Molecular and isotopic compositions of gas hydrates in the Sea of Okhotsk

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In the 1990s gas hydrates were discovered offshore Paramushir and Sakhalin Islands in the Sea of Okhotsk. Gas plumes from the sea floor and gas hydrate in a shallow sediment have been investigated offshore Sakhalin Island, the Sea of Okhotsk, within the framework of the KOMEX and CHAOS projects. We obtained hydrate-bearing sediments by using a gravity corer during the cruises of CHAOS1 and CHAOS2 on October 2003 and May 2005, respectively. Whiticar *et al.* (1986) proposed a genetic classification diagram for natural gas using methane isotopes. In the diagram, large and small delta ^{13}C values of methane indicate thermogenic and microbial origins, respectively, and delta D of methane also provides information on methyl-type fermentation or CO_2 reduction in the microbial origin. In this presentation we report molecular and isotopic compositions of hydrate-bound gas and dissolved gas in pore water obtained from the seven seepage structures in the CHAOS project.

Molecular composition ratios C_1/C_{2+} of all the seepage sites were in the range 1,500-49,000, while delta ^{13}C and delta D of methane ranged from -66.0 to -63.2 permil-VPDB and -204.6 to -196.7 permil-VSMOW, respectively. According to Whiticar *et al.* (1986), we can conclude that the microbial methane was produced by CO_2 reduction. Delta ^{13}C values of ethane and propane were -40.8 to -27.4 permil-VPDB and -41.3 to -30.6 permil-VPDB, respectively. These heavy isotopes indicate that small amounts of thermogenic gas were mixed with microbial methane. Delta D of hydrate-bound gas was 4.3 to 16.6 permil smaller than that of dissolved gas in pore water. Based on isotopic fractionation of guest gas during the formation of gas hydrate (Hachikubo *et al.*, 2007), we conclude that the current dissolved gas in pore water is really the source of gas hydrate in several sediment cores, whereas in some other cores delta D of methane in the dissolved gas in pore water changed after the formation of gas hydrate.