Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19960

Equilibrium and non-equilibrium clumped isotope signatures among microbially-mediated methane

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For the last ~10 years, doubly substituted 'clumped' methane isotopologues, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ (departure from stochastic), have been emerging as tracers of methane's origin and fate in nature. These novel tracers record kinetics or equilibrium effects associated with the methane's formation, degradation, or transport mechanisms [1].

Here we will review how $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ can help to better constrain methane-based metabolisms in natural environments. So far, their use in identifying and quantifying microbial methanogenesis has remained elusive, with laboratory and field observations resulting in somehow contradictory results [2, 3]: the former yields clear disequilibrium among methane isotopologues, while the later seems associated with near-equilibrium signatures. Whether equilibrium signatures observed in nature are inherited from methane synthesis versus from late equilibration remains debated. We will also present evidence for the role of microbial methanotrophy, whether aerobic or anaerobic, in altering $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values. We take example of two natural settings where methane is quantitatively degraded - the meromictic Lake Pavin in France and the Black sea sediments, offshore Romania – to illustrate how aerobic and anaerobic methanotrophy both promote isotopologue disequilibrium [4]. We will illustrate the spectrum of $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ behaviors associated with methanotrophy. Where aerobic methanotrophy yields to progressive depletion of both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values, anaerobic oxidation may result in extreme and yet unrecognized positive enrichments. Taken together, these findings contribute to better refine the potential bio-signatures of methane.

[1] Young et al. (2017), *GCA 203, 235-264*. [2] Wang et al. (2015), *Science 348, 428-431*. [3] Stolper et al. (2015), *GCA 161, 219-247*. [4] Giunta et al. (2022), *GCA 338, 34-53*.