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**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 the reporting period, progress was made on developing experimental and analytical protocols, and designing and carrying out initial experiments testing hypotheses #1 and #2. Several important preliminary steps had to be achieved before being able to carry out the synthesis and alteration experiments. First, it was necessary to pilot methods of Fe-oxyhydroxide synthesis as raw material for the experiments (i.e. ferrihydrite). We opted to synthesize our own Fe-oxyhydroxides rather than use natural materials because by synthesizing our own material we are able to ensure the purity and eliminate complicating factors from complex natural soil matrices. We first tested a method based on neutralization of basic iron nitrate solution (i.e. Hiemstra and van Riemsdijk, 1996). This method was successful, but time-intensive (Figure 1).

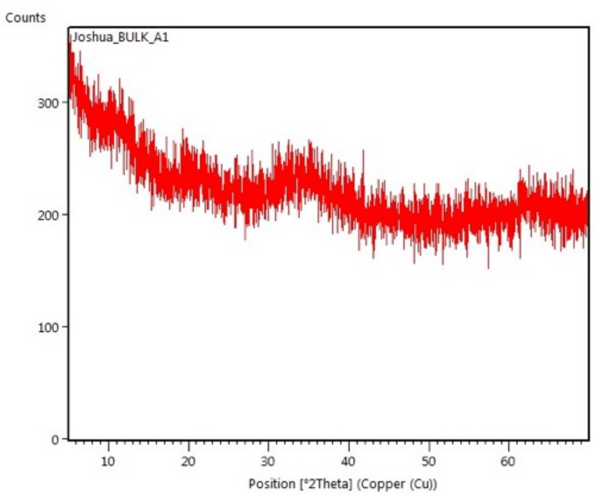


Figure 1. X-ray diffractogram of trial 1, poorly crystalline ferrihydrite synthesized from solution.

We next tested a method based on dehydration of iron nitrate salts in the presence of ammonium bicarbonate (Smith et al., 2012). This method was also successful (Figure 2), but had the added advantage of being more rapid, and involving less labor intensive benchwork, making this method more advantageous for using in undergraduate research.

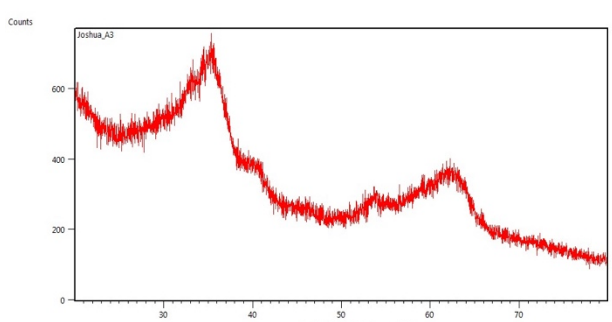


Figure 2. X-ray diffractogram of trial 2 ferrihydrite synthesized by dehydration of solid iron nitrate.

To test hypothesis #1, we obtained Clay Minerals Society Source Clay Nau-1, a well-characterized standard nontronite (Fe-rich smectite), to compare its reduction kinetics against that of the synthesized ferrihydrite. To artificially reduce the sediments, we employed the technique of Stucki et al. (1984), employing a sodium dithionite and citrate solution. We encountered difficulty in quantifying the proportions of ferrihydrite and nontronite in the synthetic mixtures, however, and found we needed to develop an X-ray diffraction protocol specifically addressing this problem.

To address this, we developed a systematic quantification method based on the ratio of integrated measurements of the nontronite 003 peak to the ferrihydrite shoulder at approximately 33˚ 2-theta (Figure 3).

Despite the poor crystallinity of synthetic ferrihydrite, the relationship between the measured and known abundances of a set of calibration standards is quite strong (Figure 4; $r^2$>0.99). This

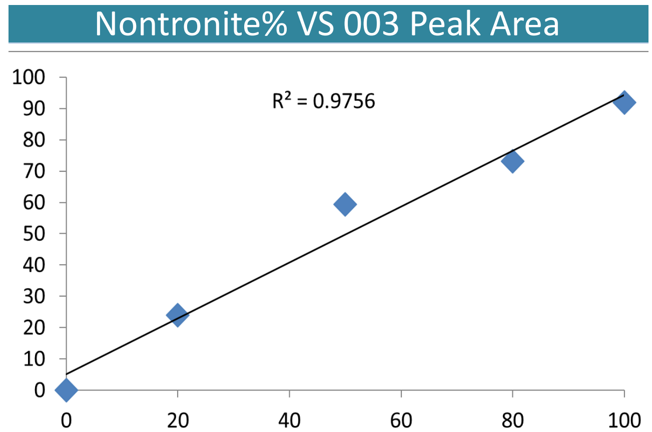


Figure 4. Relationship between Nontronite % and integrated peak area of the nontronite 003 peak.

now enables us to quantify proportional changes in the ratio of nontronite to ferrihydrite in future experiments, to test the comparative kinetics of reduction in simulated reducing pore waters. These results are generating a new way of looking at lacustrine sediment and preliminary data that will enable us to submit future proposals for more substantial funding (e.g. NSF).

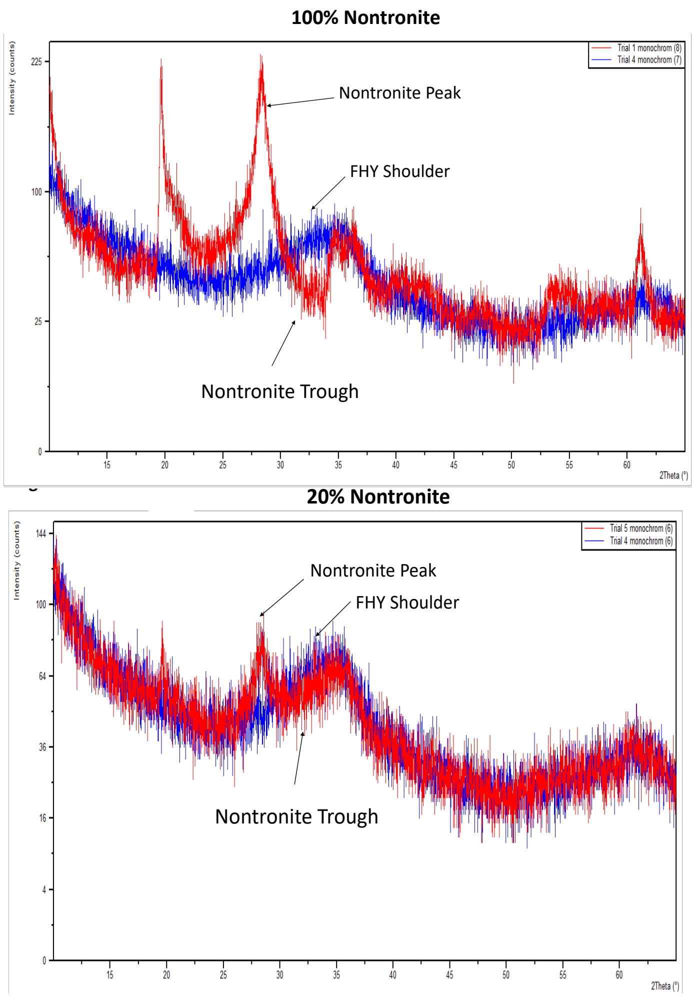


Figure 3. Example X-ray diffractograms for synthetic mixtures of nontronite (Fe-smectite) and synthesized ferrihydrite. Blue background pattern in both diffractograms is pure ferrihydrite for comparison.

**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 (Davis and Deocampo, 2018). A cohort of undergraduates is now engaged in the next stage of experiments, developed in part based on the accomplishments to date.

**References**


Davis, D.M., and Deocampo, D.M., 2018. Quantification of amorphous Fe-oxyhydroxides and phyllosilicates: Applications for the study of Fe-bearing phases in East African lakes. *Geological Society of America Abstracts with Programs*, vol. 50, no. 6, doi: 10.1130/abs/2018AM-316695.

Hiemstra, T. and van Riemsdijk, W.H., 1996. A surface structural approach to ion adsorption: The charge distribution (CD) model: Journal of Colloid and Interface Science, vol. 179, p. 488-508.

Smith, S.J., Page, K., Kim, H., Campbell, B.J., Boerio-Goteas, J., and Woodfield, B.F., 2012. Novel Synthesis and Structural Analysis of Ferrihydrite. Inorganic Chemistry, vol. 51, p. 6421-6424. Doi: 10.1021/ic300937f.

Stucki, J.W., Golden, D.C., and Roth, C.B., 1984. Effects of reduction and reoxidation of structural iron on the surface charge and dissolution of dioctahedral smectites. *Clays and Clay Minerals*, vol. 32, p. 350-355.