Computer generated reaction mechanisms to model methane isotopologue exchange rates in hydrothermal settings

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Isotope and isotopolgoue ratios of methane in geothermal fluids (e.g., volcanic fumaroles and hydrothermal vents) are used to trace its origin and thermal history. The relative abundacne of doubly substituted isotopologues ($^{13}CH_3D$, and $^{12}CH_2D_2$), for example, reflects the temperature at which the rate of isotopologue exchange reaction becomes slower than the cooling rate of the fluids. The kinetics and mechanisms of isotopologue exchange reactions, however, are poorly constrained.

We emplyed a computer model, Reaction Mechanism Generator (RMG)[1], to estimate the relative rates of chemical (CH_4/CO_2), and isotopologue (e.g., $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$ and $^{12}CH_2D_2$) equilibrium reactions in hydrothermal settings. The software generates chemical species and reacitons based on thermochemistry and reaction kinetics database, which is supplemented by structure-based model estimates.

Our model predicts the dominant mechanism for hydrogen isotope exchange is the formation of methyl radical via the reaction, $CH_4 + \cdot SH \leftrightarrow \cdot CH_3 + H_2S$. The rate of exchange is on the order of tens of years at 700K, and is a function of H_2S and H_2 concentrations. This rate is largely consistent with the maximum clumped methane isotopologues temperatures of ca. 300 to 400°C measured thus far from seafloor hydrothermal vents [2,3]. Chemical and $^{13}C/^{12}C$ equilibrium between CH_4 and CO_2 is prdicted to be slow (on the order of million years) and proceeds via intermediates, including methanol, formaldehyde and fomic acid [4], or their thio equivalent, methanethiol (CH_3SH), thioaldehyde (H_2CS), thioformic acids (SCOH) when H_2S is present.

Reference: [1] rmg.mit.edu; Gao et al., 2016, *Comput. Phys. Commun.* **203**, 212, [2] Wang et al., *Geochim. Cosmochim Acta*, **223**, 141 [3] Douglas et al., 2017, *Org. Geochem.*, **113**, 262. [4] Seewald et al., 2006, *Geochim. Cosmochim. Acta*, **70**, 446