Clumped isotope signatures of abiotic methane formed via Fischer-Tropsch catalysis and their implications

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The isotopic compositions of CH_4, such as $^{13}C/^{12}C$ and D/H ratios ($\delta^{13}C$ and δD, respectively), are widely used as a tracer for identifying the CH_4 formation processes. However, obvious defects are existent, such as partly overlapping of isotopic signatures for different CH_4 sources, difficulty in constraining CH_4 generated from two or more sources, and so on (Douglas et al., 2017). Very recently, CH_4 clumped isotope signatures has been considered as a helpful constraint to provide more information on origins of natural CH_4 (e.g. Douglas et al., 2017; Young et al., 2017).

The clumped isotope refers to molecules substituted by two or more rare stable isotopes, e.g. $^{13}CH_3D$ and $^{12}CH_2D_2$, whose abundance relative to a random distribution is temperature dependent (Stolper et al., 2014). Therefore, the formation temperatures of CH_4 can be obtained if the reactions are in isotopic equilibrium. On the other hand, kinetic effect will introduce disequilibrium clumped isotope values, which can be used in identifying specific process/mechanism (Stolper et al., 2015). Overviewing the literature of CH_4 clumped isotope, almost all of the studies focused on the microbial and thermogenic CH_4 samples so far, while limited abiotic data has been reported by Young et al. (2017) and Wang et al. (2018) only. Two preliminary results of low-temperature Fischer-Tropsch Type (FTT) reaction (Sabatier reaction) using ruthenium (Ru) as catalyst presented strongly disequlibrated clumped isotope signals, which was considered to be caused by quantum tunneling effect (Young et al., 2017). On the other hand, lack of clumped isotope data from other FTT reaction with different catalyst and reactant, limiting this technique as a tool to identify the pathways of natural abiotic CH_4 formation.

In this study, we will present the clumped isotopic signatures of laboratory produced abiotic CH_4 via gaseous FTT reactions, using various experimental parameters and catalysts, such as Ni, Fe, Ru and Co. Both $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values are analyzed using a 253 Ultra High Resolution Isotope Ratio Mass Spectrometer established in Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, following the similar procedures described in Eldridge et al. (2019). We will discuss the controlling factors of clumped isotopic signatures in laboratory produced abiotic CH_4, and try to apply these results in clarifying the producing mechanism of natural abiotic CH_4 gases, which might provide more information to illustrate the early earth environment and life origin, as well as other planet with abiotic CH_4 existent.

References: Douglas et al., 2017, Organic Chemistry; Eldridge et al., 2019, ACS Earth Space Chem.; Stolper et al., 2014, Geochim. Cosmochim. Acta.; Stolper et al., 2015, Geochim. Cosmochim. Acta.; Wang et al., 2018, Geochim. Cosmochim. Acta.; Young et al., 2017, Geochim. Cosmochim. Acta.

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