

Experimental determination of the clumped isotope signatures of abiotic methane

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Methane is observed in a variety of environments on Earth. Abiotic methane synthesis is thought to originate from reaction between CO₂ and H₂. However, abiotic synthesis of methane proceeds with substantial kinetic barriers in the laboratory. It is so sluggish that alternative pathways to methane formation have been suggested to explain the many observations of methane coexisting with hydrogen in nature.

Disambiguating methane synthesis pathways is challenging because of the lack of unambiguous signatures of the provenance of methane molecules. The abundances of mass-18 isotopologue of methane, ¹³CH₃D and ¹²CH₂D₂, could help identify occurrences of abiotic methane in nature. We performed synthesis of abiogenic methane in the laboratory and determined D¹³CH₃D and D¹²CH₂D₂. We carried out a set of 9 experiments in hydrothermal conditions, at temperatures between 130 and 300 °C. The experiments were performed by heating an aqueous solution in the presence of Fe⁰ powder and gaseous CO. We systematically extracted and quantified abiotic methane, prior to determination of d¹³C, dD ¹²CH₂D₂, and D¹³CH₃D using a Panorama gas-source mass spectrometer (Nu, Ametek).

We observe d¹³C and dD of methane to be isotopically depleted relative to the starting materials, inconsistent with equilibrium isotopic fractionations. This suggests that methane synthesis under our experimental conditions was governed by kinetics and that subsequent bulk isotope re-equilibration remained limited. We find most of the D¹³CH₃D values seem to track the temperature of abiotic methane synthesis within a permil. In contrast, D¹²CH₂D₂ data show exclusively negative values, illustrating deficits of up to 40‰ relative to equilibrium. The D¹²CH₂D₂ deficits at a given D¹³CH₃D are deeper than what is observed with microbial methane synthesized in the laboratory at temperatures under 65°C.

We interpret the data as evidence for a combinatorial effect occurring during the methane assembly. D/H fractionation associated to the various steps of hydrogen addition during CO methanation can explain the direction and the magnitude of the D¹²CH₂D₂ signatures of abiotic methane. We suggest that somewhat equilibrated D¹³CH₃D and strongly negative D¹²CH₂D₂ signatures could help identify abiotic methane in nature, should re-equilibration of C-H bonds be avoided.