Clumped Isotopologue ($^{13}CH_3D$) Fingerprinting of Methane Sources

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Methane is a significant greenhouse gas and energy resource. It is derived from diverse sources (e.g., microbial, thermogenic or abiotic) on Earth, yet differentiation between sources remains a major challenge. While carbon ($^{13}C/^{12}C$) and hydrogen (D/H) isotope ratios can tell the origin of carbon and hydrogen in methane, the abundance of a doubly substituted "clumped" isotopologue, $^{13}CH_3D$, may hold information regarding the origin of C-H bonds.

Several novel instruments have been developed for precise measurements of the clumped isotopologue of methane, including high resolution mass-spectrometers and tunable laser mid-infrared spectroscopes. Data from both types of instruments have demonstrated a wealth of additional information that can be inferred from clumped isotopologues of methane ($^{13}CH_3D$, as well as $^{12}CH_2D_2$) [1,2,3]. In particular, the abundance of $^{13}CH_3D$ can yield apparent temperatures at which methane was generated or its bonds were last equilibrated. In contrast, methane from sites supporting active microbial methanogenesis (such as wetlands and cow rumens) and from laboratory methanogen cultures, carry isotopologue abundances that are primarily controlled by kinetic processes.

I will discuss novel applications of this technique for identifying the origin of methane in the environment, including methane associated with serpentinite springs, seafloor hydrothermal vents, and gas hydrates. For some systems, estimated equilibrium temperatures of methane can be translated to the depth of generation where geothermal gradients are known.

Reference: [1] Stolper et al., 2014, *Science* **344**, 1500; [2], Wang et al., 2015, *Science* **348**, 428; [3] Young et al., 2017, *GCA* **203**, 235

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