“Collaborative Research: Kinetics and stable isotopic fractionation for abiotic and microbial transformations of elemental sulfur at seafloor hydrothermal environments”
PIs: David Fike (Wash U), Dionysis Foustoukos (Carnegie)
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Project Summary

Elemental sulfur (S^0) is a key intermediate species for biochemical sulfur cycling in chimney deposits, the shallow subsurface in diffuse flow areas, and hydrothermal plumes at mid-ocean ridges. Although the floc found in the water column after a volcanic eruption is predominantly S^0 and many microbial isolates from vents are found to utilize S^0, no significant reservoir of S^0 has been found in chimney deposits, suggesting high turnover rates of elemental sulfur in the subsurface. The kinetic rate constants for *abiotic* S^0 oxidation and reduction are unknown, even though they are critical for constraining the metastability, and thus bioavailability, of S^0 in the presence of H_2(aq) and O_2(aq) at temperatures and pH conditions relevant to hydrothermal mixing environments. Nor have the rate constants describing microbial transformations of S^0 been studied at environmentally relevant conditions. *As a result, there is a discrepancy between predictions based on energetics and the observed physiology of microorganisms that have been isolated and grown in laboratory conditions. Accurate and realistic biotic and abiotic kinetic rate constants are essential for modeling biogeochemical transformations involving intermediate sulfur species and active microbial consortia at the variable pH and redox conditions found in subsurface underlying basalt- and ultramafic-hosted hydrothermal systems*. Furthermore, the abiotic and particularly microbial sulfur isotopic fractionations associated with elemental sulfur oxidation and reduction at environmentally relevant conditions (rather than optimal growth conditions) have yet to be evaluated. By characterizing the geochemical and isotopic effect of S^0 oxidizing/reducing thermophilic autotrophs from vent systems, we can evaluate the impact of complex subsurface microbial ecological systems on associated plume environments contributing to the global ocean sulfur cycle. We propose here to evaluate the following:

- The competition between microbially mediated S^0 oxidation/reduction and abiotic losses of both electron donor (H_2) and acceptor (O_2) during S^0 reduction/oxidation under conditions of H_2-O_2-H_2O disequilibria in hydrothermal near-seafloor mixing environments.
- The effect of variable environmental conditions on $\delta^{34}S$ fractionation by S^0 oxidizing/reducing bacteria at conditions where reactants are limiting and growth conditions are non-optimal.

We propose to experimentally evaluate the kinetics of elemental sulfur abiotic oxidation/reduction at a range of T, pH and H_2(aq)-O_2(aq) concentrations relevant to the shallow subsurface of basalt and ultramafic hydrothermal systems: 250 bars, 40-120°C, pH 4-9, 0.1-20 mM H_2(aq) and 0-0.25 mM O_2(aq). Simultaneously, we will characterize the catabolic reaction rates of 3 key bacterial species that mediate elemental sulfur redox transformations, to determine if fractionation increases as environmental conditions begin to inhibit growth, as has been seen for SO_4 reducing bacteria.

Intellectual merit: The proposed evaluation of microbial and abiotic kinetics of redox reactions involving the key intermediate S^0 will provide the rate constants (abiotic and microbial) that are necessary for accurate geochemical kinetic models and facilitate the interpretation of biogeochemical processes in both basalt- and ultramafic-hosted hydrothermal systems. While the rate data can indicate the dominant sulfur speciation at relevant environmental conditions, the $\delta^{34}S$ fractionation during abiotic and microbial S^0 oxidation/reduction at hydrothermal conditions are critical for evaluating the relative contributions of S^0 reactions in the evolution and the habitability of deep-sea hydrothermal vent environments.

Broader impacts: The proposed project brings together experimental, microbial, and sulfur isotope expertise, establishes a new collaboration between the Geophysical Lab, CIW and the Dept. of Earth and Planetary Sciences, WU, and reintroduces a female scientist back into full-time research by facilitating a leading role in this project. Two distinct undergraduate research projects are supported crossing biology, geochemistry, and computer science. Furthermore, we will develop an online interactive simulation for secondary students that will allow students to use the real scientific data produced by this study in student-driven investigations trying to distinguish abiotic chemical processes from biological processes to facilitate learning the scientific method and basic concepts about Earth systems, chemical reactions, and isotopic fractionation. This educational outreach activity will also establish a working relationship with a secondary school teacher with experience adapting scientific data and methods for online learning.