

Can nitrates on Mars drive subsurface organic chemistry?

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Program: Spontaneous R&TD

Project Objectives:

- Synthesize Mars analog iron minerals in the lab, and react them with nitrates and simple organic compounds.
- Test whether nitrogen redox chemistry occurs, and whether this leads to production of ammonia (NH_3).
- **Test whether organic precursors react with these iron minerals and nitrates in Mars conditions to form amino acids.**

Benefits to NASA and JPL / Significance of Results

- **Identifying and characterizing organics on Mars is highly desired for life detection studies. However, abiotic organic chemistry is also particularly favored under Mars surface / near subsurface conditions, and is likely to produce amino acids and other products that would appear very similar to components of biological systems.** Further studies are needed to understand the extent of abiotic organic synthesis that is likely to be occurring in Mars soils and subsurface today in order to identify possible biosignatures.
- **Nitrogen (N)** is an essential component of habitability, and likely for the origin of life, on any world that may host life as we know it. On Mars, nitrogen has been found in the form of nitrates [1]; these can react with Mars iron oxides / hydroxides to produce reduced N species such as ammonia [2].
- **If reduced nitrogen products are generated in Mars iron mineral systems, then abiotic amino acid synthesis is favored.** This is seen in systems containing ammonia [3]; and various types of organic products are formed. However, on Mars nitrates are the primary N source, and this reaction has yet to be tested.
- **Our results show that organic reactions do occur under Mars conditions with oxidized and reduced nitrogen species: generating amino acids, alpha-hydroxy acids, and other as yet unidentified products. The type of organics formed depends heavily on the oxidation state of the nitrogen species, and the iron minerals. More study is required to link organic products to specific geochemical conditions.**

Experimental Conditions

A solution of Fe^{2+} with organic precursors (pyruvate or glyoxylate, both sourced from water/rock reactions and aqueous alteration of parent bodies) and a solution of nitrate (NO_3^-), nitrite (NO_2^-), or ammonium (NH_4^+) were mixed in a glove box filled with inert gas. The resulting solutions were titrated to pH 10 using NaOH in order to precipitate iron oxyhydroxide minerals that would react with the organics and nitrogen; vials were heated at 70°C in an oxygen-free atmosphere and sampled at $t=0$, $t=24\text{h}$, and $t=72\text{h}$.

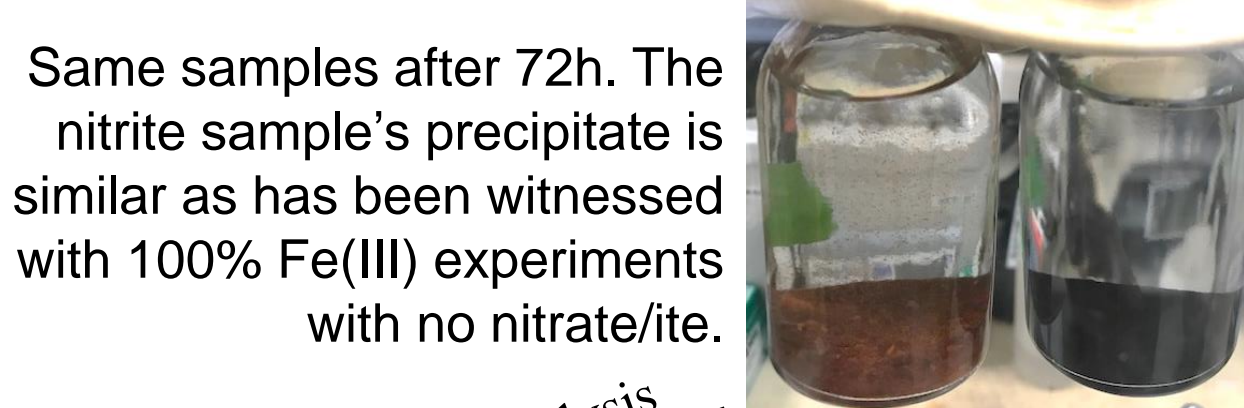
Summary of Experiments

Organic precursor	Nitrogen species	Fe(II) mole fraction in mineral
glyoxylate	NO_2^-	(1:1) Fe(II):Fe(III)
glyoxylate	NO_2^-	100% Fe(II)
pyruvate	NO_2^-	(1:1) Fe(II):Fe(III)
pyruvate	NO_2^-	100% Fe(II)
glyoxylate	NO_3^-	(1:1) Fe(II):Fe(III)
pyruvate	NO_3^-	(1:1) Fe(II):Fe(III)
pyruvate	NO_3^-	100% Fe(II)
glyoxylate	NH_4^+	(1:1) Fe(II):Fe(III)
pyruvate	NH_4^+	(1:1) Fe(II):Fe(III)

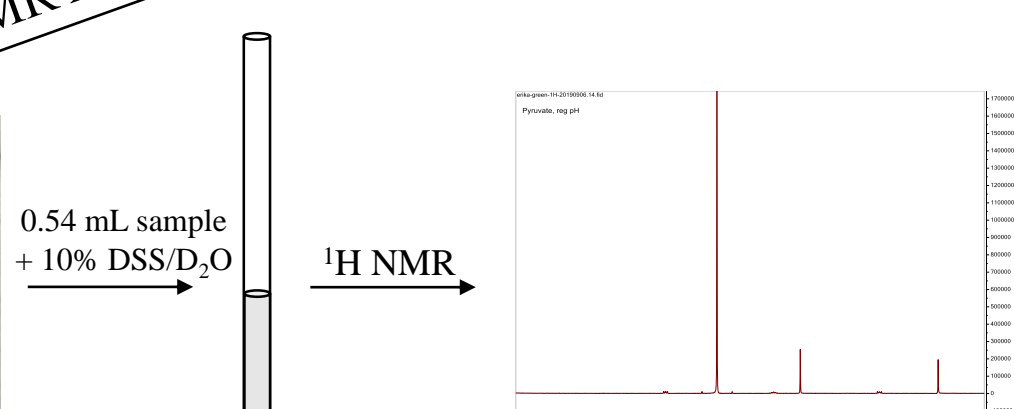
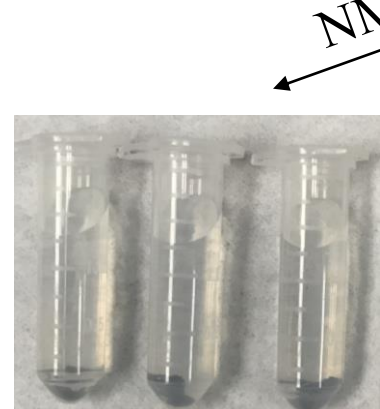
Sample Analysis via ^1H NMR and Iron Colorimetry



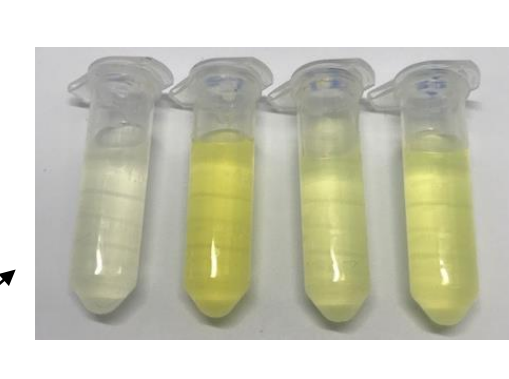
(1) Pyruvate, nitrite, (1:1) & (2) glyoxylate, nitrate, (1:1) experiments prior to titrating. Both produced gas when reacting with N source, but only nitrite produced a color change indicative of iron oxidation.



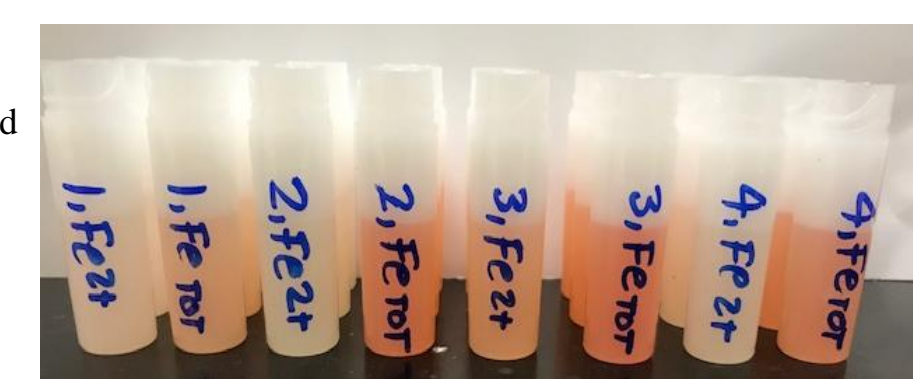
Same samples after 72h. The nitrite sample's precipitate is similar as has been witnessed with 100% Fe(III) experiments with no nitrate/ite.



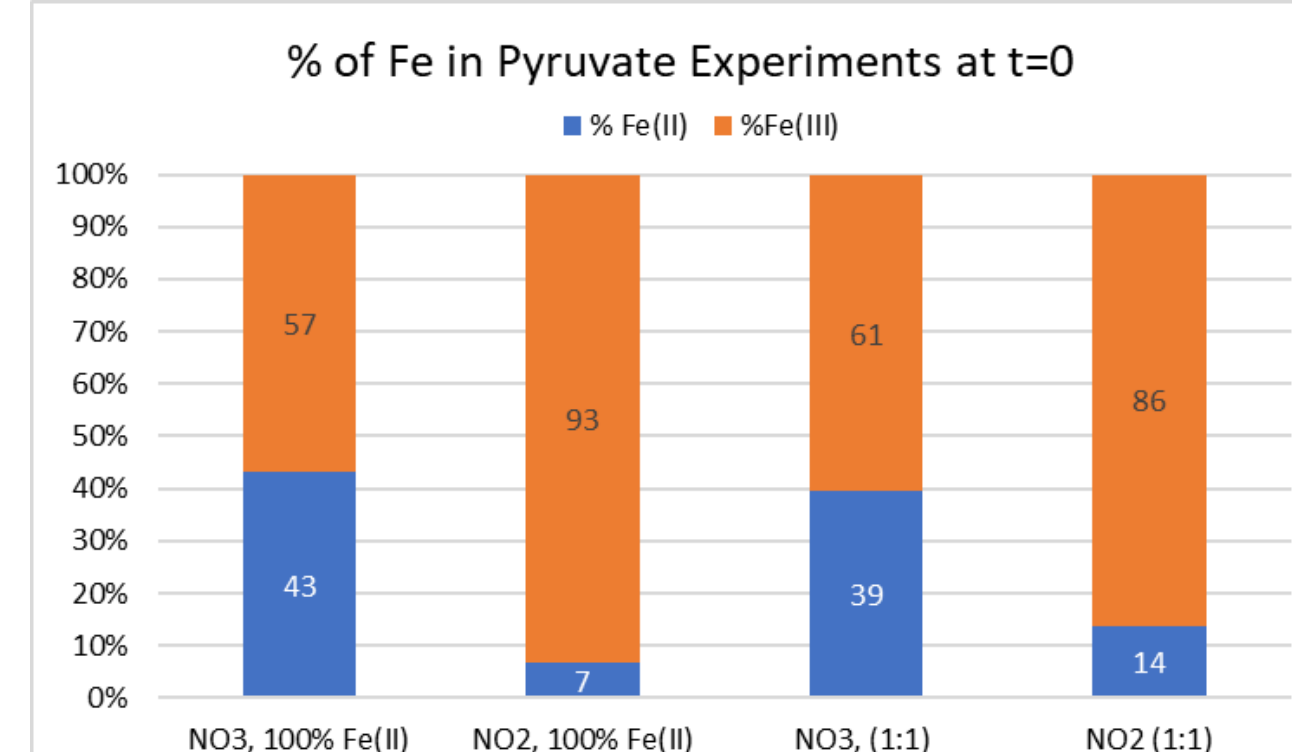
1-mL samples were taken in triplicate for each time point. 0.5 mL of 1M NaOH was added to each and centrifuged to precipitate out iron. Supernatant was transferred to NMR tube with 10% DSS/ D_2O standard and run on instrument for ^1H NMR.



Dilute and add reagents.

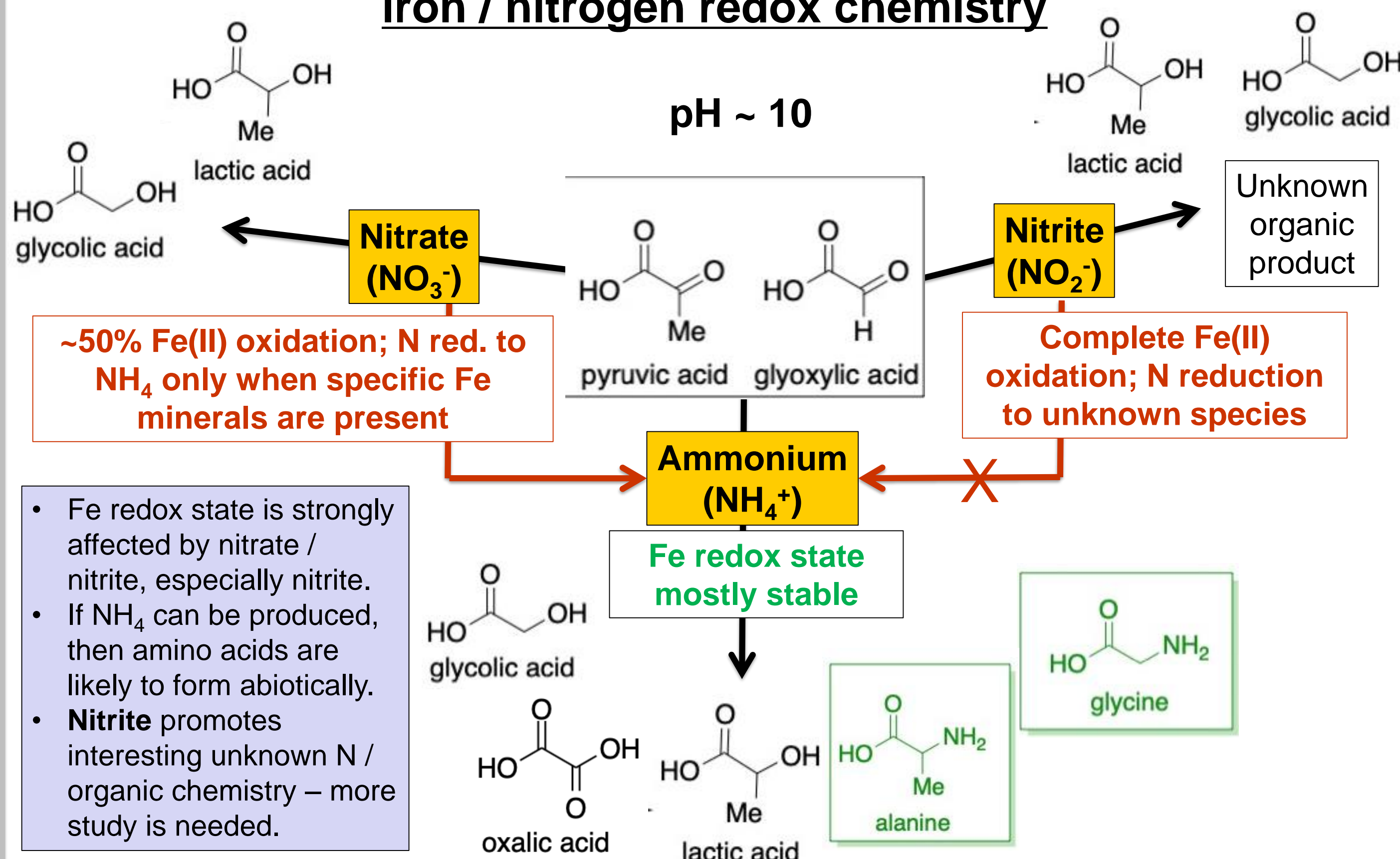


- Triplicates were taken for each experiment to which 0.5 mL of 2.5 M HCl were added to dissolve the precipitate.
- Two diluted colorimetry samples were prepared for each (one for Fe(II) and one for Fe(total) = Fe(II) + Fe(III)).
- 100 μL of ascorbic acid was added to Fe(total) samples to reduce any Fe(III) to Fe(II) and 100 μL of water was added to Fe(II) samples.
- To all samples, 100 μL of 1M HCl, 100 μL of 1M sodium acetate, and 2 mL of 0.3% 1,10 phenanthroline were added and samples were analyzed with a UV-Vis spectrophotometer after 10 minutes.



Colorimetry results show that nitrite almost completely oxidizes the iron mineral while nitrate oxidizes the mineral about 50%.

Example abiotic organic reaction cycles on Mars driven by iron / nitrogen redox chemistry



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References:

- [1] Stern JC et al. (2015) Evidence for indigenous nitrogen in sedimentary and aeolian deposits from the Curiosity rover investigations at Gale crater, Mars. PNAS 112 (14) 4245-4250.
- [2] Summers DP, Chang S (1993) Prebiotic ammonia from reduction of nitrite by iron (II) on the early Earth. Nature 365:630-633.
- [3] Barge L.M. et al. (2019) Redox and pH Gradients Drive Amino Acid Synthesis in Iron Oxyhydroxide Mineral Systems. PNAS, <https://doi.org/10.1073/pnas.1812098116>.

NMR Results

