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Combinatorial and rate effects on the multiply-substituted isotope signatures in methane during biological production and consumption

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Methane is an important energy source, a potent greenhouse gas and a potential proxy for extraterrestrial life. Constraining the sources and sinks of methane is crucial for understanding methane cycling on Earth and other planets. The relative abundances of multiply-substituted ("clumped") isotopologues $^{13}CH_3D$ and $^{12}CH_2D_2$ ($\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$) are potentially powerful tools to track processes of methane formation and destruction[1-3]. However, substantial uncertainties exist in the interpretation of clumped isotope signatures of natural methane, in part due to a lack of understanding of fractionation mechanisms by microbial methanotrophy and anaerobic methanogenesis. Recent studies show that combinatorial effect is a key factor that influences clumped isotope signatures[4]. Other studies propose metabolic rates could affect clumped isotope signatures as well[1,5]. However, more experimentation is needed to test these hypotheses.

We conduct two suites of experiments, one to test how the rate of aerobic methanotrophy affects methane clumped isotope signatures, and the other to investigate the role of combinatorial effects during different pathways of methanogenesis. In one suite of experiments, we monitor the change of $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$ during aerobic oxidation by *Methylococcus capsulatus* Bath at different growth rates controlled by temperature. In the second suite of experiments, we test the combinatorial effects resulting from enzymatically-mediated kinetic steps within a cell (endogenous) and isotopically distinct external hydrogen pools such as growth medium (exogenous) on $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$. *Methanosarcina barkeri* Fusaro was cultivated on methanol, acetate or hydrogen/carbon dioxide. We see evidence for exogenous combinatorial effects during methylotrophic and acetotrophic methanogenesis, while hydrogenotrophic methanogenesis is mainly governed by endogenous combinatorial effects. More nuanced mixing of methane from different metabolic pathways is also identified during acetotrophic methanogenesis. The broader goal is to compare our results with microbial and environmental models[4,6], and to further develop $\delta^{13}CH_3D$ and $\delta^{12}CH_2D_2$ values as indicators of methane provenance.

References:

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