**PRF # 58131-UR2**
**Iron Dynamics in Alkaline Lacustrine Systems: Implications for Deposition and Diagenesis**
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**Research Accomplished**

The purpose of this project is to understand the conditions under which oxidation-reduction reactions change lacustrine sedimentary mineralogy and geochemistry. We are using laboratory synthesis experiments to test a set of specific hypotheses generated based on studies of lacustrine sedimentary outcrops and cores in the East African Rift. These include hypotheses 1) that Fe-oxyhydroxides are more easily reduced than ferric phyllosilicates; 2) that porewater $SO_4/CO_3$ ratios control whether sulfides (pyrite) or carbonates (siderite) form under reducing conditions; 3) that pyrite morphology is controlled by degree of supersaturation, as known in marine environments; and 4) that reduction of ferric oxyhydroxides or silicates is non-reversible for the modeled lacustrine sediment matrices.

During Year 1, we developed experimental synthesis and analytical protocols for synthesizing ferrihydrite and nontronite mixtures, and characterizing them quantitatively using X-ray diffraction. During Year 2, we implemented these protocols to begin testing hypotheses #1 and #2. To test hypothesis #1, we synthesized mixtures with varying proportions of ferrihydrite (ferric oxyhydroxide) and nontronite (ferric aluminosilicate). We synthesized ferrihydrite using a solvent-free method (Smith et al., 2012), and we used Clay Minerals Society Source Clay nontronite NAU-1. We reduced the mixtures using a sodium dithionite and citrate solution method (Stucki et al., 1984), in varying ambient solution chemistries. We found that pure nontronite exhibited very little crystallographic change on reduction, limited to a small reduction in the octahedral d-spacing. In contrast, a significant portion of the ferrihydrite dissolved upon reduction. In carbonate brines, reduced samples containing ferrihydrite produced abundant siderite (ferrous carbonate). This successfully simulated a number of target African lacustrine sedimentary environments, particularly Late Quaternary sediments of Lake Malawi (Cohen et al, 2007). Moreover, we also found that the greater the proportion of ferrihydrite in the starting materials, the greater the diagenetic production of siderite (Figure 2). Therefore we interpret this to indicate that ferrihydrite is kinetically favored during reduction over nontronite.

To test hypothesis #2, we simulated brine chemistry of several different carbonate and sulfate-rich saline lakes (Deocampo and Jones, 2014), and carried out the reduction experiments. Carbonate brines uniformly produced siderite, but we were unable to synthesize pyrite in sulfide brine. This likely has to do with the degree of supersaturation, as well as kinetic barriers to pyrite precipitation. Our experiments are continuing in this area to increase the degree of

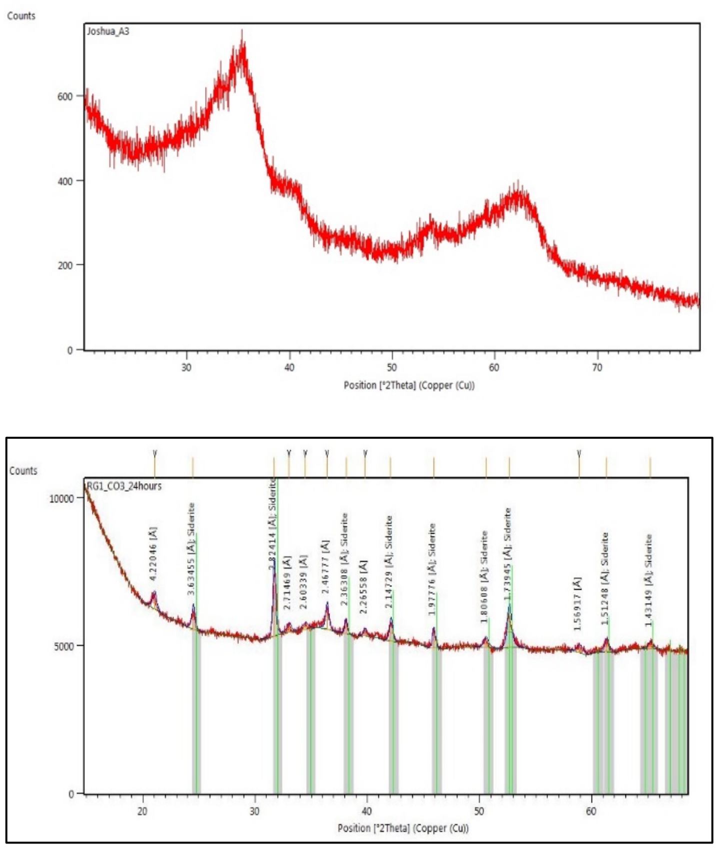


Figure 1. X-ray diffractogram of Top: pure 2-line ferrihydrite synthesized following methods of Smith et al. (2012); and Bottom: siderite produced through reduction of ferrihydrite in carbonate brine.

supersaturation as well as conduct the experiments at higher temperatures in order to induce pyrite precipitation. A small number of samples yielded magnetite unexpectedly. We preliminarily interpret the synthesis of this mineral with mixed valence as representing either incomplete reduction of ferrihydrite, or partial oxidation of ferrous oxide. Discovering a pathway to the diagenetic precipitation of magnetite in lacustrine sediments may have significant implications for the study of paleomagnetism in such sediments.

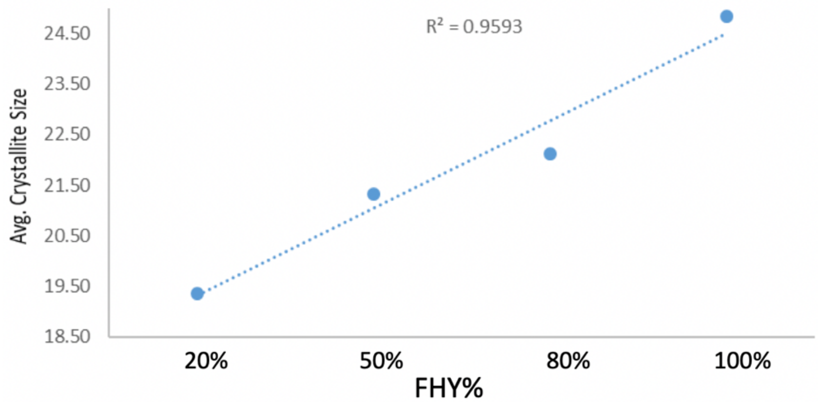


Figure 2. Crystallite sizes of experimentally produced siderite, as a function of the amount of ferrihydrite in the starting ferrihydrite/nontronite mixture. Significantly larger siderite crystals are found those with high starting ferrihydrite proportions, implying

**Impact on Students**

Several undergraduate and masters students have participated in the design, discussions, preparation, and execution of the experiments. These have involved discussions about using laboratory experiments to simulate natural environments in order to control variables and test hypotheses stemming from field-based studies. One undergraduate presented the results of his experiments at the national meeting of the Geological Society of America in 2018 (Davis and Deocampo, 2018), and three presented at GSA in 2019 (Chidzugwe et al., 2019; Davis et al., 2019; Duong et al., 2019). All of the undergraduate and graduate students involved in the project are under-represented minorities in the geosciences, and one of them is now preparing to graduate and apply to graduate degree programs. A cohort of undergraduates is now engaged in the next stage of experiments, developed in part based on the accomplishments to date.

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