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The multiply substituted isotopologue $^{12}CH_2D$ in methane differentiates biological production mechanisms

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Multiply substituted ('clumped') isotopologues of methane are well suited as tracers of methane formation pathways in general, and potential biosignatures in particular (*1*). Clumped isotopes in methane (e.g. 13CH3D, 12CH2D2) remove the difficulties associated with using bulk carbon (13C/12C) and hydrogen (2H/1H) isotope ratios on other worlds, and in hard to access environments on Earth, where the geochemical context necessary for interpreting these ratios are lacking. Still, uncertainties remain about the uniqueness of the methane isotopologue signatures in that both non-biological and biological mechanisms can make methane, and within the biological processes, a large array of substrates can be converted to methane. To mitigate these uncertainties, we performed a suite of biological and abiotic methane synthesis experiments. Here we focus only on the biological experiments.

We conducted a series of batch experiments to synthesize methane via different microbial pathways, utilizing different carbon and hydrogens sources. The mass-18 isotopologue signatures enable us to distinguish different microbial methanogenesis pathways. When two or more hydrogen sources are necessary to produce methane, product methane is isotopically distinct from single-H source methane, specifically in the more rare isotopologue, $^{12}CH_2D_2$, even when bulk $^2H/^1H$ and $^{13}C/^{12}C$ ratios are indistinguishable. This observation confirms prior theory (*2*, *3*), and experiments (*4*), that predicted the role of the so-called "combinatorial effect," the key source of the putative biosignature. The mass-18 isotopologues of methane have great potential as biosignatures if some of the lingering uncertainties about uniqueness of relating their relative abundances to specific pathways can be eliminated. This work will inform future missions about the potential benefits of including in-situ measurements of rare methane isotopologues on Mars, Enceladus, and other bodies where the origin of methane is a key geochemical and biogeochemical tracer.

[1] Young & Leavitt. 2021. *BAAS*. [2]Yeung. 2016. *GCA*; [3] Röckmann et al. (2016). *Sci.Reports*. [4] Taenzer, et al. 2020. *GCA*. **285** (2020).