$\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ signals of methanogenesis and methanotrophy

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Methanogens in marine sediments are estimated to produce between 85-300 Tg of methane (CH_4) annually, yet the net flux of CH_4 to the water column is strictly controlled by the anaerobic oxidation of methane (AOM). Hypotheses that abrupt imbalances in this delicate cycle can occur as a result of anthropogenic climate change drive our desire to better understand microbial CH_4 production and consumption in the deep biosphere. The ability to measure the relative abundances of two doubly-substituted rare isotopologues of gases with biogeochemical relevance provides new constraints on sources and sinks of these gases [1]. Here, we report the first measurements of fully resolved $^{13}CH_3D$ and $^{12}CH_2D_2$ from samples of deep biosphere CH_4 gas collected during IODP Exp. 347 to the Baltic Sea.

We measured sedimentary CH_4 samples from Bornholm Basin and Landsort Deep in the Baltic Sea for $\Delta^{13}CH_3D$, $\Delta^{12}CH_2D_2$, $\delta^{13}C$ and δD. Results are interpreted within the context of porewater geochemistry, activity measurements, and a multicomponent diagenetic model that estimates rates of CH_4 production, SO_4-AOM and Fe-AOM [2]. $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ vary with depth concurrent with changing rates of methanogenesis and methanotrophy. Samples associated with higher rates of methanogenesis exhibit disequilibrium of up to 2‰ in $\Delta^{13}CH_3D$ and 13‰ in $\Delta^{12}CH_2D_2$ while those with higher rates of methanotrophy approach intra-species thermodynamic equilibrium. We hypothesize that methanogenesis creates CH_4 in isotopic disequilibrium by combinatorial, reservoir and quantum tunneling effects, and enzymatic back reaction during AOM drives the residue towards equilibrium [1, 3-4].

[1] Young *et al.*, (2017) GCA 203,235-264. [2] Egger *et al.*, (2017) GCA in press. [3] Yeung, (2016) GCA 172, 22-38.
[4] Timmers *et al.*, (2017) Archaea 1654237.