SIMULATING ELECTROCHEMISTRY OF IRON-NICKEL SULFIDE HYDROTHERMAL CHIMNEYS.

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Introduction: Serpentinization, a water-rock interactive chemical process was responsible for creating mild-temperature, alkaline vents on the early Earth. It is possible that this type of vent could also exist on other ocean worlds, like Europa and Enceladus, which have water-rock interfaces. It has been proposed that some prebiotic chemistry responsible for the emergence of life on Earth and possibly other wet and icy worlds could occur as a result of redox potential and pH gradients in submarine alkaline hydrothermal vents [1]. Hydrothermal chimneys formed in laboratory simulations of alkaline vents under early Earth conditions precipitate membranes that contain minerals such as iron sulfides [2]. These minerals are hypothesized to catalyze reduction of CO_2 [3,4] which may be affected by other trace components in the chimney, e.g. nickel or organic molecules [3]. We have conducted electrochemical laboratory experiments to investigate catalytic properties in simulated chimneys made from iron and iron-nickel sulfides, containing organic dopants, and in slightly acidic ocean simulants relevant to early Earth.

Materials/Methods: Electrodes for the chimneys were fabricated using carbon felt, copper tinned wire, and graphite epoxy. The electrodes were then placed inside an anoxic chimney vessel with one working electrode and one reference electrode (Fig. 1). The chimney experiment was performed under an argon gas headspace, and argon-purged H_2O was used to make solutions to best approximate the oxygen-free early Earth conditions. An early Earth ocean simulant solution containing dissolved Fe^{2+}, bicarbonate (to represent dissolved atmospheric CO_2), and Ni^{2+} was added to the vessel, and was titrated to pH 5.5 – 6.5. A hydrothermal fluid simulant solution, which consisted of dissolved sulfide and optionally doped with small amounts of organics, was then slowly injected into the vessel to represent slow seepage of hydrothermal vent fluid into seawater. Chimney structures precipitated at the interface, containing metal sulfide minerals. A potential was applied to the chimney by the working electrode, in order to simulate the electron donor function that H_2 gas would have provided in prebiotic alkaline hydrothermal systems [1]. After the chimney structure visibly enveloped the working electrode, a small AC voltage amplitude of 10-100 mV was applied to the system and the reponse was measured using electrochemical impedence spectroscopy.

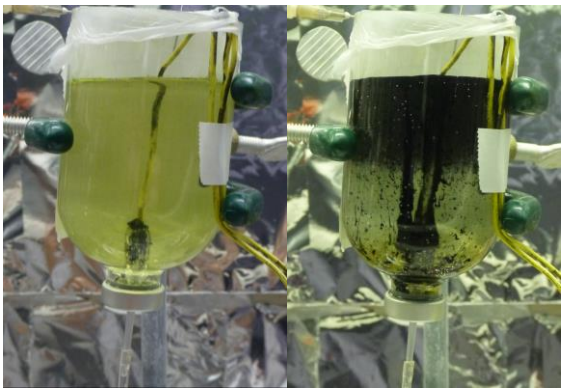

Figure 1: L: Chimney vessel with electrodes and early Earth ocean simulant. R: Hydrothermal simulant solution was injected and precipitated into a chimney that grew around working electrode.

Results/Discussion: Electrochemical properties were analyzed using electrochemical impedance spectroscopy, which allowed us to view bulk and interfacial catalytic properties of the chimney. Our simulated Fe/Ni-sulfide chimneys were observed to be electrochemically active, since they were capable of continually separating two constrasting solutions of different pH and electrical potential [2]. Simple organic acids appear to enhance the electrochemical activity (admittance) of the chimneys, while other other types of organics have little to no effect. Iron-nickel sulfides are known to be catalytic for CO_2 reduction [3,4] and are thought to have played a role in the emergence of metabolism; organic-mineral feedbacks may increase the catalytic activity of Fe/Ni-sulfide chimneys for redox reactions in prebiotic vent systems [1]. Our results imply that redox reactions driven by geochemical potentials in chimney systems may be greatly affected by 1) the mineral composition and phase that precipitates and 2) the amount and type of organics that might be present. Future work will determine the electroactive behavior of various organic/mineral composites within simulated vent chimneys.

References: [1] Russell M. J. et al. (2014) *Astrobiology* 14:308-43. [2] Barge, L. M., et al. (2015) *Angew. Chem. Int. Ed.*, 54, 8184–8187. [3] Yamaguchi A. et. al. (2014) *Electrochimica Acta* 141, 311-318. [4] Roldan A., et. al. (2015) *Chemical Communications* 51, 7501-7504.