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Experimental study of abiotic formation of organic compounds in hydrothermal systems

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A large fraction of the microbial population that has so far been identified in submarine hydrothermal systems lives by heterotrophic metabolism, which raises the question of the source of the organic matter they consume as food. One possibility is that these organisms consume organic compounds which are synthesized abiotically within the hydrothermal system itself. Indeed, methane and other organic compounds with a possible abiotic origin have been identified in submarine hydrothermal environments. However, the ubiquitous presence of biologically-derived organic matter in these environments makes it difficult to know with certainty whether or not the organic compounds are actually the products of synthesis within the hydrothermal system.

Surprisingly little is known about chemical pathways for abiotic synthesis of organic compounds under the conditions that prevail in geologic environments. For instance, the most commonly cited pathway for the abiotic formation of organic compounds within hydrothermal systems is Fischer-Tropsch (FT) synthesis, which is a well-known industrial process for the surface-catalyzed conversion of gaseous CO to hydrocarbons. Yet, it has never been demonstrated that this process can proceed with a dissolved carbon source (as is often inferred for hydrothermal systems) or with the minerals found in subsurface hydrothermal environments (although magnetite is often cited as a FT catalyst, this mineral must first be treated to form native Fe or Fe-carbides on the surface to be catalytically active).

We will summarize our recent efforts to explore conditions that allow synthesis of organic compounds under hydrothermal conditions. In one series of experiments performed under strongly reducing conditions with a variety of different minerals present, we have not observed reduction of dissolved CO₂ to organic compounds more complex than methane, suggesting that synthesis of complex compounds may require a separate vapor phase. Current experiments are focusing on carbon isotope fractionation during FT synthesis. Initial results indicate that the volatile products exhibit an isotopic trend that is distinct from that produced by thermal decay of biologically-derived organic matter. On the other hand, more complex hydrocarbons exhibit C isotope fractionations of the same magnitude as those derived from biological processes, which may make it difficult to differentiate between abiotic and biotic sources for complex organic matter using carbon isotopes.

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Quenching, mixing, reaction progress, and the hydrothermal support of the biosphere

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The supply of chemical energy to the biosphere by hydrothermal fluids is a direct consequence of sluggish rates of uncatalyzed oxidation-reduction reactions at lower temperatures. The dominant life-supporting reactions are in the H-O-C-S-Fe-N chemical system. Owing to the compositional variations among and within hydrothermal systems, subsets of this chemical system may become predominant suppliers of biologically-useful energy. The energy supply at the lowermost fringe of the subsurface biosphere in a hydrothermal system may differ considerably from other locations within the biocap. In every case, the interplay among relative rates of abiotic oxidation-reduction reactions determines which reactions can be tapped by biotic energy-conserving catalysis. It follows that major controls on the potential community structure of microorganisms in hydrothermal ecosystems have geologic as well as geochemical origins.

Geologic structures, fluid flow paths, and differences in composition of host rocks each constrain the potential for quenching, mixing, and the extent of reaction progress in hydrothermal systems. Quenched fluids that do not mix with groundwater or surface waters are nevertheless capable of providing energy in reactions involving H₂ as a reactant, because equilibrium H₂ activities at higher temperatures and pressures nearly always exceed those at lower temperatures and pressures. Greater amounts of energy often accompany mixing of quenched fluids with groundwaters, seawater, and surface waters, or during contact with the atmosphere. The presence of O₂ in these mixed systems can permit a greater variety of energy-yielding reactions than systems without mixing.

Insights gained from fieldwork, laboratory analyses, and thermodynamic modeling of hydrothermal ecosystems at Yellowstone provide clues about how the energy supply that influences microbial community structure depends on underlying geologic controls. The ranking of oxidation-reduction reactions as suppliers of energy is strongly affected by compositional changes, most easily generalized by pH variations. This means that differences in energy supply reflect complex variations in the composition of host igneous rocks, the proximity of ancient sediments, the flux of magmatic gases, the extent of silicification, and the gradients of mixing between deep hydrothermal fluids and near-surface groundwaters. This suggests that changes in microbial community structure can be predicted through an analysis of the extent of reaction progress among and within hydrothermal systems.