

Investigating Mineral-Organic Chemistry with Mars Analog Iron-Bearing Minerals

Matthew E. Luna¹, Dennise D. Valadez¹, Jessica M. Weber¹, David D. VanderVelde², Laura M. Barge¹

¹NASA Jet Propulsion Laboratory, California Institute of Technology; ²Department of Chemistry, California Institute of Technology

matt.e.luna@jpl.nasa.gov



My Digital Business Card!

Introduction

- Iron-bearing minerals, which have been known to drive prebiotic chemistry, have been detected/inferred to be in mudstones located in Gale Crater on Mars, [1, 2].
- Abiotic organic precursors such as pyruvate [3] could have been present on early Mars, as well as other potential organics.

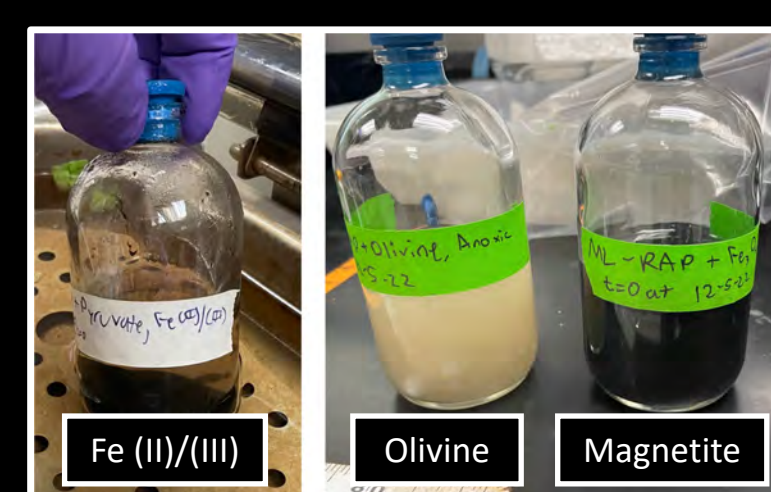
Methodology

Figure 1: Six experiments. Iron (oxy)hydroxides: A & B, Magnetite: C & D, and Olivine: E & F



- We have performed reactions with magnetite, olivine, and synthetic mixed-valence iron oxyhydroxide minerals combined with pyruvate in aqueous solution, along with ammonia, in order to investigate prebiotic reactions including the reduction of pyruvate to lactate, which can be driven by Fe (II) [2].

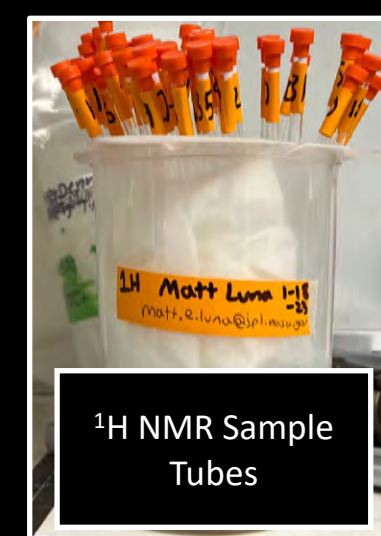
Figure 2: The solutions (left) were combined together with N₂ purged water in a nitrogen-filled chamber, then submerged in a hot water bath at 70°C once sealed.



- The solutions were titrated to pH 10 and sampled at 4 different time points: 0, 1, 3, and 7 (days).
- Iron colorimetry and liquid ¹H Nuclear Magnetic Resonance (NMR) Spectroscopy were performed on the samples. Iron colorimetry [4] and NMR were performed to determine iron redox state and organics respectively.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Figure 3: To prepare for the NMR spectroscopy, the samples were treated with NaOH to remove any excess soluble iron. The remaining supernatant was transferred to tubes containing 60μL DSS/D₂O (left). Each sample was taken in triplicate, and concentrations were measured by integrating the area of the methyl peaks.



Iron Colorimetry Analysis

Figure 4: Samples were taken in triplicate for iron colorimetry, and additional HCl was added to dissolve all solids. The samples were then partitioned into two separate vials (left), and different reagents were added to each to test for either Fe (II) or Fe (total) concentration using a spectrophotometer (λ=510 nm).



$$\text{Fe (total)} - \text{Fe (II)} = \text{Fe (III)}$$

Results

Iron Redox State Measured from Iron Colorimetry

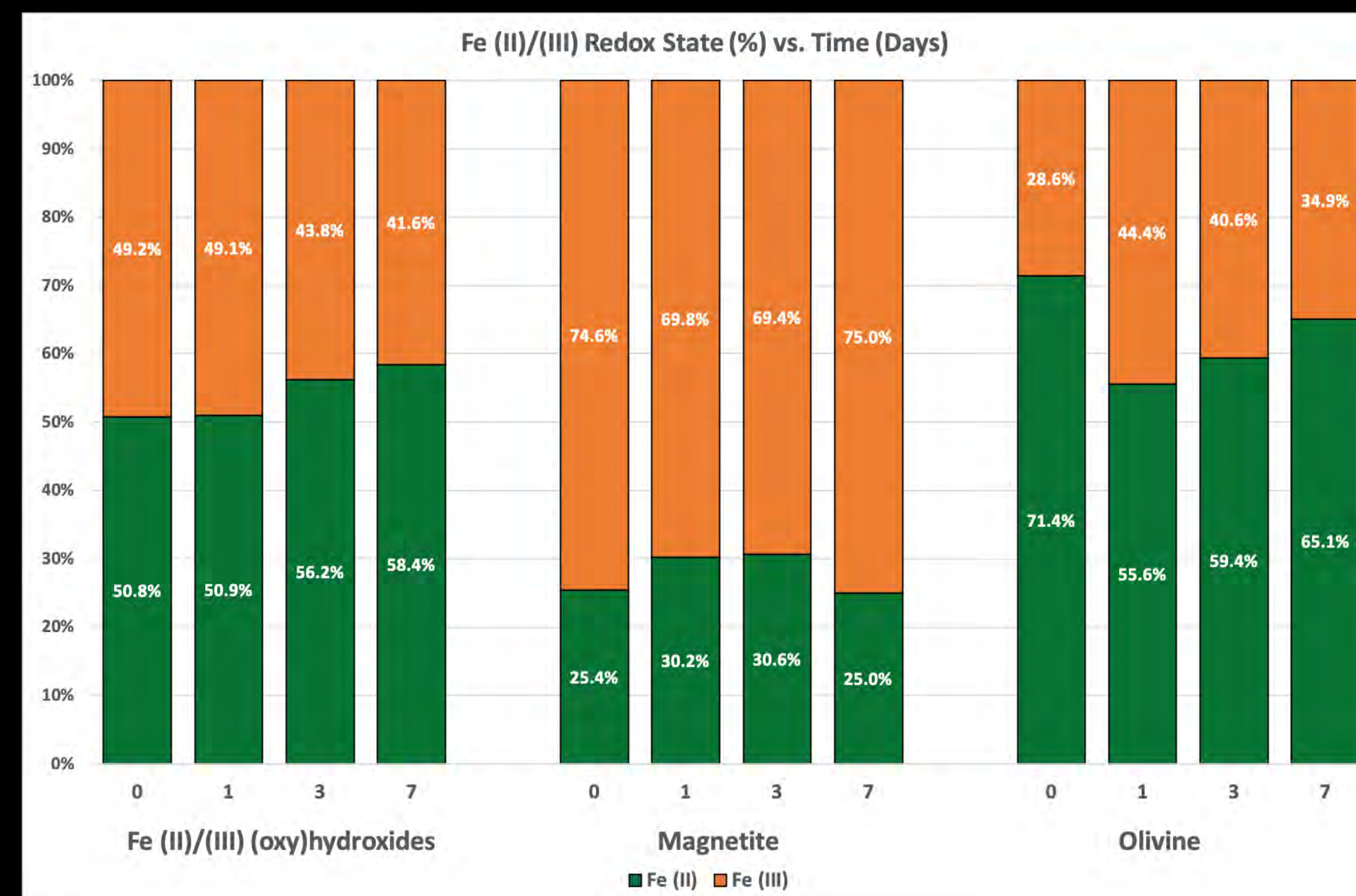


Figure 5: Changes in Fe redox state observed over the course of triplicate experiments with iron (oxy)hydroxides, magnetite, and olivine analyzed through iron colorimetry. The minerals were tested in a suspension with ammonia and pyruvate. The results of the triplicates were averaged to determine the overall redox trend of each mineral. The percentage in each column represents the average percent concentration of either Fe (II) or (III) in the system.

Lactate Production Over Time

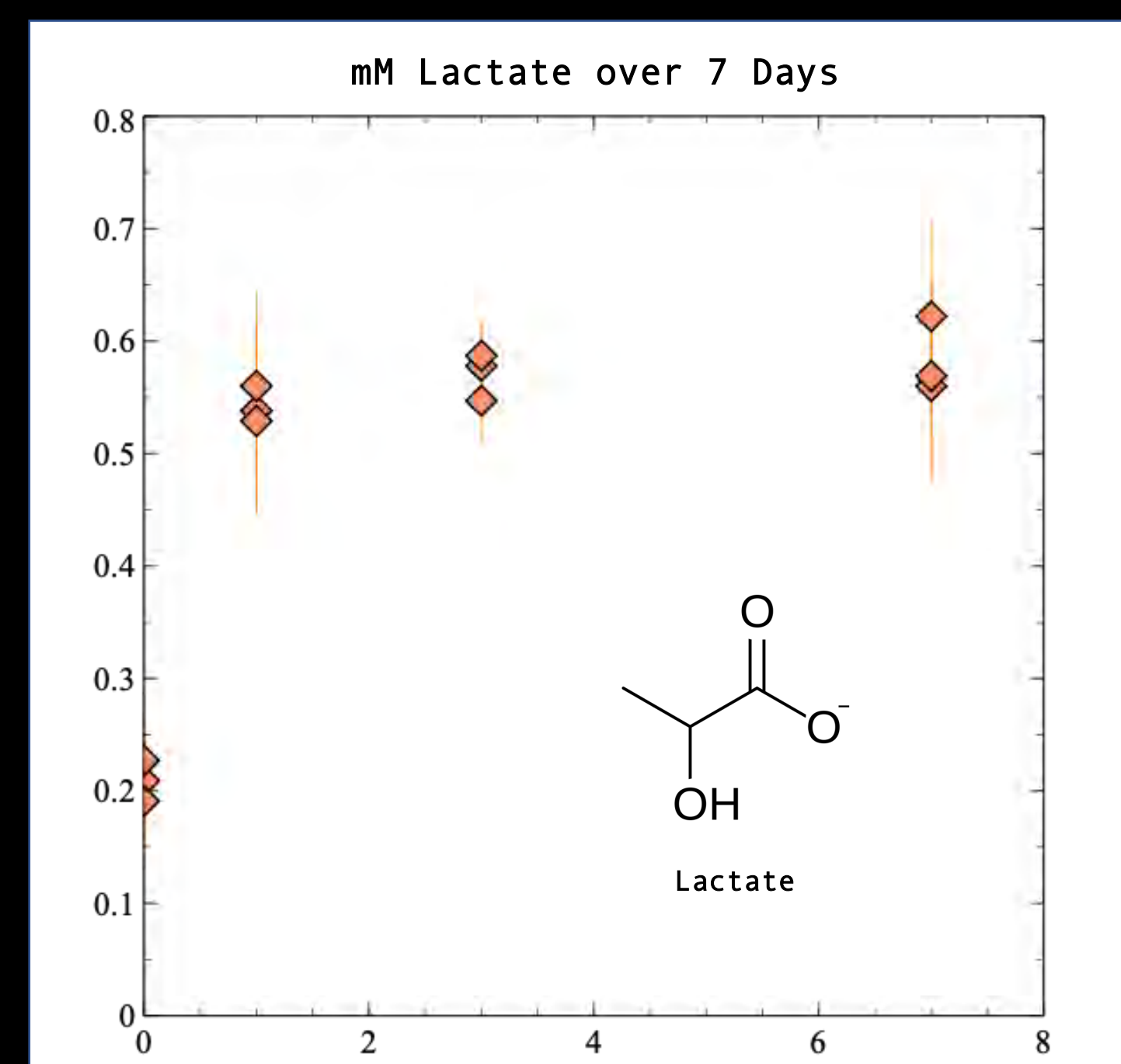


Figure 6: Graph of the millimolar (mM) concentration of the pyruvate reduction product lactate produced in the iron (oxy)hydroxide suspensions. The graph depicts the mM concentration in the system over the sampling cadence, 0, 1, 3, and 7 days.

¹H NMR Spectra of Three Experiment Types

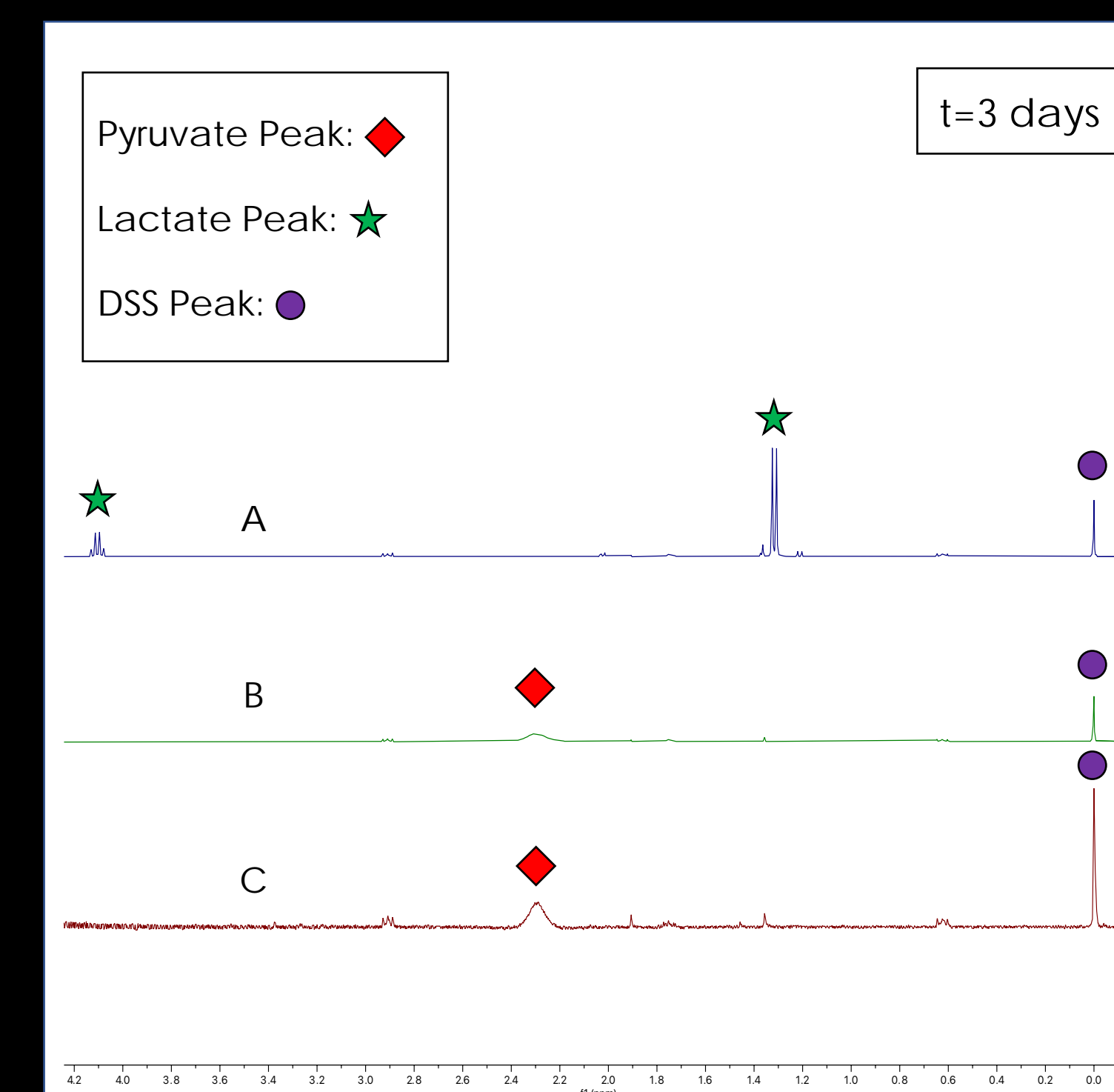


Figure 7: Liquid ¹H NMR spectra examples of each mineral type at the sampling time of t=3 days. A: Fe (oxy)hydroxides. B: Magnetite. C: Olivine. All minerals are individually reacted with pyruvate. The lactate and pyruvate peaks are labeled as well as the standard DSS at 0 ppm.

Conclusions

- Iron (oxy) hydroxides started out at a redox ratio of 50% and overwent a slight oxidation over 7 days. (Figure 5).
- Magnetite and olivine contained both Fe (II) and Fe (III), however these minerals are very insoluble, and so the colorimetry data has a higher error (Figure 5).
- An increase in lactate production over time occurred in the iron (oxy)hydroxide experiments, exhibited by the mM concentration graph (Figure 6).
- The liquid ¹H NMR results of the iron (oxy)hydroxide experiments yielded successfully lactate peak production. Olivine and magnetite show hints of lactate production, and still display the pyruvate peak. Therefore, the pyruvate is not fully reacted in the magnetite and olivine experiments. Perhaps these two minerals might need to run for a longer duration to allow for the further reduction of pyruvate to lactate (Figure 7).

Future Work

- Triplicate runs of the magnetite and olivine solutions will be performed to investigate pyruvate reactivity.
- Ammonia concentration will be increased in the system to test whether reductive amination could occur to the amino acid alanine.
- Different Mars relevant iron-bearing minerals (as well as minerals such as magnesium sulfate) and organics will be tested under similar conditions [5].
- pH and redox state of the solutions will be altered to simulate a changing early Martian environment.

References and Acknowledgments

- [1] Vaniman D. et. al. (2014) Science, 343, 6169.
- [2] Barge L. et al. (2022) Geochemica et Cosmochimica Acta, 336, 469-479.
- [3] Cody G. et al. (2000) Science, 289, 1337-1340.
- [4] Flores E. et. Al. (2021) ACS Earth and Space Chemistry, 5 (5), 1048-1057
- [5] Clark J. et. al. (2021) Minerals, 11, 475.
- Mars Science Laboratory Participating Science Program
- Background Credit: NASA/JPL-Caltech/MSSS

Alternate Text

Matthew Luna

NASA Jet Propulsion Laboratory

'Investigating Mineral-Organic Chemistry with Mars Analog Iron-Bearing Minerals'

Introduction:

- Iron-bearing minerals, which have been known to drive prebiotic chemistry, have been detected/inferred to be in mudstones located in Gale Crater on Mars, [1, 2].
- Abiotic organic precursors such as pyruvate [3] could have been present on early Mars, as well as other potential organics.

Methodology:

Figure 1: Six experiments. Iron (oxy)hydroxides: A & B, Magnetite: C & D, and Olivine: E & F

- We have performed reactions with magnetite, olivine, and synthetic mixed-valence iron oxyhydroxide minerals combined with pyruvate in aqueous solution, along with ammonia, in order to investigate prebiotic reactions including the reduction of pyruvate to lactate, which can be driven by Fe (II) [2].

Figure 2: The solutions (left) were combined together with N₂-purged water in a nitrogen-filled chamber, then submerged in a hot water bath at 70°C once sealed.

- The solutions were titrated to pH 10 and sampled at 4 different time points: 0, 1, 3, and 7 (days).
- Iron colorimetry and liquid ¹H Nuclear Magnetic Resonance (NMR) Spectroscopy were performed on the samples. Iron colorimetry [4] and NMR were performed to determine iron redox state and organics respectively.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Figure 3: To prepare for the NMR spectroscopy, the samples were treated with NaOH to remove any excess soluble iron. The remaining supernatant was transferred to tubes containing 60μL DSS/D₂O (left). Each sample was taken in triplicate, and concentrations were measured by integrating the area of the methyl peaks.

Iron Colorimetry Analysis

Figure 4: Samples were taken in triplicate for iron colorimetry, and additional HCl was added to dissolve all solids. The samples were then partitioned into two separate vials (left), and different reagents were added to each to test for either Fe (II) or Fe (total) concentration using a spectrophotometer (λ=510 nm). Fe (total) – Fe (II) = Fe (III)

Results:

Iron Redox State Measured from Iron Colorimetry

Figure 5: Changes in Fe redox state observed over the course of triplicate experiments with iron (oxy)hydroxides, magnetite, and olivine analyzed through iron colorimetry. The minerals were tested in a suspension with ammonia and pyruvate. The results of the triplicates were averaged to determine

the overall redox trend of each mineral. The percentage in each column represents the average percent concentration of either Fe (II) or (III) in the system.

Lactate Production Over Time

Figure 6: Graph of the millimolar (mM) concentration of the pyruvate reduction product lactate produced in the iron (oxy)hydroxide suspensions. The graph depicts the mM concentration in the system over the sampling cadence, 0, 1, 3, and 7 days.

¹H NMR Spectra of Three Experiment Types

Figure 7: Liquid ¹H NMR spectra examples of each mineral type at the sampling time of t=3 days. A: Fe (oxy)hydroxides. B: Magnetite. C: Olivine. All minerals are individually reacted with pyruvate. The lactate and pyruvate peaks are labeled as well as the standard DSS at 0 ppm.

Conclusions:

- Iron (oxy) hydroxides started out at a redox ratio of 50% and overwent a slight oxidation over 7 days. (Figure 5).
- Magnetite and olivine contained both Fe (II) and Fe (III), however these minerals are very insoluble, and so the colorimetry data has a higher error (Figure 5).
- An increase in lactate production over time occurred in the iron (oxy)hydroxide experiments, exhibited by the mM concentration graph (Figure 6).
- The liquid ¹H NMR results of the iron (oxy)hydroxide experiments yielded successfully lactate peak production. Olivine and magnetite show hints of lactate production, and still display the pyruvate peak. Therefore, the pyruvate is not fully reacted in the magnetite and olivine experiments. Perhaps these two minerals might need to run for a longer duration to allow for the further reduction of pyruvate to lactate (Figure 7).

Future Work:

- Triplicate runs of the magnetite and olivine solutions will be performed to investigate pyruvate reactivity.
- Ammonia concentration will be increased in the system to test whether reductive amination could occur to the amino acid alanine.
- Different Mars relevant iron-bearing minerals (as well as minerals such as magnesium sulfate) and organics will be tested under similar conditions [5].
- pH and redox state of the solutions will be altered to simulate a changing early Martian environment.

References and Acknowledgements:

- [1] Vaniman D. et. al. (2014) *Science*, 343, 6169.
- [2] Barge L. et al. (2022) *Geochemica et Cosmochimica Acta*, 336, 469-479.
- [3] Cody G. et al. (2000) *Science*, 289, 1337-1340.
- [4] Flores E. et. Al. (2021) *ACS Earth and Space Chemistry*, 5 (5), 1048-1057
- [5] Clark J. et. al. (2021) *Minerals*, 11, 475.
- Mars Science Laboratory Participating Science Program
- Background Credit: NASA/JPL-Caltech/MSSS