ELECTROCHEMICAL AND RAPID PROTOTYPING STRATEGIES FOR MORE PRECISE ANALYSIS OF GEO-ELECTROCHEMCIAL ENVIRONMENTS OF INTEREST TO ASTROBIOLOGY.

G. LeBlanc[1], D. M. Wirth,[1] H. D. Whitehead,[1] J. Yungbluth,[1] G. Ludewick,[1] L. M. Barge[2,3] and R. Cameron[2,3], [1]The University of Tulsa (800 S Tucker Drive, Tulsa, OK, gabriel-leblanc@utulsa.edu); [2]NASA Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA); [3]NASA Astrobiology Institute Icy Worlds team.

Introduction: The harnessing of geochemical energy by life is one of the most remarkable processes to have occurred on Earth, and laboratory simulations into these processes can yield insights into life's capabilities, diversity, and even its origin. The field of Astrobiology studies life's origin and mechanisms for survival in extreme environments, which is relevant to the search for life elsewhere. One particularly interesting geological environment for habitability and prebiotic chemistry is hydrothermal vents and chimneys. These hydrothermal chimneys represent "far-from-equilibrium" natural systems that have been shown to generate electrochemical energy [1] which life can harness directly from conductive mineral surfaces [2] and which may also have driven organic synthesis at the emergence of life [3]. Natural systems, however, are inherently stochastic and therefore present challenges for systematic analysis to understand the principles that govern them. Previous studies have taken advantage of more traditional electrochemical techniques, such as fuel cell analysis or three-electrode cells, to study prebiotic disequilibrium [1,3,4]. Here we present preliminary results using direct electrochemical deposition and detection methods, as well as new strategies using 3D printing, to enable more systematic analysis of hydrothermal far-from-equilibrium systems.

Electrochemical Deposition of Simulated Early Earth Minerals on the Suface of Electrodes: In order to mimic hydrothermal vents, studies have been performed that mimic the natural alkaline hydrothermal seepage process to form unique "chemical garden" mineral deposits at the interface of alkaline and acidic solutions [1,5]. Early electrochemical experiments, however, have demonstrated how the electrolysis of water can be used to dramatically change the pH of the environment at or near the electrode surface. This process leads to the deposition of pH-sensitive materials directly on the surface of an electrode without changing the properties of the bulk solutions. This strategy has previously been used for the deposition of metal oxides on electrode surfaces for different applications [6]. Here we have used this method to deposit minerals of interest, such as iron sulfides and iron hydroxides – both minerals of interest for early Earth vent systems [7] - onto the surface of electrodes. This electrodeposition technique can be adjusted to tune the roughness and thickness of the resulting mineral deposit. Because we are collecting data about the deposition while the deposition is being performed, we can analyze what parameters have the greatest influence over the deposition process. Furthermore, by using the electrode to generate the precipitate, direct electrode connection provides a simple means for subsequent analysis in different environments or by different techniques.

Electrochemical Evaluation of Products Generated by Minerals on Electrode Surfaces: The electrochemical gradient produced by hydrothermal vents have previously been evaluated for their potential in producing organic products relevant for early life [1,7]. Of particular interest is the formation of formate, formaldehyde, methanol, and methane, which have been produced as products of carbon dioxide reduction on particular iron sulfide minerals [3-4]. By coating electrode materials with these mineral systems, either by direct electrochemical processes or indirect coating methods, we can apply electrochemical overpotentials to evaluate the conditions necessary to perform reactions of interest. Furthermore, by using the inherent redox-active nature of these products we can utilize a second electrode to locally probe these systems.

Implications and Advancement for Origins of Life Research: The recent rise in rapid prototyping techniques have enable a variety of new experimental concepts in a wide range of disaplines. Here we have used 3D printing to develop a variety of experimental configurations to more systematically study simulated hydrothermal vents. These computer aided designs (CAD) can be easily changed or modified for the unique electrochemical environments to be studied. Additionally we have evaluated a wide range of materials for their suitability under different ocean (solvent) systems or as frameworks to generate more predictable chimney mimics. The digital nature of these designs allows us to share these strategies across the globe for other researchers to use for their own unique systems.

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