Low temperature S biomineralization at a supraglacial spring system in the Canadian High Arctic

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Elemental sulfur (S^0) is deposited each summer onto the ice at Borup Fiord pass on Ellesmere Island in Canada, when high (millimolar) concentrations of aqueous H_2S are discharged from a supraglacial spring system. The resulting sulfur deposits host abundant microbial communities that have been phylogenetically characterized by 16s rRNA sequencing. The clone libraries are dominated by β-proteobacteria, particularly *Ralstonia sp.,* as well as several known sulfur-cycling microorganisms such as *Thiomicrospira sp,* and ε-proteobacteria such as *Sulfuricurvales sp.*, and *Sulfurovumales, sp.*. Cultivation experiments have also been conducted to isolate psychrophilic, chemolithoautotrophic sulfide oxidizing bacteria. Light, florescence and scanning electron microscopy of the mineral aggregates produced in laboratory cultivation experiments reveal abundant filaments and sheaths variably mineralized with extracellular sulfur as a function of time and environmental conditions. 16s rRNA analysis has been used to characterize the stable sulfur-biomineralizing consortia as well as isolates. We will also present a detailed characterization of the mineral products formed in laboratory biomineralization experiments, and relate our findings to potential biosignatures for microbial sulfur cycling in cold environments on Earth and other planetary systems.

Mechanistic organic geochemistry of carboxylic acids

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Organic compounds containing the carboxyl group are present in many hydrothermal systems. In an effort to better understand carboxylic acid reactivity, geochemists have performed experiments in aqueous solutions at high temperatures and pressures, and in the presence of minerals [1]. These experiments revealed that decarboxylation ($RCO_2H \rightarrow RH + CO_2$) is a major reaction pathway for carboxylic acids, and that minerals can have an unpredictable effect on the reactivity of carboxylic acids. Despite this progress, we currently lack a mechanistic framework that allows extrapolation of experimental snapshots to the vast range of organic structures and mineralogical environments that exist in natural systems.

This project seeks to elucidate mechanisms of decarboxylation in hydrothermal systems by applying tools of physical organic chemistry. We have performed gold capsule hydrothermal experiments using derivatives of phenylacetic acid (PAA) as mechanistic probes. By changing the identity or position of substituents attached to the ring of PAA, we gain information about mechanisms of decarboxylation through observations of both reaction rates and product distributions. This type of approach, while common in the field of organic chemistry, is rarely applied to geochemical problems.

Experiments with PAA in water at 300°C and 103 MPa in the absence of minerals gave toluene as the only detectable organic product, and an apparent first-order rate constant of $9.2\times10^{-6}\ s^{-1}$. Decarboxylation of PAA is dramatically faster in water than in the gas phase, where a bond homolysis mechanism has been proposed [2]. An anionic mechanism for decarboxylation of PAA in the absence of minerals is supported by preliminary studies of kinetics and products of a PAA substituted with a strong electron-withdrawing group. In the presence of hematite, however, products indicate additional pathways, including oxidative decarboxylation and radical coupling. Experiments with other minerals are in progress.

[1] McCollom & Seewald (2003) *GCA* **67**, 3645–3664.
[2] Back & Sehon (1960) *Can. J. Chem.* **38**, 1261–1270.