Methanogenesis from hydrocarbons biodegradation: evidence from multiple isotopologue proxies in Tokamachi mud volcano, Japan

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Microbial methane production represents an important source of methane on Earth. In oil and gas reservoirs, microbial methane can be formed from secondary methanogenesis, i.e., from C_{2+} hydrocarbons biodegradation, either directly [1] or indirectly from the biodegradation products [2]. Despite its global significance [2], secondary methanogenesis is arguably challenging to detect, mainly because methane isotopic signature overlaps with that of the existing thermogenic methane in the reservoir, and is thus inferred only from indirect proxies such as high ^{13}C content of propane and CO_2.

Here, we combine methane clumped isotopes with propane position-specific isotope analysis (PSIA) of 19 samples from mud volcanoes and gas seepages located in Tokamachi area (Niigata, Japan). Previous studies have shown that both propane and CO_2 in Tokamachi natural gas samples are ^{13}C-enriched, consistent with biodegradation-associated methanogenesis [3].

Propane ^{13}C-PSIA shows a clear biodegradation trend where $\delta^{13}C$ of the central position of propane is specifically enriched as the relative amount of propane decreases [4]. Based on results from pure culture experiments, the position-specific isotope composition of propane in Tokamachi is consistent with combined bacterial and archaeal biodegradation with a 10:90 ratio.

Interestingly, the extent of propane biodegradation, as indicated by the difference between the two positions of propane ($\Delta_{Central} = \delta_{Central} - \delta_{Terminal}$), correlates with $\Delta^{13}CH_3D$ and ΔCH_2D_2 of methane, both of which tending towards equilibrium values at high biodegradation rates. This, along with the increase of $C_1/(C_2+C_3)$ ratio at high biodegradation rates, suggests the occurrence of secondary methanogenesis [2] from C_{2+} hydrocarbons biodegradation. This study emphasizes the importance of using multiple indicators to tackle hydrocarbons cycling in the subsurface, in particular methanogenesis associated with hydrocarbons biodegradation.

References:
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