Methane Clumped Isotope Compositions From Ethane Pyrolysis Experiments

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Methane clumped isotope compositions (given as $\Delta^{13}CH_3D$ & $\Delta^{12}CH_2D_2$) provide complimentary constraints on the formational environments of methane (e.g., thermogenic *vs.* biogenic) relative to traditional techniques, but uncertainty remains regarding the mechanisms by which some forms of methane obtain their clumped isotope compositions. Methane interpreted to be thermogenic (i.e., derived from the thermally activated breakdown of larger organic molecules) often, but not always, exhibits clumped isotope compositions that are consistent with equilibrium at temperatures within an expected thermogenic range (~60-220°C) both for $\Delta^{13}CH_3D$ & $\Delta^{12}CH_2D_2$ (e.g., Stolper et al., 2014; Wang et al., 2015; Giunta et al., 2019). However, it is not known how this equilibrium is achieved.

We have conducted a series of ethane pyrolysis experiments at relatively high temperatures (600°C) to investigate the rates and bulk/clumped isotope effects that accompany a thermally-induced methane formation process. We find that bulk isotopic compositions of accumulated methane (given as $\delta^{13}C$ and δD) evolve as a function of reaction progress in a manner that is consistent with a closed-system Rayleigh process. The $\Delta^{13}CH_3D$ composition of accumulated methane is found to remain relatively constant as a function of reaction progress (within analytical precision) and appears to be consistent with equilibrium at the experimental temperature. The $\Delta^{12}CH_2D_2$ of accumulated methane is found to exhibit so-called 'anti-clumping' behavior ($\Delta^{12}CH_2D_2 < 0$ ‰) that evolves with reaction progress in a manner that is consistent with a closed system Rayleigh process. We will discuss these results in the context of ethane pyrolysis mechanisms and natural thermogenic methane formation processes.

Our measurements have been made utilizing a newly installed ThermoFisher 253 Ultra at UC Berkeley. We will additionally present results of our analytical procedures that will include a newly extended experimental calibration of equilibrium $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ from 20-500°C that agree with theoretical predictions (e.g., electronic structure calculations performed at the CCSD/aug-cc-pVTZ level).