METHANE FORMATION AND CONSUMPTION PROCESSES REVEALED BY EQUILIBRIUM AND DISEQUILIBRIM SIGNATURES IN MULTIPLE ISOTOPOLOGUES. J. L. Ash[1], Issaku Kohl[2], Jabrane Labidi[2], and E. D. Young[2], [1]Department of Earth, Environmental and Planetary Sciences, Rice University (Houston, Texas, USA, jeanine.ash@rice.edu), [2]Department of Earth, Planetary, and Space Sciences, UCLA (Los Angeles, California, USA).

Methane is ubiquitous throughout the solar system. The economic significance of this simple hydrocarbon coupled with its greenhouse warming potential have stimulated much research in the past decades regarding both the genetics and the fate of methane in the Earth system. Tools often used to determine methane provenance such as bulk isotopic values and gas composition can be difficult to interpret when processes like mixing and oxidation alter a reservoir.

Recent advances in mass spectrometry now allow for the measurement of the doubly-substituted isotopologues of methane $^{12}CH_2D_2$ and $^{13}CH_3D$ [1]. In equilibrium reactions, abundances of these two isotopologues can be used to determine the temperature of methane formation. The field of stable isotope geochemistry often assumes that equilibrium signatures abound in nature (e.g. when measuring carbonates for paleotemperature); here we will show that equilibrium is rare and that many environmental samples of methane do not have $^{12}CH_2D_2$ and $^{13}CH_3D$ compositions that reflect their temperature of formation [2].

The multiply-substituted isotopologue compositions of methane representative of end-member thermogenic, microbial and abiotic sources have been measured. These studies reveal that while thermogenesis seems to create methane in molecular isotopic equilibrium, most low-temperature processes including microbial methane production and Sabatier reactions create methane with large depletions in $^{12}CH_2D_2$ relative to equilibrium, even if their $^{13}CH_3D$ compositions imply reasonable environmental temperatures.

We will discuss potential mechanisms for this low-temperature disequilibria including hydrogen-tunneling, reservoir effects and combinatorics. The $^{12}CH_2D_2$ and $^{13}CH_3D$ composition of methane from sedimentary basins, mud volcanoes, the deep biosphere and clathrates are probed to explore double isotopologue space and define fields that may be useful for interpreting provenance in extra-terrestrial methane.

References: [1] Young E.D. et al. (2016) *Internation Journal of Mass Spectrometry, 401,* 1-10. [2] Young E.D. et al. (2017) *Geochimica et Cosmochimica Acta, 203,* 235-264.