Origin of biogenic methane in the Nankai submarine mud volcano based on methane stable isotopologues

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Submarine mud volcanoes act as "natural pipelines" that transport deep hydrocarbons, including methane, to the overlying hydrosphere and atmosphere. In 2012, we explored one of the active submarine mud-volcanoes in the Kumano forearc basin of the Nankai Trough, off the Kii Peninsula of Japan using the deep-sea drilling vessel *Chikyu* (33°67.581N, 136°56.8085E, 1986.7 m in water depth). Gas samples were recovred from sediment core samples drilled down to 200 m below the summit using a hydraulic piston-coring system and a gas-tight hybrid-pressure coring system (Hybrid-PCS).

Relatively high C_1/C_2 ratios (670±390) in the headspace gas suggest the contribution of biologically produced methane. The average $\delta^{13}C$ value of methane (–34.3±2.3‰) is within the typical range of thermogenic methane. In contrast, the hydrogen isotopic compositions of methane (–181±2‰) as well as the magnitude of ^{13}C-isotopic difference between DIC and methane (73.9±3.5‰) are fully consistent with substantial contribution of methane from hydrogenotrophic methanogenesis. The abundance of $^{13}CH_3D$, a multiply substituted "clumped" isotopologue, in two Hybrid-PCS samples obtained from 6.5 m and 61.5 m below seafloor, indicates apparent equilibrium temperatures ($\Delta^{13}CH_3D$ temperatures) of ca. 29°C and 31°C, respectively. Assuming two endmember mixing of biogenic and thermogenic methane, we estimated that as much as 90% of methane was microbially produced at 17–30°C. Combining these constraints with the *in-situ* temperature profile (29°C km^{-1}), we estimate the depth of mud pools from which methane was sourced to be around 400–1,000 m below seafloor. Our results indicate that microbial activity in the deep mud-volcano biosphere strongly impacts on the biogeochemical carbon cycle in the Nankai accretionary complex.