



Toward estimation of origin of methane at ancient seeps — Carbon isotopes of seep carbonates, lipid biomarkers, and adsorbed gas

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Methane is generated mainly by microbial or thermal degradation of organic matter, and the origin of methane can be estimated based on its stable carbon isotopic signature. Seafloor seepages of methane-charged fluids have been a major source of methane to the ocean, and knowing the origin of methane at the methane seeps can provide valuable insights into the subsurface fluid circulation and biogeochemical processes. Methane seeps in the geological past are archived as authigenic methane-derived carbonate rocks, which precipitate via an alkalinity increase facilitated by microbially mediated anaerobic oxidation of methane. Here we attempted to estimate origins of methane at ancient seeps, based on several proxies preserved within the seep carbonates. We examined methane-seep carbonate rocks in the Japan Sea region, collected from lower Miocene to middle Pleistocene sediments at 11 sites on land, and also carbonate nodules collected from the seafloor off Joetsu, where thermogenic methane is seeping. Carbon isotopic compositions of the carbonates and lipid biomarkers of methane-oxidizing archaea within them were analyzed. In order to directly know original isotopic signatures of methane, we also attempted to extract adsorbed methane through acid dissolution of the powdered carbonates.

Early-diagenetic carbonate phases show various $\delta^{13}\text{C}$ values between -64.7 and -4.7‰ vs. VPDB, suggesting either biogenic or thermogenic, or both origins of methane. A lipid biomarker pentamethylcosane (PMI) extracted from the ancient carbonates has $\delta^{13}\text{C}$ values mostly lower than -100‰ , whereas that from the modern methane-derived carbonate nodule has a higher value (-80‰). The $\delta^{13}\text{C}$ values of the seeping methane (-36‰) and PMI in the modern Joetsu seep carbonate shows an offset of -44‰ . If this carbon isotope offset was similar at the ancient seeps, the $\delta^{13}\text{C}$ values of PMI indicate that methane at ancient seeps in the Japan Sea region was biogenic in origin, with $\delta^{13}\text{C}$ values lower than -50‰ .

Acid dissolution of the Miocene to Pliocene carbonates released methane with $\delta^{13}\text{C}$ values mostly around or higher than -50‰ , which conflicts with the estimation based on biomarkers. Moreover, the Pleistocene and modern samples released only trace amounts of methane. It is thus highly possible that the extracted methane was mostly adsorbed on the carbonates within zones of thermogenic generation of hydrocarbons during burial.

In conclusion, we can roughly estimate origins of methane at ancient seeps based on $\delta^{13}\text{C}$ values of carbonates and biomarkers. However, in order to directly analyze methane contained in ancient seepage fluids, exploration of gas or fluid inclusions trapped within carbonate crystals is necessary.