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Effects of pH and Redox Gradients on Prebiotic Organic Synthesis and the Generation of Free Energy in Simulated Hydrothermal Systems

L. M. Barge¹, E. Flores¹, Y. Abedian¹, T. Maltais¹, R. Cameron¹, N. Hermis¹, K. Chin¹, M. J. Russell¹, M. M. Baum²

¹NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109, ²Oak Crest Institute of Science, 132 W Chestnut Ave, Monrovia, CA 91016

* laura.m.barge@jpl.nasa.gov

Planetary water-rock interfaces generate free energy in the form of redox, pH, and thermal gradients. These disequilibria are particularly focused in hydrothermal systems where reducing, heated vent fluid feeds back into the more oxidizing ocean. The sediments and chimneys precipitated in alkaline hydrothermal vents on the early Earth would have contained reactive iron minerals such as iron (-nickel) sulfides and iron oxyhydroxides (including green rust). These minerals could have promoted carbon fixation and amino acid synthesis, as well as further organic synthesis, and concentrated the products, along with phosphate species, through ad- and absorption. We have developed methods for investigating the effects of geochemical gradients on important prebiotic reactions in these systems, including the formation of simulated hydrothermal precipitates in a gradient (mimicking the electronic / protonic gradients that would be generated across hydrothermal chimney walls) [1]. We have also been able to synthesize hydrothermal minerals over a range of pH / redox states particular to the reactive sedimentary pile at a submarine alkaline vent. It has been shown that simulated hydrothermal minerals can reduce carbon dioxide [2-4] and we observed that the presence of pyruvate in iron-nickel sulfide precipitates increases the electrochemical activity of the chimney/ocean chemical system. These results carry the implication that the generation of organic precursors in hydrothermal sediments and chimneys could be the result of ever increasing mineral-organic feedbacks [5]. We also observed that gradients of pH and redox state affect the synthesis of amino acids from pyruvate [6]; in particular, the oxidation state of the iron minerals affects the yield of amino acid produced. Amino acids may concentrate further on, and within, charged mineral surfaces and be condensed to peptide nests harboring sulfide clusters and phosphate [5,7]. Phosphorus is also readily concentrated into reactive iron hydroxide minerals [8]. However, the suite of amino acids that may be found in a particular mineral system is a combination of what is synthesized there, what is preferentially concentrated / retained there, and what is preserved against degradation. In this way the chemistry of peptides formed in hydrothermal systems would depend on the ad- and absorptive capacity of the ambient minerals. We observed that at alkaline pH (~9) the presence of amino acids affects the absorption of phosphate and phosphite into iron hydroxide minerals. Further work is needed to determine how this depends on pH and redox gradients as well as the forced diffusion of products to a site of contrasting disequilibria. Many of the factors prompting interest in alkaline hydrothermal vents on Earth may also have been present on early Mars, and presently within icy worlds such as Europa or Enceladus. Thus, an understanding of the disequilibria that may have driven prebiotic chemistry in these systems can be put to use in assessing the habitability of other bodies in the Solar System and, eventually, the growing number of promising extra-solar planets.

References: [1] Barge LM et al. (2015) *Journal of Visualized Experiments* DOI:10.3791/53015 [2] Cody GD et al. (2000) *Science* 289, 5483:1337-1340 [3] Yamaguchi A. et. al. (2014) *Electrochim. Acta* 141, 311-318. [4] Roland A et. al. (2015) *Chem. Comm.* 51, 7501-7504. [5] Russell MJ et al. (2014) *Astrobiology* 14, 308-43. [6] Novikov Y and Copley SD (2013) *PNAS* 110, 33:13283-13288. [7] Milner-White J and Russell MJ (2005) *OLEB* 35:19-27. [8] Barthélémy K et al. (2004) *J. Colloid Interface Sci.* 384:121-127.