INVESTIGATING THE ROLE OF IRON SULFIDES IN THE HYDROTHERMAL VENT MODEL FOR THE EMERGENCE OF LIFE. L. M. White[1,2], R. E. Mielke[1,2], M. J. Russell[2], G. D. Stucky[1], I. Kanik[2]
[1]Department of Chemistry & Biochemistry, University of California at Santa Barbara, Santa Barbara, CA. 93106,USA [2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA. 91109,USA

Introduction: Scientists have postulated since the discovery of hydrothermal vents known as "black smokers" that these ocean floor structures may be important for the emergence of early life on Earth. However, sulfur-rich vent fluids from black smokers exhibit temperatures upwards of 400°C and are driven by energy derived from magmatic processes [1-2]. Therefore, it is difficult to remedy the unstable conditions of a black smoker system with the ability to concentrate organics to form life. For this reason, Russell et al. [3-5] proposed the early earth could produce a more stable, low temperature alkaline vent with conditions allowing the concentration of organic molecules. Such a vent was later discovered by Kelley et al. near Lost City [1]. Known as off-axis alkaline vents, these structures vent fluids below 100°C rich in methane along with minor formate and are driven by chemical energy derived from serpentinization as well of that residing in the Earth's crust. Now recognized as the "alkaline hydrothermal model" for the emergence of life [6], this model offers lower temperatures and porous chimney structures composed of iron-nickel sulfides set in silica gel and clays capable of promoting and concentrating amino acids and peptides [7-8].

Christensen et al. (in prep) show that a Hadean Ocean, rich in dissolved CO_2 from an early Earth atmosphere, can readily be reduced by the supply of hydrogen from serpentinization of earth's crust to produce hydrocarbons such as methane [9]. Based on the effluent of these experiments, Mielke et al. [10] proposed a chimney structure in a Hadean ocean would be rich in iron-nickel sulfides capable of catalyzing the formation of formate, acetate and methane from the vent fluid and a CO_2-rich ocean. In an ancient oxygen free ocean, nickel and ferrous iron and would be readily available for precipitation with sulfur venting from the crust and forming iron-sulfide alkaline chimneys different from today's calcite and brucite-rich alkaline vents. Rickard et al. [7] show that mackinawite [(Fe>>Ni)S] adsorbs formaldehyde, thus favoring the formation of greigite over pyrite, significant because of the structural similarities between thecrystal lattices of mackinawite and griegite to enzymes including ferredoxin and co-enzyme A synthase. Because ferredoxin appears to be the enzyme with the longest pedigree [7-8] we envision life may have derived such enzymes from precursor inorganic chemcals precpitated at alkaline hydrothermal vents. Thus, we hypothesize early off-axis chimneys were likely composed predominantly of mackinawite and griegite which could catalyse the formation of, and concentrate, organic molecules. Here we describe the results of the fabrication and analysis of iron sulfide precipitated chimney-like structures under anoxic hydrothermal conditions as a step toward understanding the structure and surface chemistry bringing about the emergence of life on any wet, rocky planet.

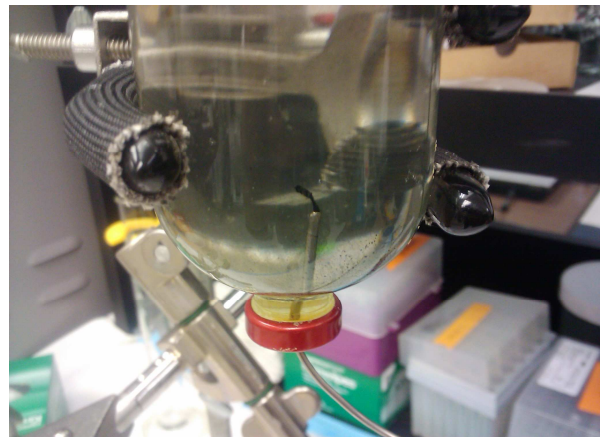

Figure 1: Example of Fe/S chimney grown from simulated hydrothermal vent fluid flowing into an acidic salt solution indicative of an early Earth ocean.

Methods. To simulate alkaline (hydrothermal) seepages, we inject aqueous alkaline salt solutions at both 25°C and 70°C containing sulfide and silicate into acidic ocean-like iron(II) salt solutions by way of motorized pipettes at rate of ~0.2ml/hour (Fig. 1). Reactant concentrations were derived from previously reported hydrothermal reactor experiments where the serpentinization process is simulated to obtain "initial conditions" similar to fluid venting from a Hadean crust [10]. All solutions were continuously purged with N_2 (g) to ensure the anoxic conditions in the carbonic Hadean Ocean. The pH of the receptacle (acidic ocean) solution was obtained both before and after injection in order to derive, via arithmetic reckoning, a potential energy across the chimney membrane. Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive X-Ray Spectroscopy (EDX) were used to observe the structure and elemental composition of precipitated chimney structures. Fe/S mineral phases in

the resulting precipitates were obtained by Raman Spectroscopy.

Results:

Room Temperature Experiments. Upon injection of the model hydrothermal solution into the acidic ocean solution, a smooth and homogeneous chimney begins to form almost immediately. After a period of 20-25 hours, these chimneys develop a cap, indicating the surface areas of the membranes are extensive enough for diffusion through the walls. ESEM analysis shows the resulting precipitates are hollow, chimney-like structures ranging from 1-2mm in length. Nanoclusters lining the chimney interior appear similar to framboidal structures typical of greigite or pyrite mineralization. EDX spectroscopy indicates an iron/sulfide-rich composition over the entire precipitate. In some cases, calculated Fe/S ratios exhibit nearly a 1:1 relationship indicative of a mackinawite-like composition. Nanometric hollow spheres (Fig. 2) were also observed in chimneys by ESEM of a comparable size to large living cells (~30μm – 1mm).

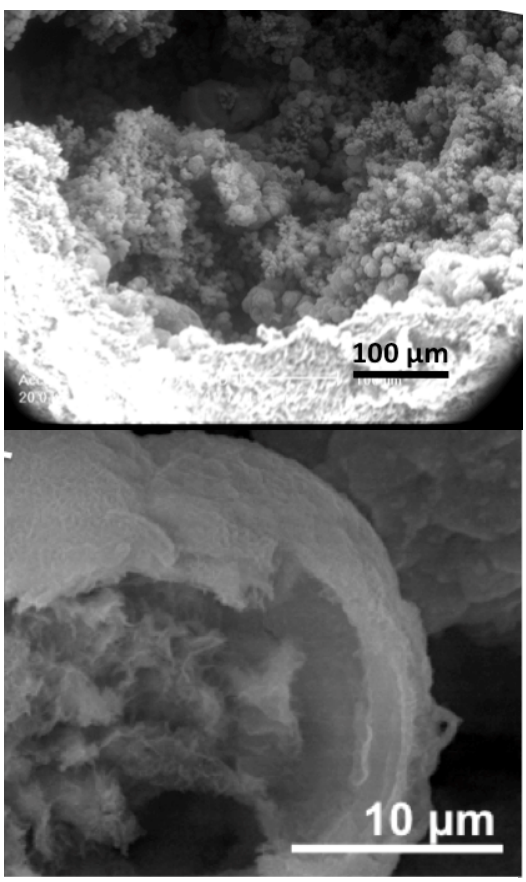

Figure 2: ESEM images showing porous structure of precipitate Fe/S chimneys with pore diameters similar to cell-like structures.

Hydrothermal Temperature Experiments. Experiments were repeated at temperature typical of off-axis hydrothermal vents (~70°C) though at otherwise similar conditions. Just as in the case of the room temperature experiments, a smooth and homogenous chimney begins to form almost immediately upon injection, with capping occurring after 20-24 hours. High relative abundances of sulfide over iron were observed along chimney membranes by EDS with ratios close to a griegite-like Fe/S phase, i.e., 3:4.

Conclusions: According to the alkaline hydrothermal hypothesis, iron-nickel sulfides may have been the inorganic precursors to catalysts or protoenzymes essential to the emergence of life. Fe/S nanoclusts are shown to precipitate readily in the formation of chimney-like structures under simulated Hadean Ocean conditions. Fe:S ratios from precipitate chimneys indicate a mackinawite and/or griegite phase under stable, low-temperature (25° or 70°C) conditions. Such mineral phases are known to promote the formation of organic compounds and may be the key to understanding the formation of early life on earth.

Previous studies indicate hydrothermal vent fluids are capable of reducing carbon dioxide to methane by way of serpentinization of Earth's crust in a pathway comparable, if much more sluggish, to the operations of the methanoarchaea. Thus, understanding the surface inorganic chemistry of alkaline chimney structures that may have catalyzed the prebiotic components of life may be relevant not only to the emergence of life on Earth, but on any wet, rocky planet of sufficient mass to retain a carbon dioxide/nitrogen atmosphere.

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