

Nitrogen Reduction on Metal Sulfide Surfaces under Hydrothermal Conditions Alexander D. Gordon^{1,3}, Soujanya SingiReddy^{1,3}, Riley Murphy^{1,3}, Alexander Smirnov^{2,3}, Martin A.A. Schoonen^{2,3}, Daniel R. Strongin^{1,3}: Temple University, Department of Chemistry, Philadelphia, PA 19122 (alex.gordon@temple.edu, Soujanya@temple.edu, riley.murphy@temple.edu, dstrongi@temple.edu); ²Department of Geosciences, Stony Brook University, Stony Brook, NY 11794 (mschoonen@notes.cc.sunysb.edu and asmirnov@ms.cc.sunysb.edu); ³Astrobiology Biogeochemistry Research Center, Montana State University, Bozeman, MT 59717

A hypothesis in this research is that there may have been a transition period on early Earth where inorganic iron-sulfur clusters were adapted for use by the biological world. It has been proposed by others that prebiotic chemistry originated on the surface iron sulfides within the extreme environment of hydrothermal vents (i.e., the “iron-sulfur world”) on the ocean floor [1]. Currently our studies are attempting to answer the question as to whether iron sulfide minerals can catalyze biologically relevant chemistry under hydrothermal conditions. In short, did this chemistry precede the chemistry that we now associate with enzymes (such as nitrogenase) containing Fe-S active sites?

Under current study is the conversion of dinitrogen to ammonia, presumably a key reaction that would precede the assembly of biologically relevant molecules. Prior studies have shown that dinitrogen can be converted to ammonia in the presence of iron sulfide under hydrothermal conditions [2,3], adding support to the “iron-sulfur world” hypothesis [4,5]. Current literature lacks studies that have investigated the surface chemistry involved in this chemical transformation. In this work we will present results from laboratory based experiments using *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to investigate the fixation of dinitrogen under hydrothermal conditions in the presence of iron sulfides (and nickel sulfides) and hydrogen sulfide at pressures up to 100 bar and temperatures up to 200°C. Using ATR-FTIR we will present data that helps to determine the composition of the iron sulfide surface during the conversion of the dinitrogen to ammonia under hydrothermal reaction conditions. Experimental results will be presented for FeS, FeS₂, and NiS mineral phases.

[1] Wächtershäuser, G. (1988b) *Syst. Appl. Microbiol.*, 10, 207-210. [2] Schoonen, M.A.A., Xu, Y. (2001) *Astrobiology*, 1, 133-142. [3] Smirnov et al, (2008), *Geochemical Transactions*, 9 [4] Wächtershäuser, G. (1990b) *Origins of Life*, 20, 173-176 [5] Wächtershäuser, G. (1992) *Prog. Biophys. Molec. Biol.*, 58, 85-201