# Prebiotic reactions in a Mars analog iron mineral system: effects of nitrate, nitrite, and ammonia on amino acid formation

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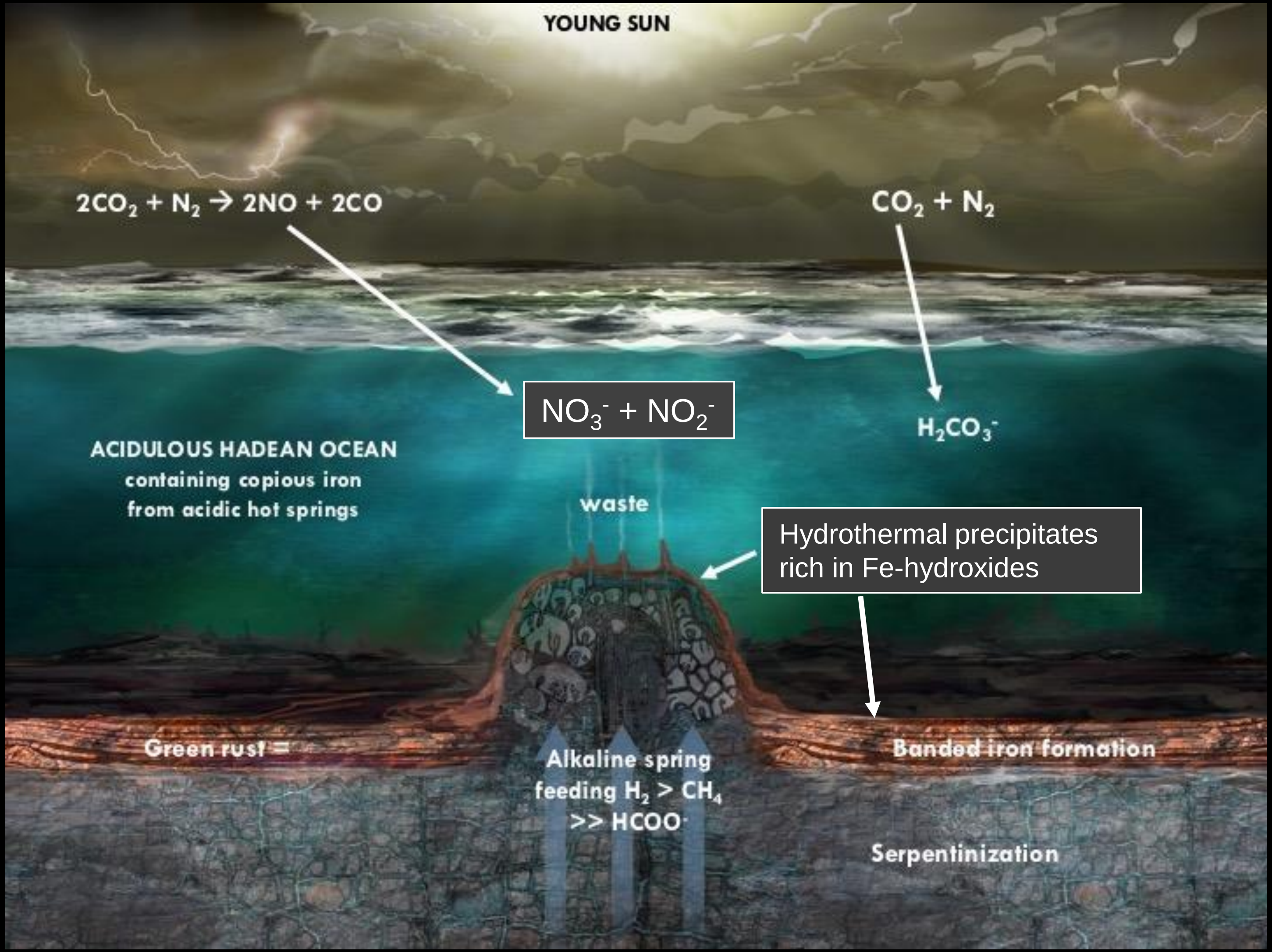
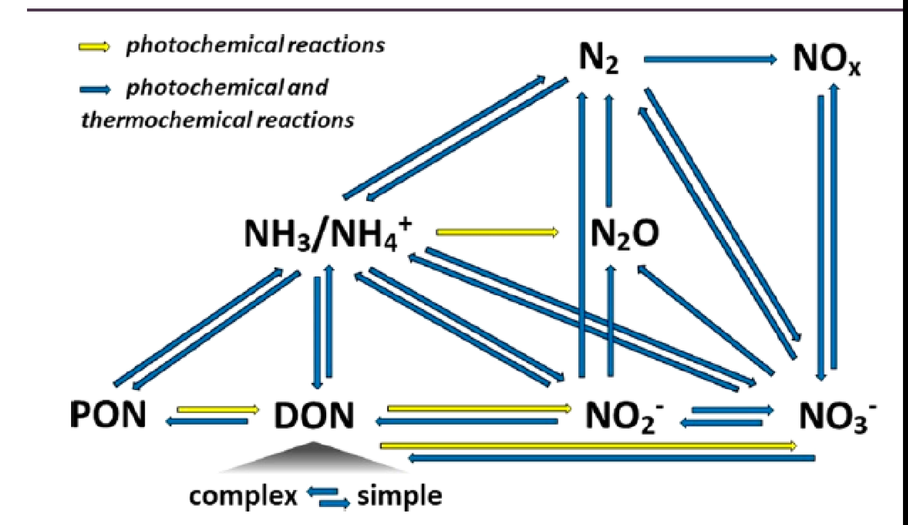
Geochimica et Cosmochimica Acta (2022), 336, 469-476,
https://doi.org/10.1016/j.gca.2022.08.038

# Abiotic Nitrogen species in a prebiotic environment




Modified from Branscomb and Russell, 2018, BioEssays, 41, 1800208.
Also: Wong et al. 2017; Astrobiology, 17, 975–983




Doane 2017; ACS Earth Space Chem, 1, 411−421

$NO_3^-$ + $NO_2^-$ can be reduced to $NH_3/NH_4^+$ by $Fe^{2+}$ and/or Fe(II)-bearing minerals

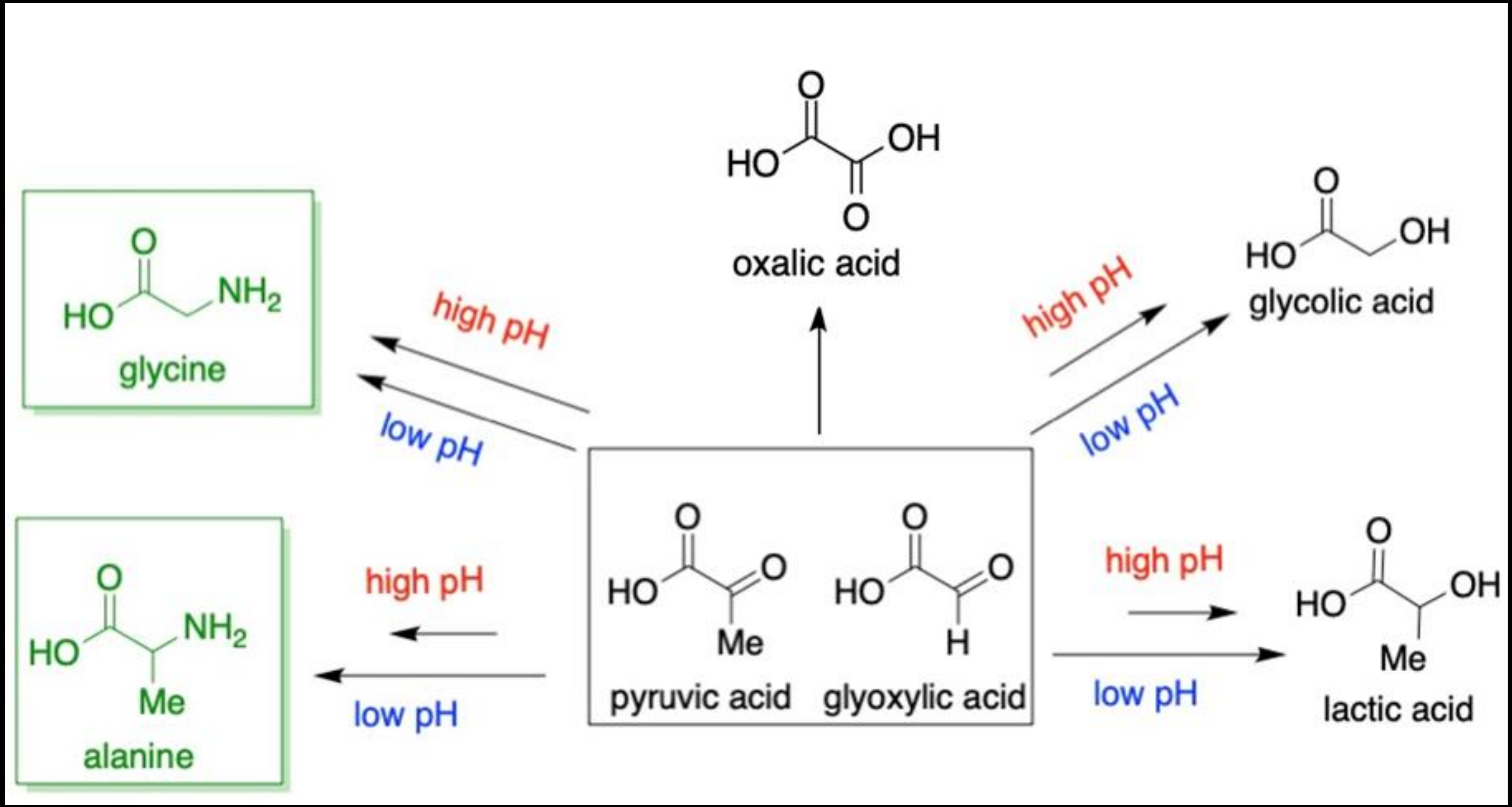
Dörr et al. (2003) Angew. Chem. Int. Ed. 2003, 42, 1540 – 1543
Hansen et al. 1996; Environmental Science & Technology, 30(6), 2053–2056
Summers and Khare 2007; Astrobiology, 7, 333–341

$NO_2^-$ is rapidly reduced by Fe(II) so is not thought to persist as much as $NO_3^-$ in surface waters

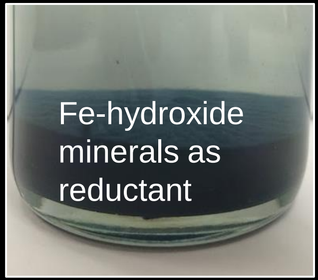
Ranjan et al. 2019, Geochemistry, Geophysics, Geosystems, 20, 2021–2039

# Example organic precursors: pyruvate and glyoxylate

**Amino acids** form when $NH_3/NH_4^+$ is added



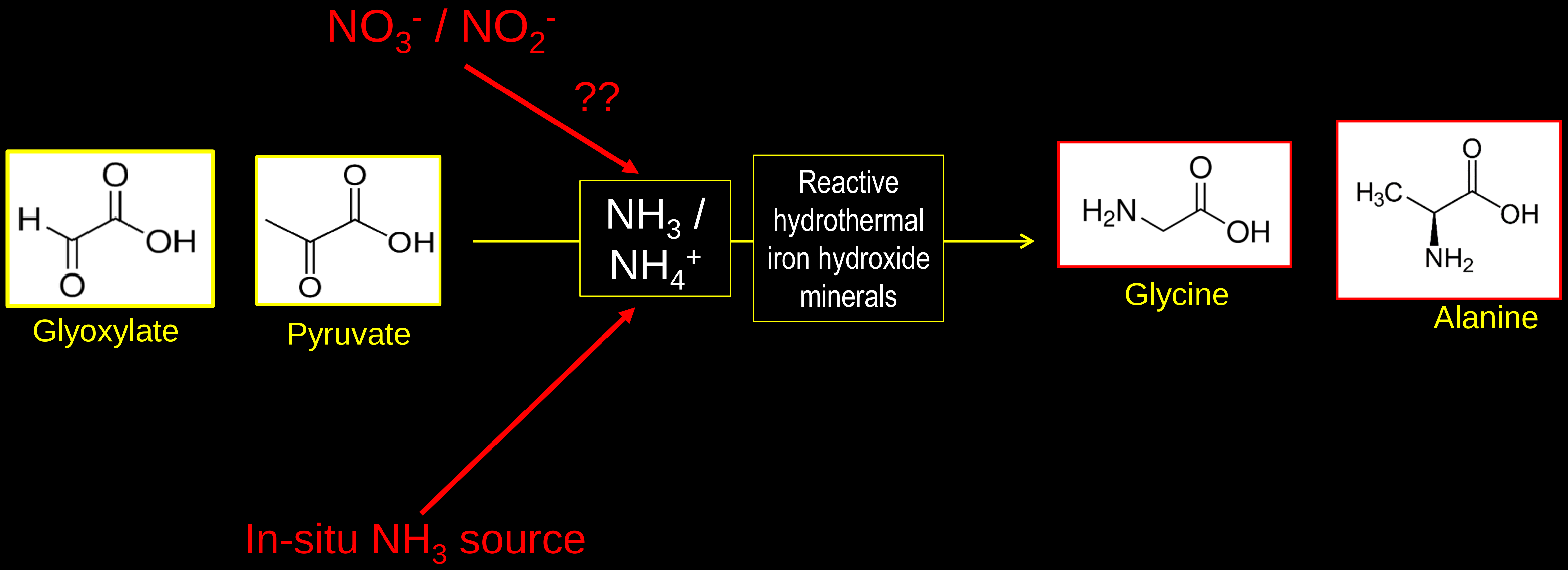

Reduction also occurs to form hydroxy-acids




Barge et al. (2020) Effects of Geochemical and Environmental Parameters on Abiotic Organic Chemistry Driven by Iron Hydroxide Minerals. *JGR-Planets,* e2020JE006423.
Barge et al. (2019) Redox and pH Gradients Drive Amino Acid Synthesis in Iron Oxyhydroxide Mineral Systems, *PNAS* 116 (11) 4828-4833.

# Questions for this study:

Can nitrate/nitrite generate the $NH_3$ to form amino acids in these reactions?
Or is an *in-situ* $NH_3$ source required to abiotically make amino acids?



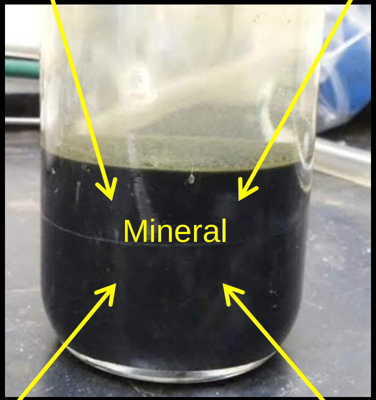
# Methods:

50 mM

$Fe(II)Cl_2 + Fe(III)Cl_3$

50 mM

NaOH




$NaNO_3$, $NaNO_2$, and/or $NH_4Cl$

various

Pyruvate or Glyoxylate

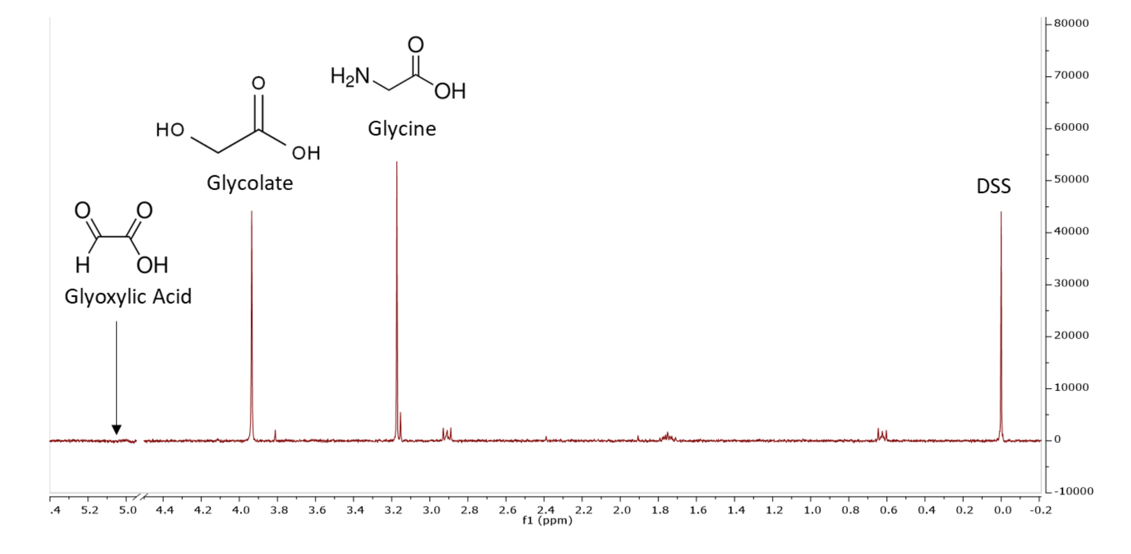
2.5 mM

Exp at pH 10, 70 C, 50 or 100% Fe(II)

Shake, sample, centrifuge

Freeze-dry solids for XRD

Analyze liquid (organic products)




$^1H$ liquid Nuclear Magnetic Resonance (NMR) spectroscopy (and confirmed with Q-TOF/MS)

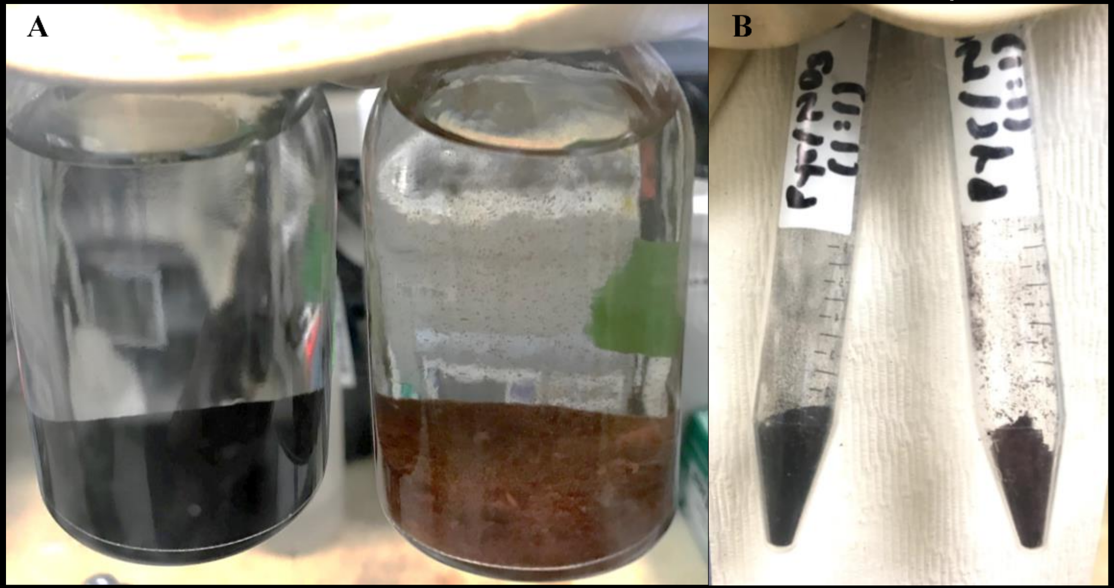
Dissolve in acid
Analyze liquid + solid (colorimetry), IC

Fe(II) / Fe(III) ratio
$[NO_3^-]$, $[NO_2^-]$
$[NH_4^+]$

# Results: Nitrate / nitrite-driven Fe oxidation

t = 4 days

Dried samples




Glyoxylate / $NO_3^-$
Fe(II):Fe(III) = 1:1

Pyruvate / $NO_2^-$
Fe(II):Fe(III) = 1:1

Pyruvate / $NO_3^-$ or $NO_2^-$
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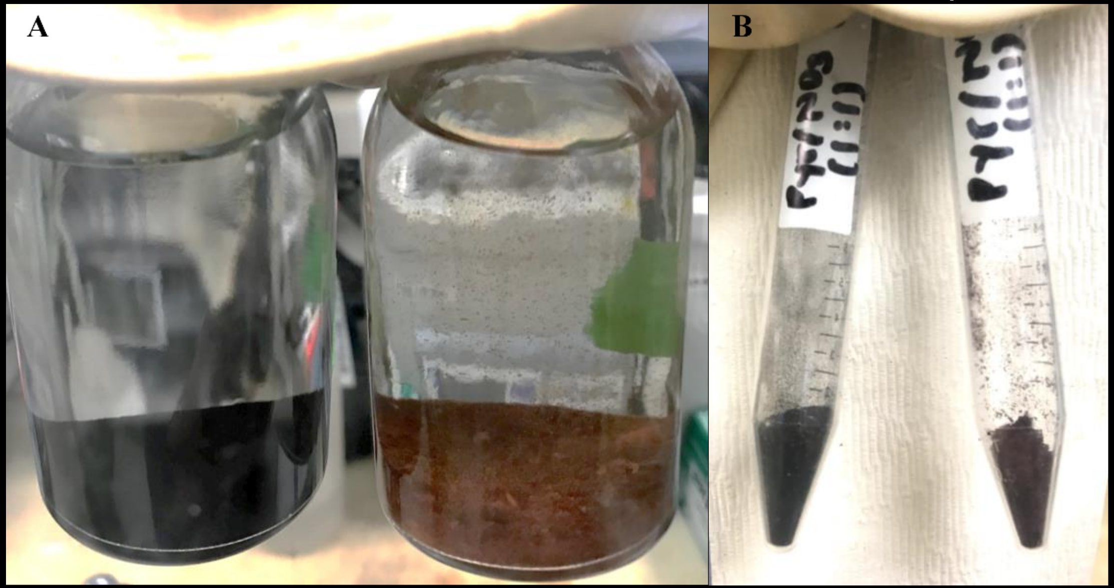


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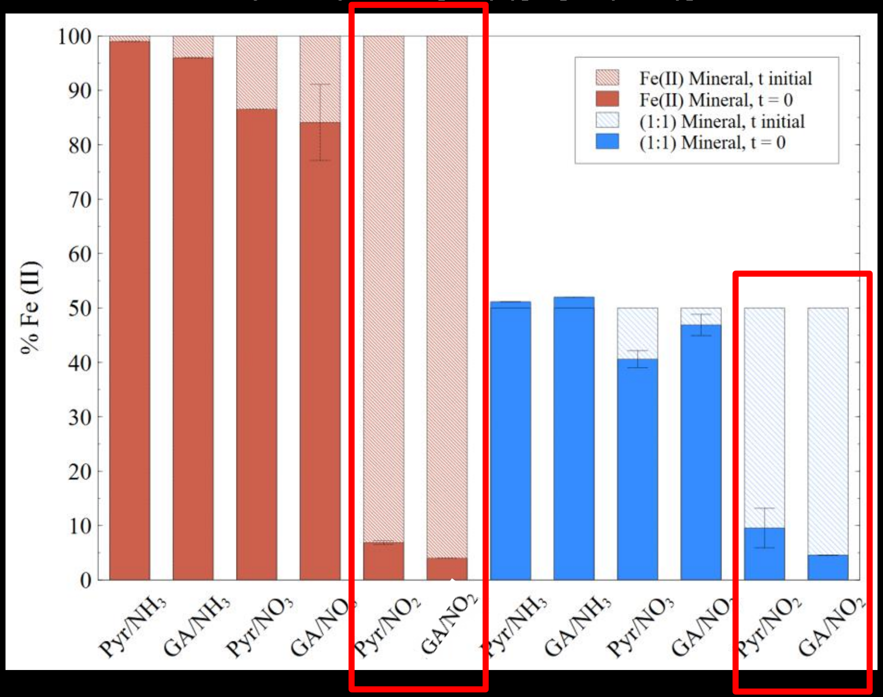
Colorimetry analysis of [Fe(II)] / [Fe(total)]




**$NO_2^-$ containing experiments exhibit a high degree of Fe oxidation**

$NO_3^-$ containing experiments also exhibit some Fe oxidation

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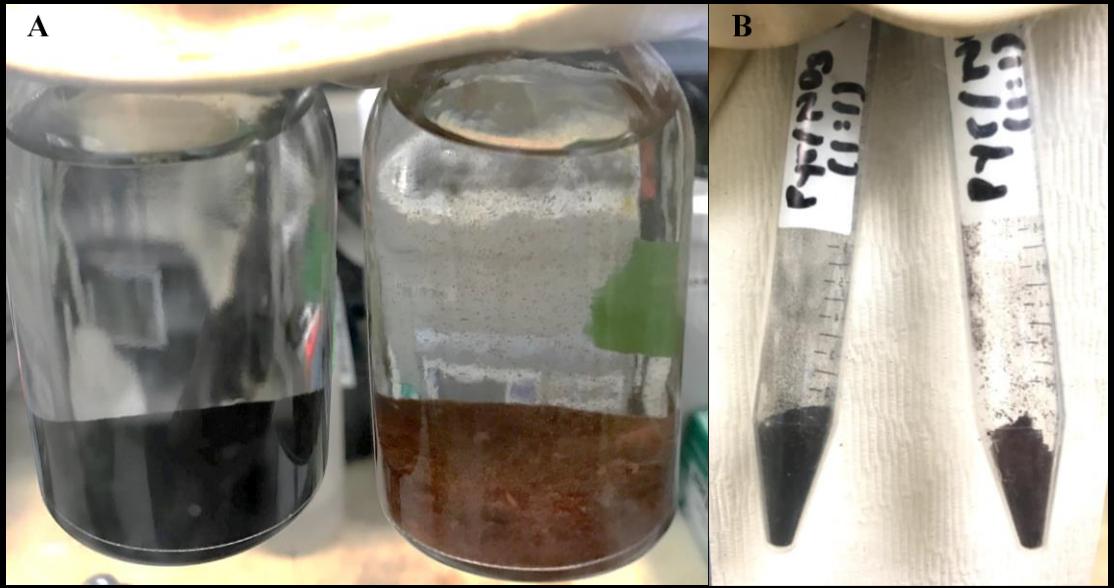


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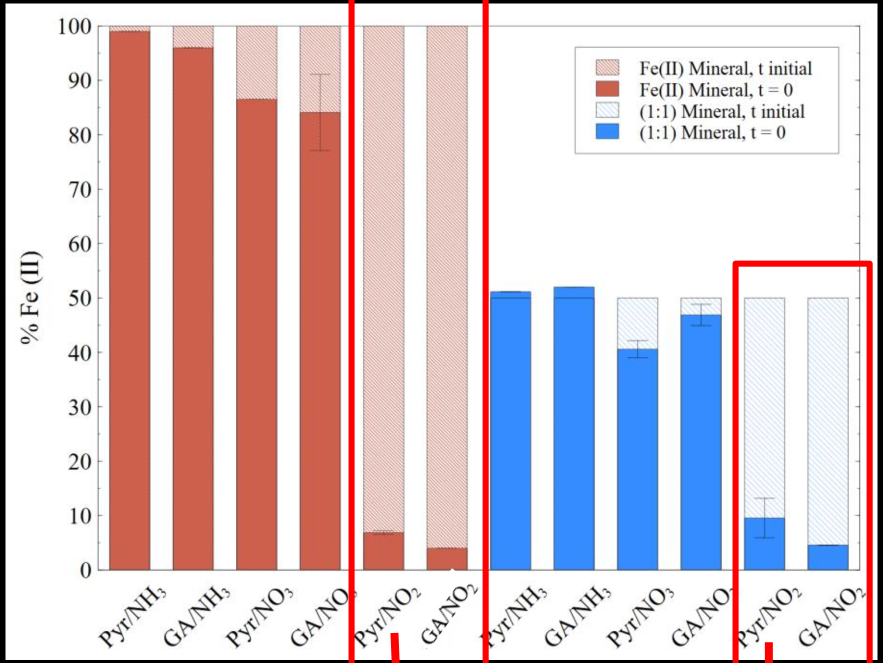


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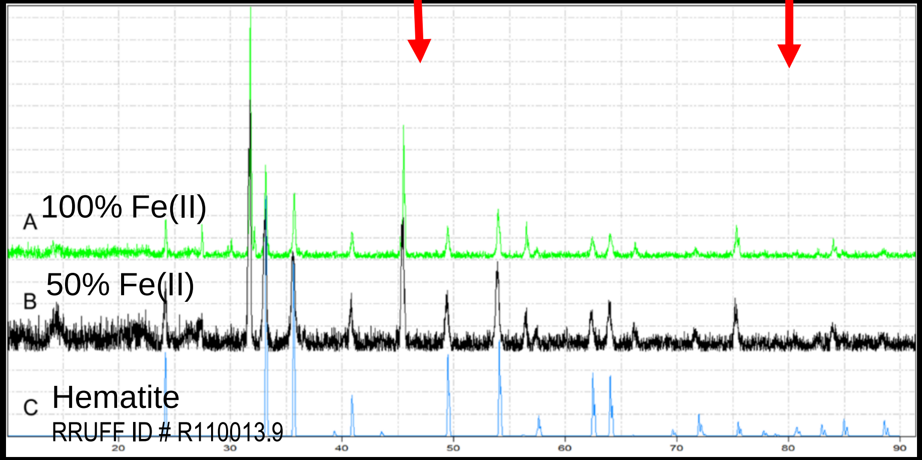
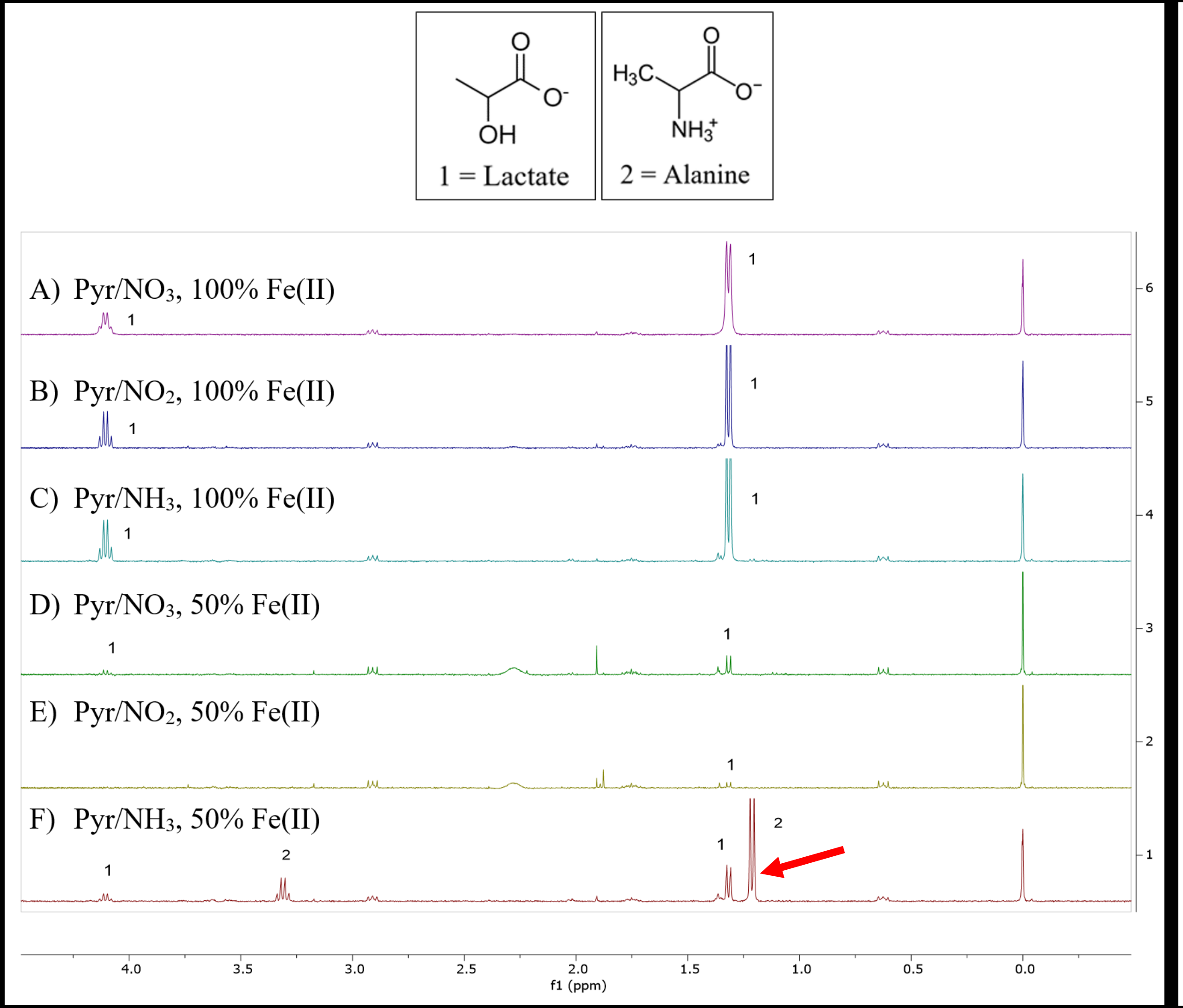
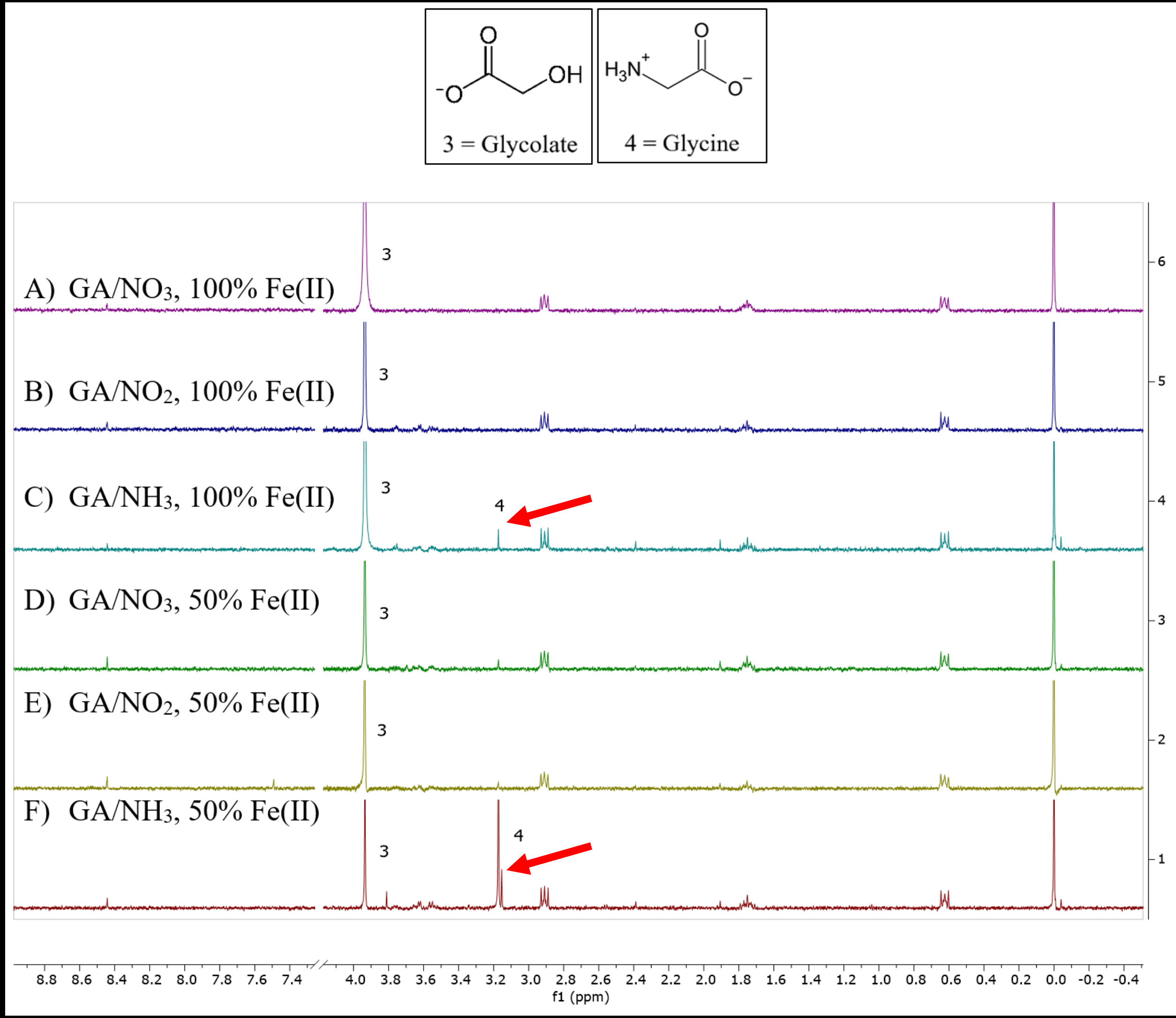



XRD: Pyruvate / $NO_2^-$ experiment

Precipitates from $NO_2^-$ containing experiments match well to hematite (Fe(III)-oxyhydroxide)

# Results: Organic reactions

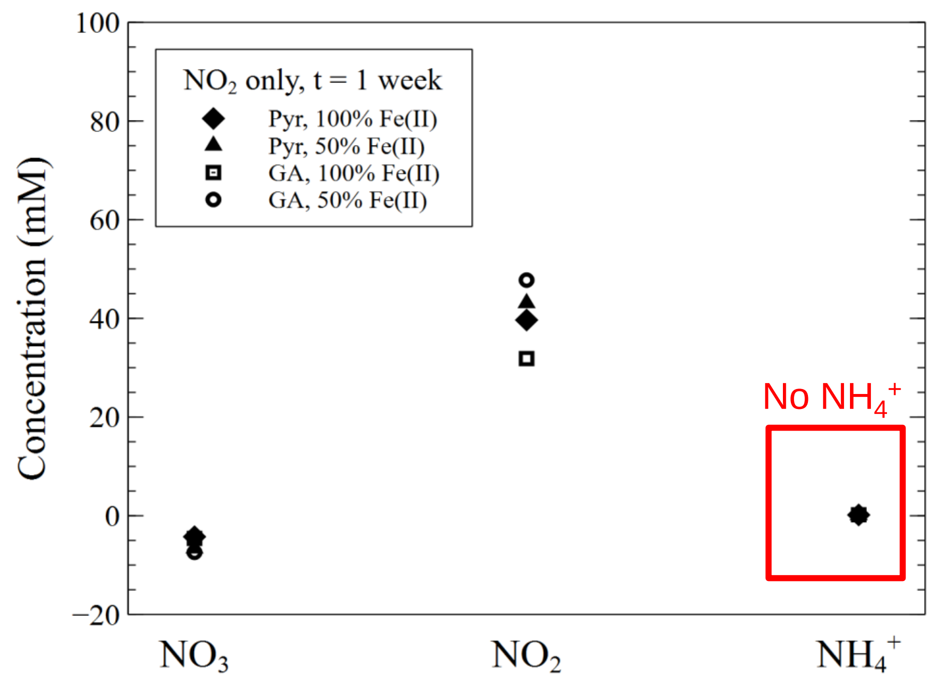


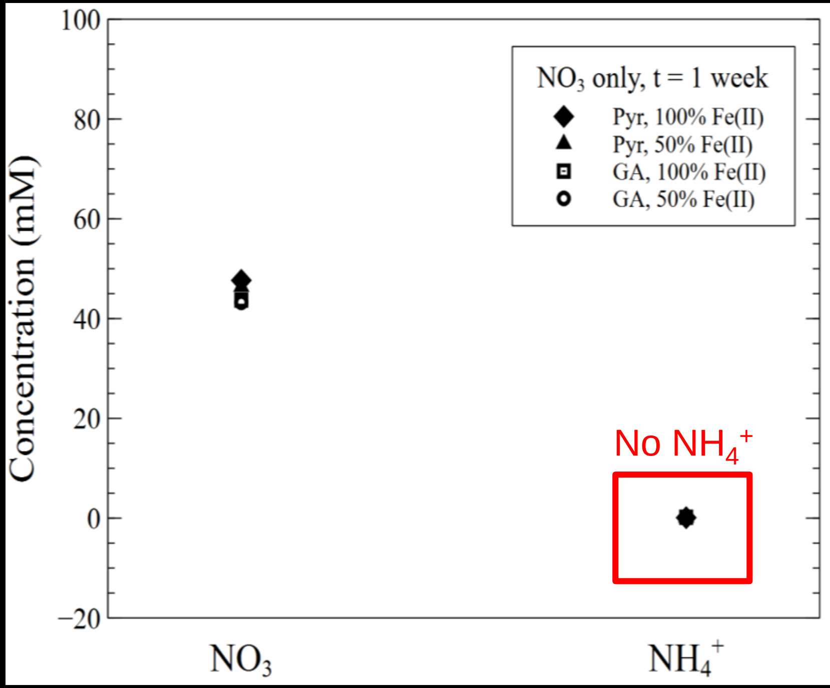

No amino acids formed in experiments with only nitrate or nitrite, despite evidence that nitrate/nitrite reduction was occurring.

# Results: Organic reactions

50 mM $NO_2^-$




50 mM $NO_3^-$



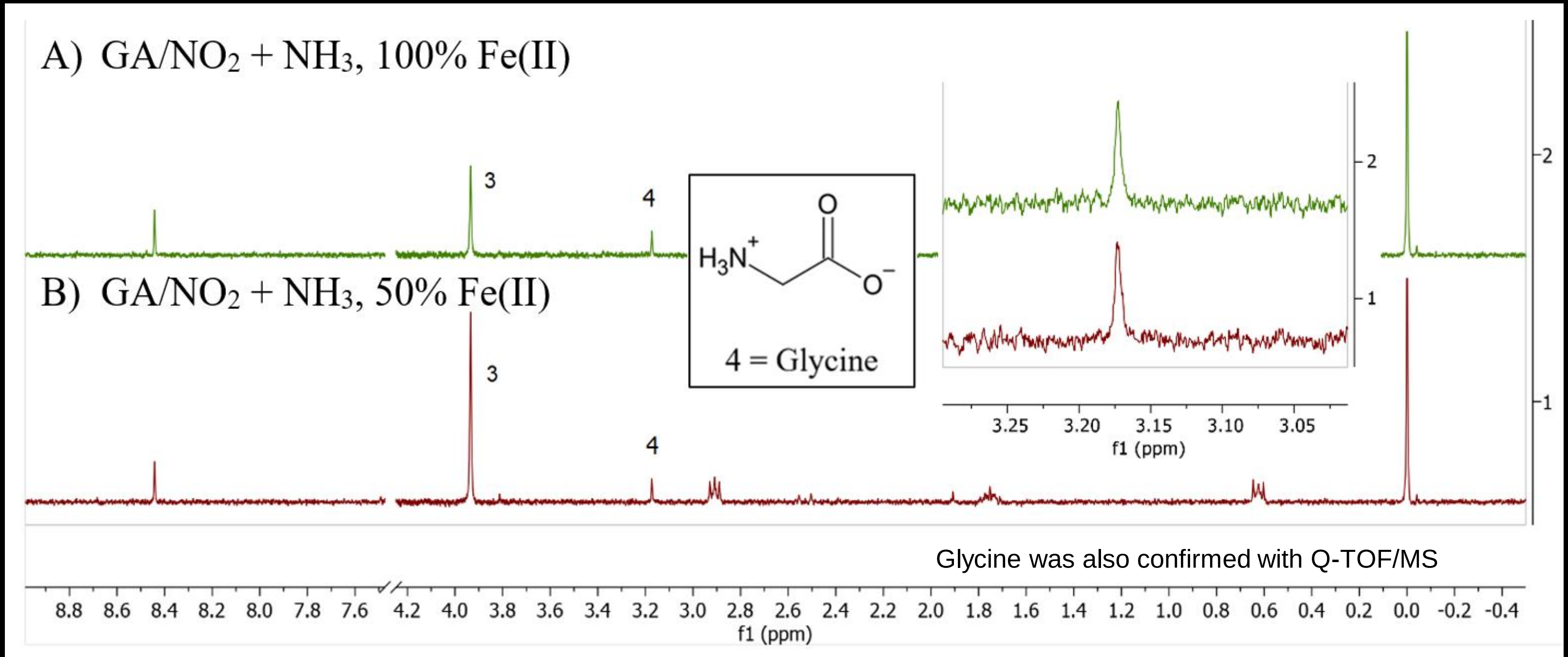

But $NO_3$ / $NH_4$ colorimetry analysis indicates that $NH_4$ is not present.

Is $NO_3^-$ / $NO_2^-$ reducing to different products?

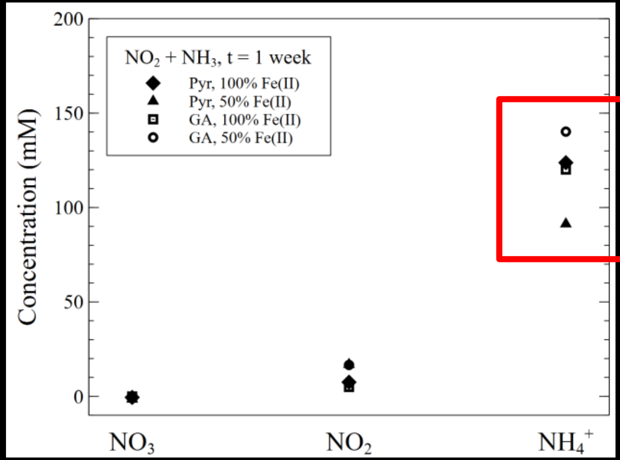
Or is $NH_4$ being produced and then being consumed by some other process?

**Test: Add more $NH_4$ to the $NO_2^-$ experiments and see if AA's form.**

# Results: Organic reactions




The $NH_4$ we added is still there after 1 week, so it is not being otherwise consumed




25 mM $NO_2$ + 50 mM $NH_3$

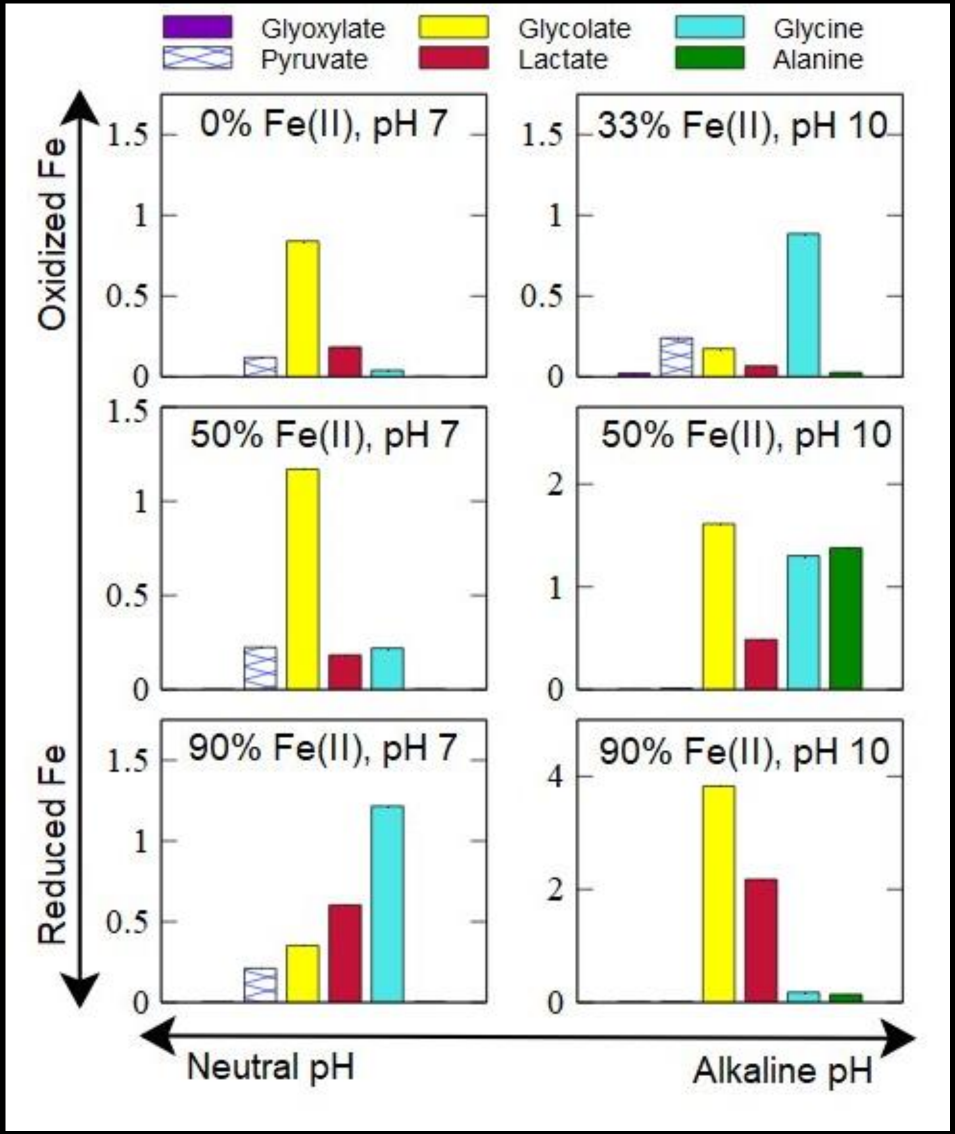
**Addition of 50 mM $NH_4Cl$ to a 25 mM $NO_2^-$ + glyoxylate experiment did lead to detectable glycine formation.**

We did many versions but this was the only ‘ammonia addition’ experiment that formed any AA’s.

# Discussion: Amino acid formation

- Our previous work showed that the **%Fe(II) in the Fe-hydroxide mineral** is a primary driver of whether amino acids form from pyruvate and glyoxylate (+ $NH_4$).
  - Even at low [$NH_4$] we saw AA formation, BUT only at the right %Fe(II) mineral values.

- In our $NO_2^-$ experiments,
  - a) $NH_4$ is not being generated
  - b) the Fe mineral oxidation prevents AA formation under most conditions, even if $NH_4$ is added.




Barge et al. (2020) JGR-Planets, e2020JE006423.

# Conclusions

- We observed Fe oxidation in experiments containing $NO_2^-$ / $NO_3^-$
- However, there is no indication of $NH_3$/$NH_4^+$ formation from $NO_2^-$ / $NO_3^-$ reduction.
- Amino acids only formed when an extra source of $NH_4^+$ was added
- This is probably because the Fe(II)/Fe(III) ratio in the mineral is a main factor in AA formation from these precursors; and $NO_2^-$ drives near complete Fe oxidation.
- For astrobiology: it is important to understand how Fe / N redox chemistry affects prebiotic reactions, to predict environments where AA's could form on early Earth or Mars.