implies that dynamic activity occurs after gas hydrate formation.

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Keywords: gas hydrate, X-ray CT, 3D observation

Chemical analysis of LV59 sediment pore waters retrieved off Sakhalin Island, Russia

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The Sakhalin Slope Gas Hydrate Project (SSGH) is an international collaborative effort by scientists from Japan, Korea, and Russia to investigate natural gas hydrates (GHs) that have accumulated on the continental slope off Sakhalin Island, Okhotsk Sea. In 2012, the field operation of the SSGH-12 project was conducted as the LV59 cruise of the R/V Akademik M.A. Lavrentyev. GH-bearing and -free sediment cores were retrieved using steel hydro- and gravity corers.

The pore water was sampled on board using squeezers designed and constructed at the Kitami Institute of Technology (KIT). A 10-cm depth interval of the sediment core was drawn into the squeezer, and pore water was then directly collected into a polyethylene syringe connected to the discharge tube of the squeezer. The other end of the syringe was connected to a membrane filter cartridge containing a 0.2- μ m filter. Seawater samples were obtained from the top of the corer. All water sample was filtrated through a 0.2- μ m filter and then taken into a polypropylene bottle.

The concentrations of anions in the pore waters were measured at KIT. Sulfate concentrations decreased linearly with depth to the sulfate methane interface (SMI). The linearity of these profiles suggested that sulfate depletion is largely driven by an upward flux of methane, rather than by the flux of organic matter from above, and the anaerobic oxidation of methane (AOM) at the SMI. The linear sulfate profiles are formed in a steady state based on sulfate and methane co-consumption at the SMI and the balance of sulfate and methane fluxes. The SMI of the GH-bearing LV59-27HC core was 0.5 m below the seafloor (m bsf). Since the depth of the SMI depends on the intensity of the upward methane flux, we can conclude that intensive methane flux was observed at the GH-bearing core.

Keywords: gas hydrate, pore water, chemical analysis, Sakhalin Island, Russia

Natural gas hydrates retrieved at the Terpeniya Ridge and the Tatar Trough, off the Sakhalin Island

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We report molecular and isotopic compositions of hydrate-bound hydrocarbons in the new seepage sites of offshore Sakhalin Island, the Sea of Okhotsk. Sakhalin Slope Gas Hydrate (SSGH) project was started from 2007 and we retrieved sediment cores off northeastern Sakhalin Island in 2009-2011. We also sampled some cores at the Terpeniya Ridge, southeastern Sakhalin Island in these cruises; however, we could not retrieve hydrate-bound cores at the area. Because gas plumes ascend and the dissolved methane in pore water was very rich, existence of gas hydrate crystals in the shallow sediment layers were expected. In August 2012, we visited the Terpeniya Ridge again and the Tatar Trough (southwestern Sakhalin Island) and got hydrate-bound sediment cores from both fields in the cruise of SSGH12. We sampled gas hydrate crystals and stored into liquid nitrogen tank. We also obtained the samples of hydrate-bound gas and dissolved gas in pore water on board, and we measured molecular and stable isotope compositions of them in our laboratory. Empirical classification of the methane stable isotopes; delta ¹³C and delta D according to Whiticar *et al.* (1986) indicated that the gases obtained at the Terpeniya Ridge are microbial origin via carbonate reduction, whereas some cores at the Tatar Trough showed typical thermogenic origin (methane delta ¹³C = -47 permil). Because ethane delta ¹³C of the all gas samples suggested their thermogenic origin, microbial methane is mixed with the small amount of thermogenic gas at the Terpeniya Ridge. Results of Raman spectroscopic analysis revealed that the hydrate crystals of both Terpeniya Ridge and Tatar Trough belonged to the structure I, and the hydration number was 6.0 in the both fields. Small amount of hydrogen sulfide was also enclathrated with methane.

Whiticar MJ, Faber E, Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate fermentation - Isotope evidence. *Geochim Cosmochim Acta* **50**: 693-709

Keywords: gas hydrate, stable isotope, Terpeniya Ridge, Tatar Trough, Sea of Okhotsk, Raman