PRF#: 58813
Project Title: Experimental Determination of C-H Bond Isotope-Exchange Kinetics for Singly and Multiply Substituted Methane Isotopologues
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2019 Narrative Progress Report

Background: Methane is an important reactant and product in numerous geological, atmospheric, and biological processes and important energy resource in accumulations of economic hydrocarbon deposits. A first step in the study of methane accumulations in the environment is to determine the source of the methane. A variety of approaches exist to do this, but a routine and well-established technique is to measure the hydrogen isotopic composition of methane, which reflects its source (e.g. biogenic or thermogenic). A motivating question behind this proposal is what conditions are necessary, post methane formation, for the hydrogen isotopic composition of methane to change. In other words, what are the rates of hydrogen isotope exchange of methane in the subsurface? We proposed to answer this by measuring the rates of hydrogen isotope exchange for both single substituted ($^{12}CH_3D$) and multiply isotopically substituted ($^{13}CH_3D$ and $^{12}CH_2D_2$) methane molecules (i.e. clumped isotopes) in both hydrous and anhydrous laboratory experiments. These were new measurements for my laboratory group and new experiments and so the first year of the project was devoted to working out measurement and experimental methodologies, which have now been accomplished, paving the way for more experiments in the second year of the project.

Progress: (1) Over the past year, my lab has set up the clumped isotope measurement technique needed for measurements of abundances of multiply isotopically substituted methane molecules. Such measurements are needed to be able to measure rates of clumped isotope exchange discussed above. Graduate student Andrew Turner, who is funded by this grant, aided in this set up by helping generate methane in isotopic equilibrium as a function of temperature to calibrate the measurement. The work describing the calibration has been submitted to an ACS journal. This methods development and calibration now allows us to make the proposed measurements of experimental products for clumped-isotope measurements in year two

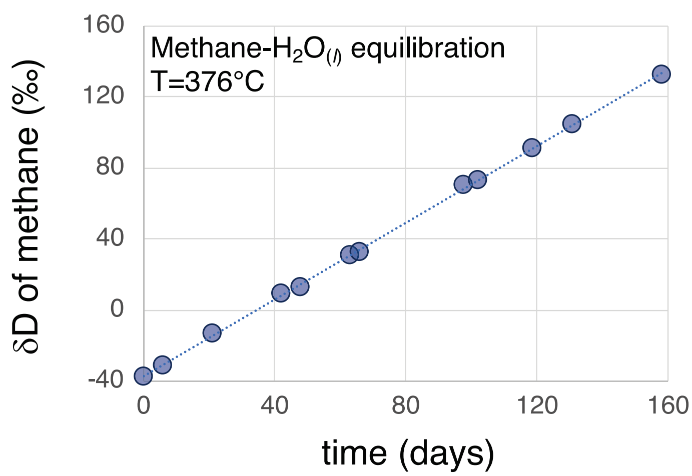

Figure 1: Experimental demonstration of hydrogen-isotope exchange between methane and water at 376°C.

(2) For the hydrous experiments, we designed, set-up and performed the first hydrogen isotope-exchange experiment. This was done in hydrothermal gold bag reactors. We additionally developed sampling protocols and measured the isotopic composition of methane over the course of an experiment. We present the data from a successful experiment in Figure 1 demonstrating a clear change in the δD of methane as a function of time. This is a promising result demonstrating our ability to do these experiments.

Next Steps: In the second year of the grant we plan to quantify bulk methane hydrogen isotope exchange rates in hydrous experiments at elevated temperatures compared to the experiment presented above. We will fit these data to models to extract activation energies and prefactors that describe the rate constant as a function of temperature. We will also sample these hydrous experiments not only for bulk hydrogen isotope-exchange rates, but also exchange rates of clumped isotopologues. In tandem, we will perform anhydrous experiments to examine clumped isotope exchange rates in the presence and absence of minerals.

Impact: By working on this project, graduate student Andrew Turner has learned laboratory skills including the measurement of δD values of hydrocarbons, the use of vacuum glass lines, the use of hydrothermal reactors. He has also learned computational skills including modeling of data calculation of isotopic fractionation factors based on theoretical considerations. These skills have provided Andrew fundamental training in core techniques for geochemistry that will provide a basis of skills for all future work in his PhD. This work has had a critical impact on my research by providing funding to perform these experiments and demonstrate that this approach is viable and yields useful results. Additionally, the first publication from my laboratory has been submitted based on support from this grant.

Publications: Eldridge DL, R Korol, MK Lloyd, AC Turner, MA Webb, TF Miller III, DA Stolper (in review). Comparison of Experimental vs. Theoretical Abundances of $^{13}CH_3D$ and $^{12}CH_2D_2$ for Isotopically Equilibrated Systems From 1-500°C. *ACS Earth and Space Chemistry*.