Reduction of Mixed Nitrate/Nitrite via Green Rust Chloride and Sulfate

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Life is said to have originated in primordial oceans from reduced nitrogen compounds, such as ammonia.[1] Prior to this, acid rain from Early Earth's non-reducing atmosphere provided a sink for the marine accumulation of oxidized nitrogen species, namely, nitrate and nitrite. The highly redox active ferrous-ferric double layer hydroxide (DLH) mineral, green rust, has the potential to reduce oxygenated nitrogen species and could have been responsible at least partially for the production of fixed nitrogen precursors for life.[2,3]

Previous studies have attempted to colorimetrically follow the reduction of nitrate or nitrite to ammonia via biogenic and synthetic green rusts. Even so, few (if any) studies have attempted to quantify the kinetics of ammonia formation by rigorously synthesized green rust samples. The production of additional reaction products, including gaseous compounds, in the reduction of nitrite and nitrate is reported in an attempt to completely account for the nitrogen balance. Some of the observed reaction products have not been reported from these mixed systems. Herein we report GC-MS and LC-MS/MS reaction data from nitrate/nitrite reduction with highly pure green rust chloride and sulfate, novel colorimetric methodology used to elucidate the amount of ammonia in the green rust lattice versus solution, and finally, reactions with mixed nitrate/nitrite species as opposed to solely unmixed nitrate or nitrite solutions.

Our experiments allude to the differing chemistry and reaction kinetics of mixed nitrate/nitrite species compared to their pure nitrate or nitrite counterparts during green rust catalysis. Additionally, the association of produced ammonia within the green rust lattice and in solution is assessed during the reaction progress – illuminating a complex equilibrium.

[1] Summers et al. (1993), *Nature* 365, 630-633,
[2] Halevy et al. (1993), *Nature Geoscience* 10: 135-139,
[3] Russell et al. (2017). *Astrobiology* 17: 1053-1066.