Methane clumped isotope signature of anaerobic oxidation of methane

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Microbial anaerobic oxidation of methane (AOM) significantly mitigates atmospheric methane emissions on Earth and represents a thermodynamically favorable metabolic strategy for astrobiological targets where methane has been detected. The bulk carbon and hydrogen isotope ratios produced by AOM have been used to probe the thermodynamic drive for intracellular reactions that involve the bi-directional enzymes of the methanogenesis pathway. Recently, measurements of the abundance of doubly-substituted methane isotopologues provide another dimension for assessing kinetic and equilibrium isotope effects and thus the AOM process itself. Towards this end, we measured methane clumped isotope ratios of residual methane in AOM-active microbial incubations using sediment slurry and/or fracture fluid from Svalbard methane seeps, Santa Barbara Channel methane seeps, Nankai Trough, and Beatrix Gold Mine. We also analyzed methane isotopologue abundances in sub-seafloor fluids from a Mariana mud volcano where AOM occurs. Extremely high $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values were found in the Svalbard sediment slurry and the Mariana fluids where minimal reversibility of AOM intracellular reactions preserved signatures of kinetic fractionation of clumped isotopologues. When conditions were consistent with a low thermodynamic drive for AOM, however, methane isotopologues approached intramolecular quasi-equilibrium. This was notably observed in the microbial incubations of the deep biosphere samples from Nankai Trough and Beatrix Mine. This presentation will highlight the environmental controls on the enzymatic activity of intracellular pathways and the reversibility of AOM, and their intrinsic link to methane isotopologue ratios.