Clumped isotope systematics of biogenic methane

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Methane is an important constituent of the global carbon cycle. Nonetheless, the fluxes of methane are not well constrained, and it is often difficult to determine whether this gas is generated by microbial or geochemical (thermogenic or abiogenic) processes. The temperature of formation for methane, or temperature at which methane is equilibrated, may be revealed by studying the multiply substituted isotopologues, or clumped isotopes, of methane, $^{13}CH_3D$. Because the currently known upper temperature limit of life is around 120°C and thermogenic methane often forms at temperatures greater than 150°C, clumped methane analysis is expected to provide critical constraints on the source of methane and to eliminate confounding variables associated with conventional isotope studies. The $^{13}CH_3D$ thermometry scale was calibrated between 200°C and 400°C by heating methane over a platinum or nickel catalyst [1]. The goal of this study is to extend the calibration to lower than 200°C, at which inorganic isotope exchange becomes sluggish.

Methane produced in batch cultures of methanogens, *M. thermolithotrophicus*, *M. jannaschii*, and a novel strain of *Methanocaldococcus*, grown between 40°C and 90°C was analyzed using novel high precision tunable infrared laser direct absorption spectroscopy. The relative abundance of $^{13}CH_3D$ species measured corresponded to higher than actual growth temperatures by 100°C or more. To test whether this discrepancy was the result of closed system isotope effects or non-thermodynamic methane production associated with microbial enzymatic processes (e.g., hydrogen tunneling), we are carrying out a time series study for the clumped methane isotope fractionation of biogenic methane grown in batch cultures at a range of temperatures. We will report the results of this experiment and prospects of using $^{13}CH_3D$ to understand the clumped isotope systematics of microbial metabolism and sources of natural methane.

[1] Ono *et al* Goldschmidt 2014.