

ELECTROCHEMICAL DEPOSITION OF IRON SULFIDES AND IRON HYDROXIDES: MIMICKING HYDROTHERMAL VENT SYSTEMS RELEVANT TO ORIGIN OF LIFE STUDIES. D. M. Wirth¹, G. LeBlanc¹, H. D. Whitehead¹, J. Yungbluth¹, G. Ludewick¹, L. M. Barge^{2,3}, and R. D. Cameron^{2,3}, ¹The University of Tulsa (800 S Tucker Drive, Tulsa, OK, gabriel-leblanc@utulsa.edu), ²NASA Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA), ³NASA Astrobiology Institute Icy Worlds team.

Introduction: Chemical garden systems, including hydrothermal vent chimneys, have been proposed as a possible system leading to the formation of life [1]. Hydrothermal vents are composed of semi-permeable inorganic membranes, formed from the interaction of solutions of contrasting pH and ionic composition. For laboratory studies, these systems are generally formed by one of two methods: a solid “seed” containing a metal cation is dissolved in a solution containing an anion, or through an injection method in which a basic solution containing the metal cation is injected into an acidic solution containing the anion [2]. It has been demonstrated that these mineral membranes maintain chemical and electrochemical gradients enabling the energy necessary to fuel organic synthesis, and thus various biochemical reactions involved in metabolism and the emergence of life [3-4]. To better characterize these mineral membranes, we present new methods for interfacing these systems with electrodes in order to evaluate their electrochemical properties.

Electrochemical Deposition of Simulated Hydrothermal Minerals: As an alternative method of mimicking these hydrothermal vent systems, an electrode can be used to split water to create local acidic and basic environments. This allows the mineral deposit to form directly on the electrode surface instead of using separate acidic and basic solutions [4]. Rather than attaching electrodes to the mineral, risking damaging the structure or forming weak connections, voltage and current information can easily be obtained. Additionally, since data is being collected during the deposition process, more information can be obtained regarding the electrochemical behavior of the mineral membrane during its actual formation. The electrodeposition of the iron sulfide and iron hydroxide minerals can be accomplished through constant potential or cyclic voltammetry experiments using various electrolyte solutions containing the needed reactants, as well as numerous different electrode materials. Due to the robust connection between the mineral and the electrode, the mineral modified electrodes can be subsequently analyzed using a variety of additional ex-situ techniques.

Pulsed Electrochemical Deposition of Natural Minerals: During the electrodeposition process described above, where a potential is continuously being applied, hydrogen molecules are formed. Numerous hydrogen gas molecules can clump together, forming a bubble that blocks the electrode and prevents mineral

formation in those regions, as can be seen in **Figure 1**. To prevent this, a pulsed electrodeposition method can be used to prevent the agglomeration of H₂ molecules [5]. This unique strategy therefore allows for dramatic pH changes at the electrode surface while allowing H₂ molecules to diffuse away before they interfere with the deposition process.

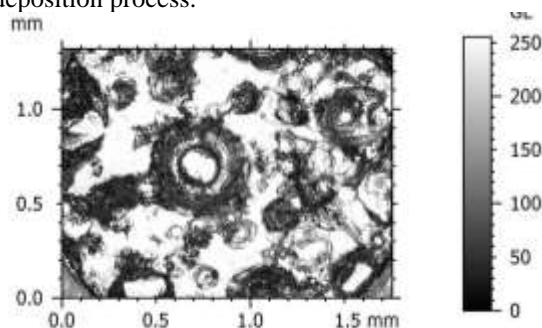


Figure 1. Optical profilometry image of an iron hydroxide deposit on the surface of an electrode.

Evaluation of Mineral Byproducts Using a Secondary Sensing Electrode: Since it is hypothesized that the energy from hydrothermal vents may have driven organic synthesis, the presence of by-products such as formate, methane, methanol, and formaldehyde are of great interest. To evaluate any products that may be formed following the electrodeposition of iron sulfides and iron hydroxides, a secondary sensing electrode can be used. Essentially, the second electrode will be placed close to the area of mineral formation on the first electrode and used to detect electrochemically active products arising from the mineral modified electrode. This provides the opportunity to explore regional differences in the electrochemical activity, providing new insights into the structure-function role of these mineral systems.

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