Origin of methane at ancient seeps inferred from carbon isotopic signatures of biomarkers of methane-oxidizing archaea

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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. Submarine methane seeps 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 biogeochemical processes and fluid circulation. Methane seeps in the geological past are archived as authigenic methane-derived carbonate rocks, which form via an alkalinity increase facilitated by microbially mediated anaerobic oxidation of methane. Although these carbonates inherit methane-derived carbon, they also incorporate non-methane-derived carbon such as seawater dissolved inorganic carbon, which masks original isotopic compositions of methane. Here we attempted to estimate origins of methane at ancient seeps based on carbon isotopic compositions of lipid biomarkers of methane-oxidizing archaea, which can more directly reflect isotopic signatures of methane. 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. Early-diagenetic carbonate phases show various δ^{13}C values between −64.7 and −4.7‰ vs. VPDB, suggesting either biogenic or thermogenic, or both origins of methane. A lipid biomarker pentamethylicosane (PMI) extracted from the ancient carbonates showed δ^{13}C values mostly lower than −100‰, whereas that from the modern methane-derived carbonate nodule showed a higher value (−80‰). The δ^{13}C values of the seeping methane (−36‰) and PMI in the modern Joetsu seep carbonate showed an offset of −44‰. If this carbon isotope offset was similar at the ancient seeps, the δ^{13}C values of PMI indicate that methane at the ancient seeps in the Japan Sea region was mostly biogenic in origin, with δ^{13}C values lower than −50‰. This suggests that methane was supplied mainly from the shallow subsurface, and the migration of thermogenic gases from the deep subsurface to the seafloor through pathways such as faults was minor at the studied ancient seeps. Further attempts to constrain original isotopic signatures of methane by extraction of residual methane from carbonates is also ongoing. Future works need to examine other proxies to know origins of seep fluids, such as rare earth elements in seep carbonates, which would also help to know origins of methane at ancient seeps.

Keywords: Methane, Cold seep, Biomarker, Cenozoic, Japan Sea

