

INVESTIGATING ABIOTIC MINERAL-ORGANIC CHEMISTRY WITH IRON OXYHYDROXIDES.

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Introduction: Iron hydroxides and oxyhydroxides have been detected/inferred to be in mudstones located in Gale Crater on Mars [1]; these are reactive minerals that are known to drive prebiotic chemistry [2]. Various organic precursors could have been present on early or present day Mars; for example pyruvate, which can be synthesized abiotically [3]. An understanding of the potentially abiotic/prebiotic reactions driven in Mars-relevant environments is key for the separation of intricate chemistry types; abiotic from potential prebiotic reactions. In this work, we are studying reactions of select Mars relevant minerals (Fe-oxyhydroxides, magnetite, and olivine) with abiotic organic precursors (pyruvate and glyoxylate). Preliminary reactions have been performed with synthetic mixed-valence iron oxyhydroxide minerals combined with pyruvate in aqueous solution, along with ammonia, in order to investigate reactions perhaps including reductive amination to an amino acid alanine, and reduction of pyruvate to lactate. These preliminary experiments will pave the way for more detailed investigations of organic/mineral reaction environments with additional Mars-relevant geochemical components, e.g. sulfate or perchlorate [4].

Methods: An aqueous solution of a 1:1 ratio of Fe (II) to Fe (III) was created for a total concentration of 50 mM Fe, along with 10 mM of ammonia and 2.5 mM of pyruvate. The solution was transferred into a nitrogen-filled glove box to simulate Martian anoxic conditions. The solution was titrated to ~ pH 10 with NaOH, which resulted in precipitation of the dissolved $\text{Fe}^{2+} / \text{Fe}^{3+}$ as an iron oxyhydroxide mineral (**Figure 1**).

The vial was sealed and kept at 70°C for the duration of the experiment (~3 days with sampling at $t=0$ and $t=2$ days). The samples were then prepped for ¹H NMR and colorimetry analysis. Iron colorimetry was performed to determine the concentrations of Fe (II) and Fe (III) in the solution, both during the initial $t=0$, and at $t=2$. Iron colorimetry was taken at these different time points to analyze how the iron oxidized when in the presence of ammonia and pyruvate [2].

Results: In the colorimetry analysis, the iron redox states were found to be roughly equivalent over the various sampling dates. At the initial colorimetry date; $t=0$, the Fe (II) and Fe (III) concentrations were found to be relatively similar, as shown in **Figure 2**. At $t=2$ days, there is a slight increase in the Fe (III) (**Figure 2**). This is most likely due to the gradual oxidation of the samples as they are exposed to air. ¹H NMR spectroscopy



Figure 1: Aqueous solution of Fe (II)/(III), ammonia, and pyruvate, created under anoxic conditions and kept at 70°C in a hot water bath.

was also taken at both time points $t=0$ and $t=2$ days. The goal of this analysis was to determine if the organic – pyruvate – successfully reduced to the hydroxy-acid lactate [2]. In the NMR analysis, lactate peaks were observed in both $t=0$ and $t=2$ days (**Figure 3**) samples.

Conclusion/Future Work: The iron redox states of the synthetic mineral remained largely the same throughout the experiment and after the organic reaction process. The successful reduction of pyruvate to lactate occurred, and the NMR data was largely similar in triplicate. No visible reduction to the amino acid alanine was observed, and future work involving greater concentrations of ammonia could be performed to assess reductive amination feasibility of pyruvate with iron oxyhydroxides. Further studies could involve the reduction of other organics with the iron (oxy)hydroxides, such as glyoxylate and possibly alpha-ketoglutarate. Different minerals will also be used, starting with magnetite and olivine, to investigate how organics might react with various iron-containing Mars minerals. Altering the pH and redox states of the organic reactions is another future step that could be beneficial in understanding the potentially abiotic/prebiotic reactions proposed to have occurred in early Mars environments.

References: [1] Vaniman D. et. al. (2014) *Science*, 343, 6169. [2] Barge L. et al. (2022) *Geochimica et Cosmochimica Acta*, 336, 469-479. [3] Cody G. et al. (2000) *Science*, 289, 1337-1340. [4] Clark J. et. al. (2021) *Minerals*, 11, 475.

