

## Experimental study of adsorbed methane in a methane-seep carbonate from the upper Miocene in Joetsu City, Niigata Prefecture

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Submarine methane seeps where methane-charged fluids seep out of the seafloor have been regarded as major sources of methane which is a main component of natural gases and a potent greenhouse gas. In methane seeps, anaerobic oxidation of methane (AOM) by microbial consortia increases alkalinity and induces methane-derived authigenic carbonate precipitation. Ancient methane seeps can be recognized from low stable carbon isotopic compositions derived from methane and lipid biomarkers of microbes performing AOM recorded in carbonate rocks hosted in sedimentary strata. They have a great significance as direct evidences of generation, migration, and emission of methane in the geological past. Methane is generated by microbial or thermal degradation of organic matter in shallow or deep sediment depths, respectively, and the origins of methane can be distinguished by proxies such as carbon isotopic compositions of methane. Identifying the origin of methane in ancient seep fluids can provide an insight into origin and pathway of seep fluid, and oil and natural gas generation in the past, but the way to directly estimate origins of methane in ancient seeps has not been established yet. Authigenic carbonates are reported to adsorb hydrocarbon gases in surrounding sediments (Ijiri et al., 2009). If ancient seep carbonates could also adsorb "paleo-methane" dissolved in seep fluids, it may be possible to estimate the origins of methane in ancient seeps by analyzing isotopic compositions of the adsorbed methane. This study attempted to extract adsorbed gas from an ancient seep carbonate and analyze stable carbon isotopic compositions ( $\delta^{13}\text{C}$  values) of methane to estimate its origin. Studied material is a methane-seep carbonate collected from the upper Miocene Nodani Formation in Joetsu City, Niigata Prefecture, central Japan. This carbonate mainly consists of dark-grey matrix of micritic aragonite and has abundant void spaces rimmed with creamy-colored acicular aragonite cements. Both of the micritic part and acicular aragonite have low  $\delta^{13}\text{C}$  values ( $-42.6$  to  $-15.4\%$  vs. PDB), and the former contains lipid biomarkers of anaerobic methanotrophic archaea, pentamethylcosane and crocetane, showing that the carbonate was precipitated in a methane seep. Adsorbed methane was liberated by dissolution of carbonate powders by adding phosphoric acid, and then introduced into GC-IRMS to analyze concentration and  $\delta^{13}\text{C}$  values of methane. Methane was successfully extracted from all samples, and the  $\delta^{13}\text{C}$  values of methane ranged widely from  $-60.7$  to  $-40.0\%$ . This suggests that the extracted methane is composed of a mixture of biogenic and thermogenic methane in various ratios and/or contains biogenic methane enriched in  $^{13}\text{C}$  due to fractionation through AOM. The  $\delta^{13}\text{C}$  values of the extracted methane and those of the carbonate powders from which gases were extracted showed a weak positive correlation, and void-filling acicular aragonite mostly have lower  $\delta^{13}\text{C}$  values of extracted methane and carbonate than those of micritic parts. This result implies that the methane contained in the seep fluid could be trapped in the host carbonate phases during their precipitation, and there was some relation between precipitation of each carbonate phase, either in sediment or void, and origin and/or flux of methane trapped in it. Because it is also possible that the methane was adsorbed after precipitation and during burial of the carbonate, further investigation of the preservation state of the gases in the seep carbonate is required to elucidate where and how the methane was trapped within the carbonate.

Keywords: Methane seep, Carbonate, Miocene, Joetsu City, Adsorbed gas