COORDINATION CHEMICAL MODEL OF PYRITE BULK AND [100] SURFACE. C. J. Koll, M. J. Vance, and R. K. Szilagyi, Astrobiology Biogeochemistry Research Center, Department of Chemistry and Biochemistry, Montana State University, P.O. Box 173400, Bozeman, MT 59717 (szilagyi@montana.edu)

Introduction: Recent discovery of a reduced iron-sulfur surface at the ABRC by the Minton and Szilagyi groups in molecular beam experiments and X-ray absorption spectroscopic measurements provides further evidence for the possibility of iron-sulfur systems being involved in conversion of abundant pre-biotic molecules, such as N₂, H₂, CO₂, CO, and CH₄, into simple organic molecules such as amino acids, sugars, and N-containing heterocycles. In order for these processes to take place, access to catalytic active sites is required which can carry out bond breaking/formation, atom transfer, reduction/oxidation with good yields, and reasonable selectivity at thermally or radiolitically sustainable rates.

While the recreation of early earth conditions in the laboratory is challenging due to the several unknown physico-chemical parameters, the use of computational chemistry can be a fruitful approach in simulation of molecular potential energy surfaces and correlation of these with the desired pathways.

A limitation of this approach for mineral surfaces is the need to use complex periodic boundary condition-based simulation methods, which are not yet as well developed for potential energy surface studies as the alternative localized, molecular-based methodologies [1]. Here we report our initial results in the creation of a coordination chemical model for bulk and [100] pyrite. Since catalytic reactions on mineral surfaces are thought to occur at defect sites (localized), we argue that such a simulation methodology has the potential to provide the reasonable potential energy surface description of mineral surface and particle reactivity.

Methodology: The crystal structure of bulk pyrite was evaluated using molecular graphical tools that are commonly applied to metalloprotein active sites such as hydrogenase or nitrogenase. From this analysis, the inner sphere and several layers of outer sphere atoms/interactions were identified. Fe centers beyond the outermost layer were treated as point charges for charge neutralization of the coordination chemical model. Dangling truncated persulfide bonds were terminated by hydrogen atoms. Using this bulk model, three different [100] surface models were generated depending on the nature of terminating atoms: Fe, terminal S, bridging S.

Results: The 107 atom model of the bulk pyrite is shown in Figure 1. Structural optimization using BP86 density functional theory and LANL2DZ effective core potentials show small structural distortions upon optimization and thus indicate the adequacy of these computational models for the bulk structure of pyrite. For example, this model can be used to study the geometric and electronic structural effect of doping various heterometals.

Figure 1: Front (left) and top (right) view of the coordination chemical model of an Fe site in bulk pyrite. Central Fe atom is in pink, inner shell persulfides are in ball&stick presentation, terminating H atoms are in white.

Figure 2: Terminal S(left), bridging S(center), Fe(right)-terminated [100] pyrite surface models.

Figure 2 shows three surface models of the [100] cut of pyrite. These are relevant to the experimental reactivity studies of a H/Ar beam exposed [100] surface. They provide the starting structures for the mapping of potential energy surfaces of reduced Fe surface formation. Unexpectedly, we found that even in these truncated surface models the spin state of the Fe²⁺ centers remain low spin, which is an ideal organometallic electronic structure for the binding and activating of small molecules with multiple bonds.

Conclusions: We present a promising new approach for generating molecular, coordination chemistry-based computational models for periodic Fe-S mineral bulk and surfaces with localized defect sites. Furthermore, our approach will also be applicable for simulation of the geometric structure, electronic and magnetic properties of small Fe-S particles. Potential energy surface pathways explaining the molecular processes leading to reduced iron formation in molecular/beam experiments are being evaluated and results will be presented.