PRF# 56306-ND2
Project Title: Field study of the impact of burial diagenesis on stable isotopic and organic molecular records
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Organic molecular biomarkers are preserved in sedimentary systems over geologic timescales and provide a record of past environmental conditions, micro- and macroecological assemblages, and secondary processes that alter organic matter after deposition. As a result, these compounds offer a novel means of reconstructing past environments, hydrocarbon source or thermal history, and are increasingly utilized to understand terrestrial climatic and tectonic evolution. Despite the utility of molecular records of past systems, the effect of burial diagenesis on the isotopic composition of biomarkers is still poorly constrained. In particular, *how does the isotopic composition of different molecular classes change as a function of time, temperature and/or pressure? How does the presence of water or clay minerals affect isotopic alteration?*

Accurate application of stable isotopic organic molecular proxies requires an answer to three key questions: 1) how do molecular distributions or isotopic composition change during the process of diagenesis, 2) how does the isotopic composition of H or C of target molecules change as a result of isotopic exchange or generation of secondary products and 3) how does the presence of specific soil minerals catalyze isotopic or molecular alteration during this process?

Over the period of funding for this project, PI Hren and students conducted several sets of experiments to assess changes in the distributions of organic biomarkers and their stable isotopic composition. These experiments were conducted in the presence or absence of air, water and oxygen, under conditions associated with microbial degradation of compounds, and in the presence of different clay minerals. These experiments are designed to mimic a range of conditions found in nature and to quantify of the effect of cracking on stable isotope compositions and organic molecular distributions. There are several key results and products that have been generated from this work:

Products 1 and 2: Carbon and hydrogen isotope alteration of biomarkers during controlled heating.

We conducted controlled heating experiments of organic soil extracts to assess the alteration of C and H isotopes of normal alkanes during heating in the presence and absence of air and water. Results were published in Wang et al. (2017) and a second manuscript entitled "Stable carbon isotopes and reaction kinetics of *n*-alkanes during heating experiments in hydrous and anhydrous systems" has been submitted for review. Results show a clear shift in molecular distributions during the heating process associated with cracking of complex molecules, and clear isotopic fractionation associated with this cracking process (Figure 6 of Wang et al. 2017). However, results show that isotopic fractionation is clearly tied to cracking in the presence of oxygen, such that hydrogen isotopes change by up to 15‰ during the degradation process.

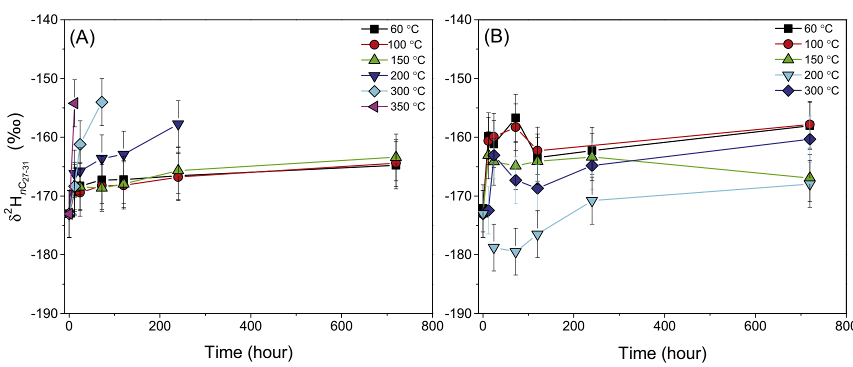

Figure 1. Hydrogen isotope alteration of long-carbon chain n-alkanes in open (a) and closed (b) systems during heating experiments. (From Wang et al., 2017)

Product 3: Microbial degradation of sedimentary biomarkers and isotope fractionation.

During the process of organic transport and sedimentary burial, microbes degrade and transform organic matter, changing both the distribution of compounds and isotopic compositions. Maturation experiments designed to assess the potential effect of microbial activity in sediments on the hydrogen and carbon isotope composition of *n*-alkanes were paired with DNA analyses of sediments to assess whether any changes in molecular distributions or isotopic composition were associated with changes in microbial communities. We show that storage of sediments can affect microbial activity, driving changes in molecular distributions and isotopic composition. (Brittingham et al., 2017).

Work in progress (Products 4 and 5):

As part of the funded ACS research, there are two manuscripts that will be submitted for publication in Winter 2019.

Product 4: Glycerol dialkyl glycerol tetraethers are a group of compounds produced by microorganisms in low oxygen environments. The distribution of these compounds is used to constrain past temperature in terrestrial or marine settings. Prior work on these compounds shows preservation of molecular distributions at temperatures of up to ~250°C. We conducted a series of heating experiments to assess how temperature affects GDGT distributions. Results show significant temperature effects on isoprenoidal GDGTs that are related to different reaction kinetics for molecular breakdown. Results will be submitted for publication in Winter 2019.

Product 5. Clay minerals provide a template for catalyzing cracking reactions of complex organic compounds in sedimentary environments. At present, it is unknown how clay-organic reactions affect the hydrogen and carbon isotopic composition of biomolecules. New heating experiments show distinct patterns of molecular degradation and molecular production due to thermal cracking and heating in the presence of different clay mineralogies. Results of this work have implications for understanding sedimentary biomarker isotope records as well as the role of clays in organic catalysis reactions. A manuscript draft is in preparation and will be submitted in Winter 2019.

Impact of Research and Funding on PI and Students

Organic biomarkers are a key tool for understanding the production and movement of hydrocarbons, interpreting paleoenvironments, and quantifying the links between paleoenvironmental conditions and carbon burial. Results from this funded work have provided key insight into factors that shape the isotopic compositions of biomarkers in sediments. This work has fundamentally shaped how the PI applies biomarker records for interpreting past environments. In addition, support for this project has been instrumental in the establishment and growth of the Stable Isotope and Organic Molecular Biogeochemistry Laboratory at the University of Connecticut and has resulted in the publication of two papers, one in submission and two in preparation, and six abstracts at international meetings. In addition, through direct and indirect support of graduate and undergraduate students, this award has affected the research and career trajectories of four graduate students and four undergraduate students.

One graduate student who worked on this project (C. Wang) has completed her PhD and is now employed as an isotope and organic geochemist. A second student (A. Brittingham) will graduate in 2019 and will continue as a Postdoctoral scientist working on related research. A third (J. Smolen) is a 3rd year PhD and is continuing dissertation research on clay-organic interactions that grew out of the work funded above.