Mineralogy, Morphology, and Organic Modifications of Iron-Based Hydrothermal Chimney Simulants. Arden C. Hammer[1,2], Brian C. Corbit[2,3], Ivria J. Doloboff[2,4], and Laura M. Barge[2,4], [1]Department of Chemistry and Biochemistry, Oberlin College, Oberlin, Ohio 44074, United States; [2]NASA Astrobiology Institute, Icy Worlds Team; [3]Tulsa Community College, Tulsa, Oklahoma 74115, United States; [4]NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, United States.

Background: Practically all known extant life powers organic synthesis by maintaining electrochemical gradients across membranes [1]. Some researchers suggest that the bioenergetic systems fundamental to life arose from analogous far-from-equilibrium geochemical conditions [1-3]. One geological system operating far from equilibrium that has been proposed as a possible environment for origin of life is off-axis alkaline hydrothermal vents or seepages [3]. At these sites, serpentinization of ultramafic crust at moderate temperatures produces an alkaline, reducing fluid which feeds into the ocean. Where this vent fluid interfaces with the ocean, the dissolved anions react with cations from the seawater, producing porous, inorganic, tubular precipitates called hydrothermal chimneys [3]. Catalytic mineral phases within a chimney may couple dissipation of the electrochemical gradient between the seawater and vent fluid to organic synthesis, paving the way for the emergence of metabolism [4]. Here, we simulate an iron-rich hydrothermal chimney, reminiscent of those which may have existed on the early Earth, and which may also have existed on Mars, or on the icy moons of Jupiter and Saturn [5].

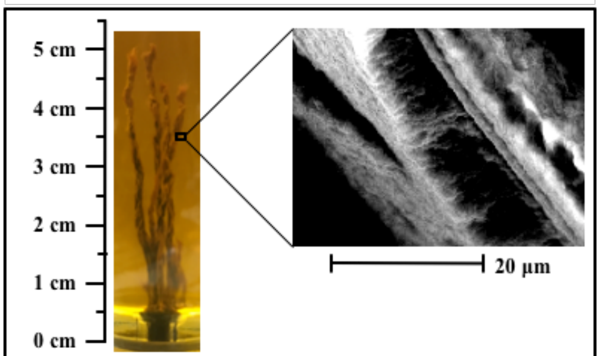

Figure 1: Simulated hydrothermal chimney.

Methods and Results: We simulated a hydrothermal chimney by anaerobically injecting aqueous sodium hydroxide into a reservoir of aqueous ferrous and ferric chloride. A "chemical garden" precipitate structure formed as the injection proceeded. ESEM and Laser Raman Spectroscopy showed that our growing chimney simulants formed hollow, porous stalks composed of magnetite and iron oxyhydroxides. The walls of each stalk consisted of concentric layers, each layer displaying a rugged, crystalline outer surface and a smooth, rounded inner surface (Fig. 1). The walls of each stalk also displayed concentric mineralogical zoning – akaganéite near the outer surface of the stalk, lepidocrocite in the middle of the wall, and goethite near the interior – perhaps owing to the chloride gradient between the reservoir and injection solutions [6].

When pyruvate or cysteine was also present in the injection solution, the resulting chimneys had weakened walls lacking visible crystalline morphology. When alanine was present in the injection solution, the resulting chimneys had walls containing new morphologies including rounded disks and crossed spines. This suggests that small functionalized organic compounds may interact with inorganic motifs in a chimney and become embedded within the chimney's walls.

Impact: Our results show that iron-based hydrothermal chimneys may have compositional gradients reflective of the chemical conditions in which they formed [5]. The mineralogical diversity associated with these gradients is beneficial in an origins of life scenario because different mineral phases may be best suited to catalyze different reactions within a larger metabolic pathway. In the search for life, compositional gradients like those we show in our experiments may indicate the presence of far-from-equilibrium, potentially biogenic systems. Our results also show that small organic compounds may modify hydrothermal chimneys. This is significant for origins of life research because it supports the theory of ligand accelerated autocatalysis; that is, that while hydrothermal chimneys unmodified by organics are not potent enough catalysts to promote the synthesis of large polymers characteristic of extant life, monomers and smaller polymers synthesized in a hydrothermal chimney may interact with mineral fragments from the chimney and increase their catalytic efficiency, opening the possibility for further polymerization [7]. Future work will examine the effects of short peptides in the walls of the chimney.

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