ALKALINE HYDROTHERMAL VENTS: ASSEMBLING THE REDOX PROTEIN CONSTRUCTION KIT ON ICY WORLDS. Lauren M. White[1], Michael J. Russell[2], Randall E. Mielke[1,2], Takazo Shibuya[3], Lance Christensen[2], Rohit Bhartia[2], Morgan L. Cable[4], Amanda Stockton[4], Galen D. Stucky[1,5] , Isik Kanik[2]

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Introduction: For life to emerge on a terraqueous world there must be a medium across which electrochemical gradients are put to work to drive CO_2 reduction over the initially unfavorable thermodynamic steps. One theory for the emergence of life hypothesizes that iron-sulfide bearing compartments of off-axis submarine alkaline hydrothermal vents could provide the appropriate catalytic environment to synthesize the organic building blocks of proto-enzymes—the first step to the emergence of metabolism [1]. Russell et al. propose that the carbon dioxide dissolved in an early ocean from an atmosphere rich in CO_2 can be readily reduced by the supply of hydrogen from serpentinization of a wet rocky planet's crust to form methane [1]. Experiments by McCollum and Seewald (2003) to simulate such conditions show hydrothermal CO_2 reduction can lead to the production of formate [2]. Furthermore, Mielke et al. (2010) proposed a chimney structure in a Hadean ocean that would be rich in iron-nickel sulfides capable of catalyzing the formation of formate, formaldehyde, and methane from the vent fluid and a CO_2-rich ocean [3]. In an ancient oxygen free ocean, Fe^{2+} and Ni^{2+} would be readily available for precipitation with venting alkaline fluids from the crust forming Fe(Ni)S-bearing chimneys that contrast with today's calcite and brucite-rich Lost City vents [4-6]. Specifically, iron-sulfide minerals such as mackinawite [FeS] and greigite [$(Fe{>>}Ni)_3S_4$] could catalyze CO_2 reduction and assemble activated acetate from CO and CH_3SH [7]. Since the lattice structures of mackinawite and greigite have affinities with the activation centers of metalloenzymes, including ferredoxin, carbon monoxide dehydrogenase (CODH) and acetyl coenzyme-A synthase (ACS) found in archaea and bacteria, their presence in a hydrothermal vent would also enable their sequestration by peptides generated in the hydrothermal mound [8] We conduct iron-sulfide precipitation experiments to recreate the proposed early conditions at an off-axis spreading center in order to identify and quantify Fe-S phases which are most abundant at a range of hydrothermal temperatures (40-80°C). We also conduct experiments using an in-house built hydrothermal reactor to attempt CO_2 reduction to CH_4 and longer chain organic molecules at hydrothermal pressures (100 bar), temperatures (≤100 °C) and atmosphere (anoxic).

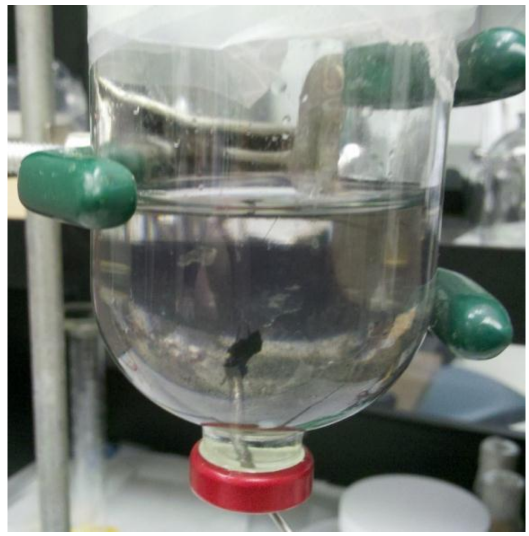

Figure 1: An example of precipitated single-tube FeS chimneys fabricated under Hadean conditions.

Precipitated Iron-Sulfide Chimneys. Iron sulfide chimneys are precipitated as an alkaline (pH=11.0) hydrothermal salt solution containing sulfide and silicate is introduced into a stimulant of a salty acidic (pH=5.0) carbonic ocean containing dissolved ferrous iron. The hydrothermal fluid is allowed to flow for 72 hours into the ocean solution heated to a range of temperatures under anoxic atmosphere. Single-tubular chimneys are observed to form (figure 1) and are characterized by Raman Spectroscopy. Comparing over 150 spectra from each chimney precipitated at each temperature, we observe a relatively high abundance of greigite and nanocrystalline mackinawite in chimneys peaking around 70°C.

Catalysis in a Hydrothermal Reactor. We use a hydrothermal reactor system [3] to mix a hydrogen-rich hydrothermal simulant solution with a CO_2-rich early ocean simulant. Both solutions flow for 72-91

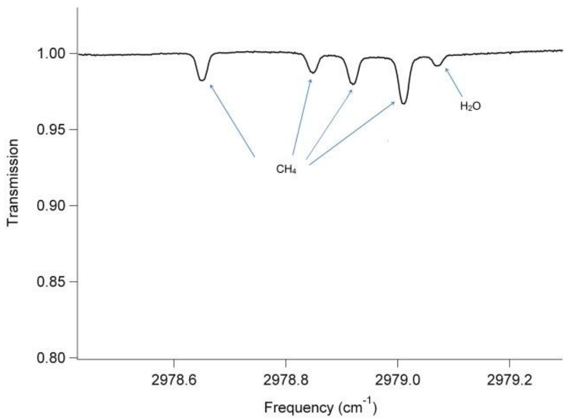

Figure 2: A spectra collected during a hydrothermal reactor experiment revealing detection of methane.

hours over a reactor bed packed with varying compositions of ocean crust materials including pentlandite [(Fe,Ni)S], rock wool (basalt), and komatiite (ultramafic). All experiments are conducted at hydrothermal pressures (100 bar) and temperatures (100°C). Tunable Diode Laser Absorption Spectroscopy is used to detect CH_4 (g) during reactor experiments (figure 2). A newly developed Mars Organic Analyzer microchip capillary electrophoresis system [9] is used to characterize dissolved organics in solution and reveals the possible synthesis of aldehydes.

Conclusion. Both experiments use newly developed analytical tools to contribute to our understanding of how life may have emerged from alkaline hydrothermal vent systems early in the development of any icy and rocky world with a CO_2-dominated atmosphere.

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