

**DESIGNING FAR-FROM-EQUILIBRIUM EXPERIMENTS FOR ORIGIN OF LIFE AND PLANETARY HABITABILITY.** L. M. Barge<sup>1</sup>, M. J. Russell<sup>1</sup>, P. Sobron<sup>2</sup>, M. M. Baum<sup>3</sup>, I. Kanik<sup>1</sup>, <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA, laura.m.barge@jpl.nasa.gov), <sup>2</sup>SETI Institute (189 Bernardo Ave, Mountain View, CA), <sup>3</sup>Oak Crest Institute of Science (2275 East Foothill Boulevard, Pasadena, CA).

**Introduction:** One of the most important considerations for understanding origin of life and planetary habitability is to investigate environments that could provide geochemical free energy for life and develop reliable methods for characterizing these environments *in situ*. A ubiquitous properties of life on Earth, and perhaps of any life elsewhere, is that it utilizes geochemical and electrochemical disequilibria and converts such free energies. Planetary water-rock interfaces generate energy in the form of redox, pH, and thermal gradients, and these disequilibria are particularly focused in hydrothermal vent systems where the reducing, heated hydrothermal fluid feeds back into the more oxidizing ocean. The energetic environment of a hydrothermal chimney is an ideal habitat for chemosynthetic life, and alkaline hydrothermal vents have been proposed as a possible location for the origin of life on the early Earth due to various factors including the ambient hydrothermal pH /  $E_h$  gradients that resemble the ubiquitous electrical / proton gradients in biology, the catalytic hydrothermal precipitates that resemble inorganic catalysts in enzymes, and the presence of electron donors and acceptors in hydrothermal systems (e.g.  $H_2 + CH_4$  and  $CO_2$ ) that are thought to have been utilized in the earliest metabolisms [1-3]. Minerals that precipitate at alkaline hydrothermal vents can serve various functions for life, including: concentrating the organics, phosphates and other biologically relevant components emanating from the subsurface, and potentially driving formation of peptides, oligomers, and evolution of RNA; abiotically catalyzing redox chemistry and even reducing  $CO_2$  and oxidizing  $CH_4$  to generate organic carbon [4-7]; and redox-sensitive minerals could serve as electron donors / acceptors for microbes that can transfer electrons directly to/from minerals via extracellular electron transfer [8,9] – thus perhaps linking spatially separate redox reactions to support a biosphere in a relatively low energy environment. Many of the factors prompting interest in alkaline hydrothermal vents on Earth may also have been present on early Mars, or even presently within icy worlds such as Europa or Enceladus.

The potential energies between available electron donors and acceptors at vents or water/rock interfaces determines the metabolisms that could exist in that system, and hydrothermal chemistry produces various catalytic minerals that can affect and effect prebiotic reactions and habitability. Whether particular geo-

chemical gradients in active hydrothermal systems on the early Earth (or on other worlds) were capable of providing sufficient free energy to drive the emergence of life, can, for the most part, be simulated experimentally. Testing habitability and origin-of-life hypotheses regarding far-from-equilibrium geochemical and biochemical systems requires new types of experimental design, utilizing methods from electrochemistry, materials science, microfluidics, and rapid *in situ* analysis techniques.

**Experimental considerations:** Some important processes that we can test in the laboratory include:

- 1) Simulate the interface between various ocean compositions and the hydrothermal fluids produced by serpentinization; measure the electronic / protonic gradients that would be generated at particular water-rock interfaces on specific worlds using flow-through reactors [10, 11];
- 2) Test the catalytic and disequilibria converting abilities of common hydrothermal minerals (e.g. trace-metal doped iron sulfides / oxyhydroxides) particularly with regards to electron transfer and redox chemistry; use real-time *in situ* analytical methods such as electrochemical and spectroscopic analysis to observe reactions and mineral oxidation state;
- 3) Test how mineral-catalyzed phosphorus and organic reactions are affected by geochemical  $E_h$ /pH gradients, employing modern fuel cell technologies to experimentally couple specific gradients to specific reactions, in order to test possible mechanisms by which emerging life could harness these gradients [12, 13].

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