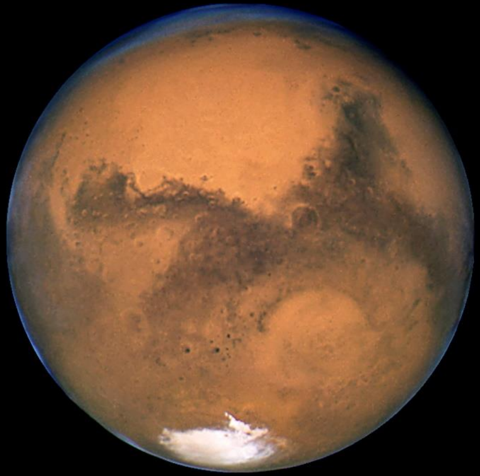
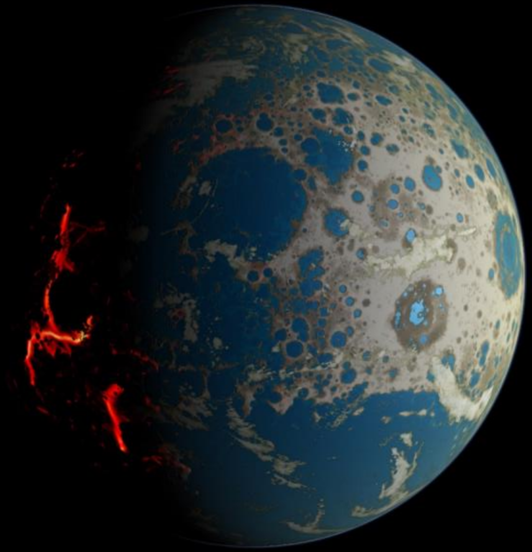
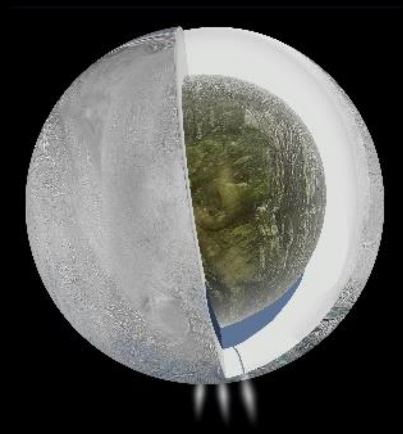
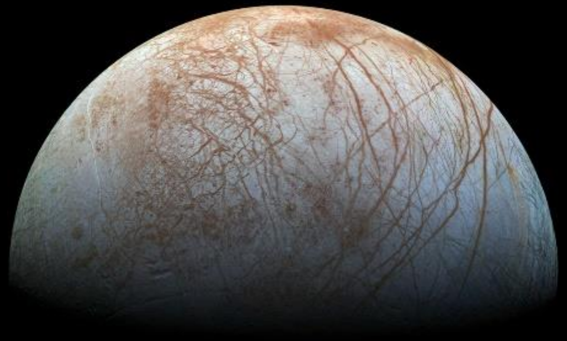
Abiotic / Prebiotic Organic Synthesis







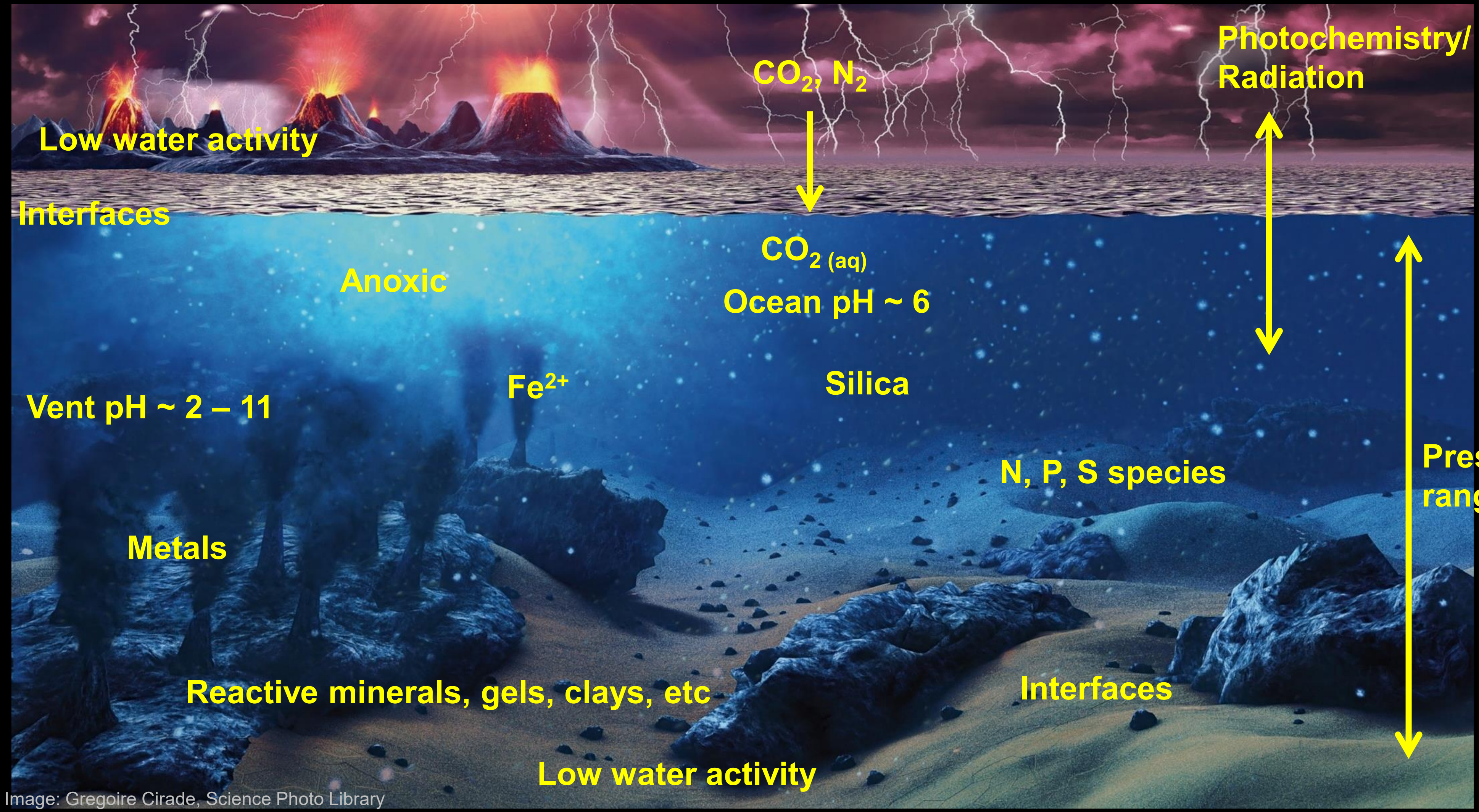


Laurie Barge, Ph.D.

Senior Research Scientist, NASA Jet Propulsion Laboratory
California Institute of Technology

Image: Gregoire Cirade, Science Photo Library

Early Earth



Early Earth

Many varied environments, each containing multiple different reaction conditions

Example of an environment with varying conditions: Hydrothermal vents

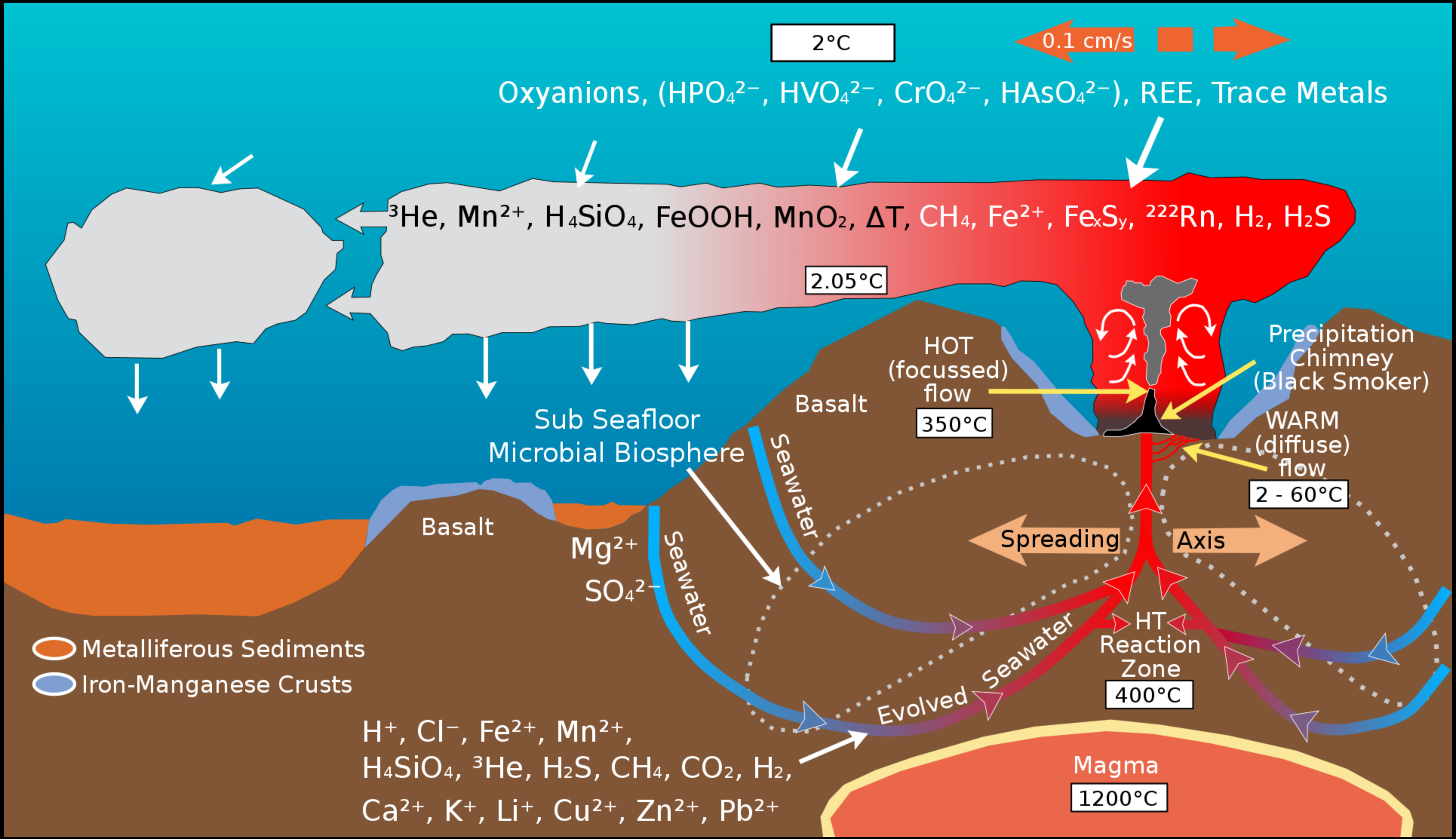
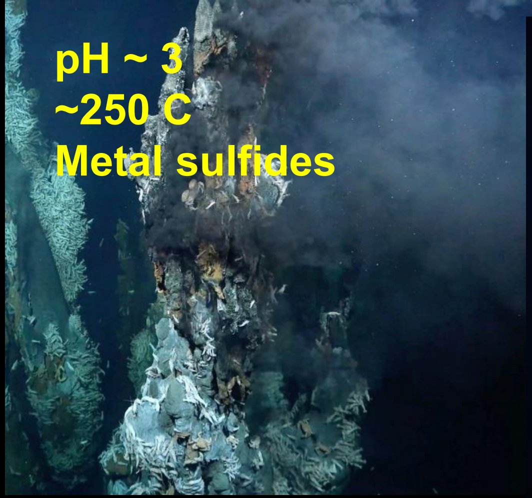


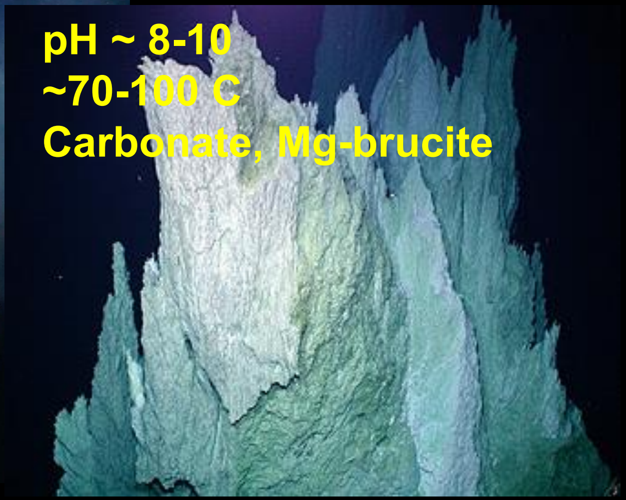
Image: NOAA

Hydrothermal systems contain many different conditions

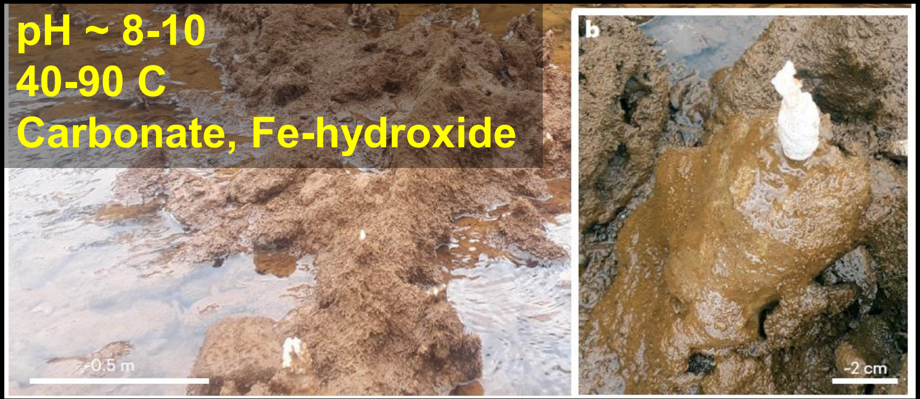
Strytan Hydrothermal Field, Iceland



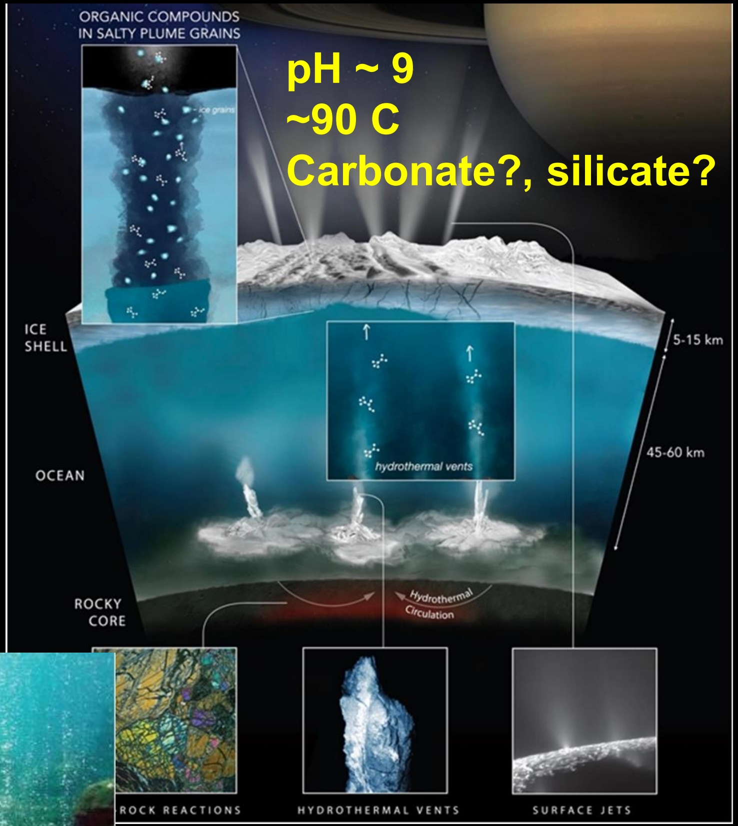
Puy des Folles Seamount, MAR



Lost City Hydrothermal Field



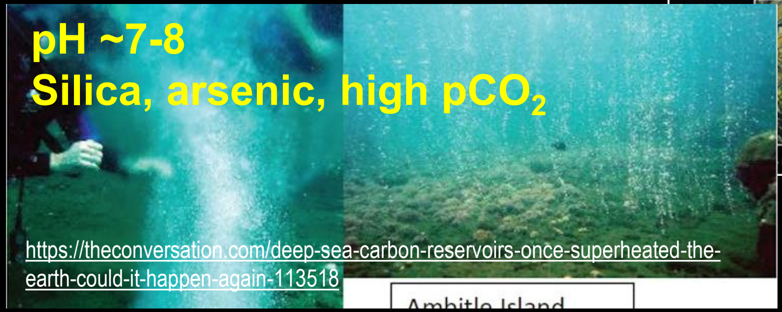
Prony Hydrothermal Field, New Caledonia



Saturn's moon Enceladus

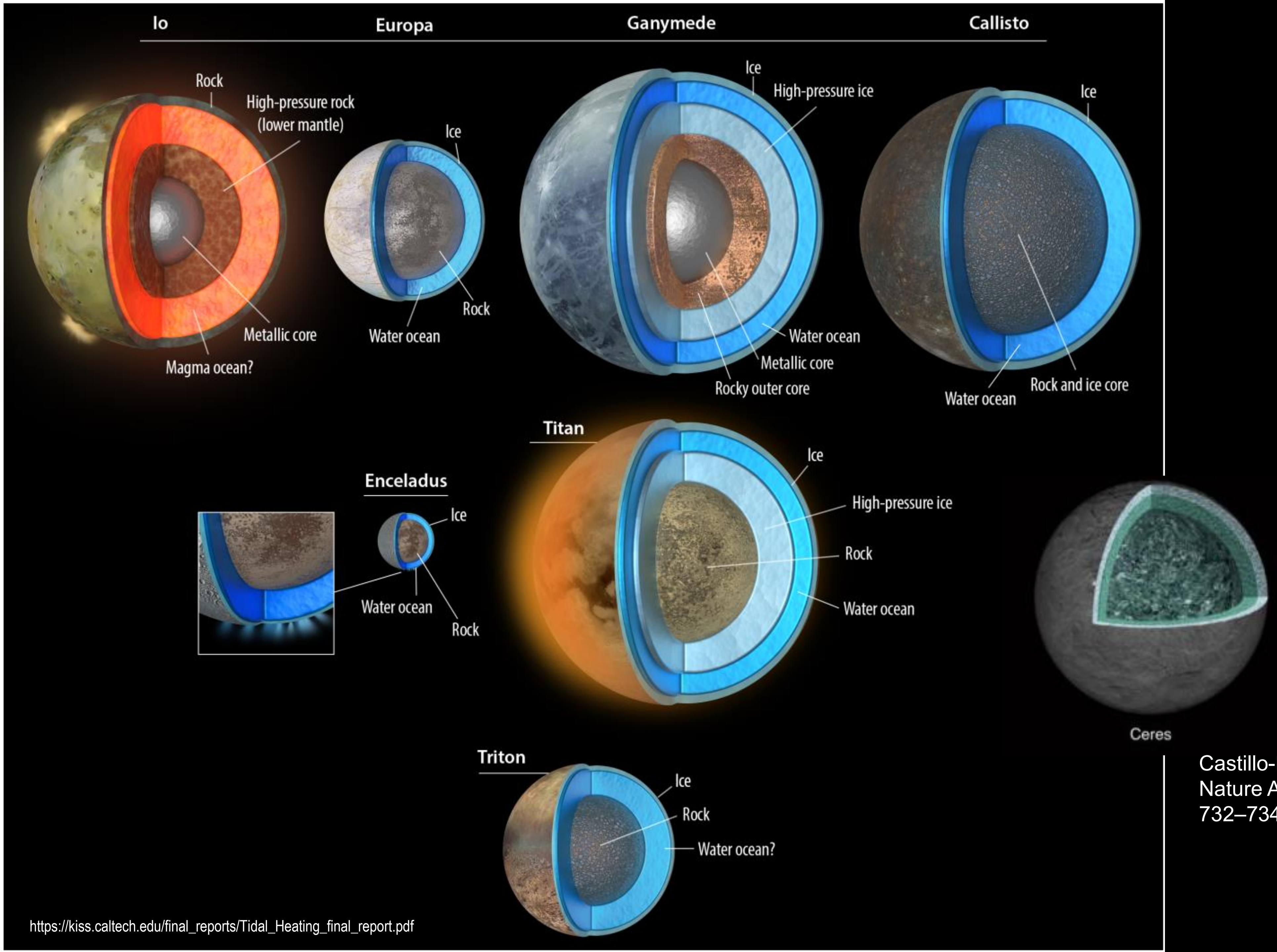
Old City Hydrothermal Field, SW Indian Ridge

Carbonate, Mg-brucite



Ambitle Island, Papua New Guinea

Ocean Worlds



Ceres

Castillo-Rogez, 2020
Nature Astronomy 4,
732–734

Example of an organic reaction affected by changing conditions

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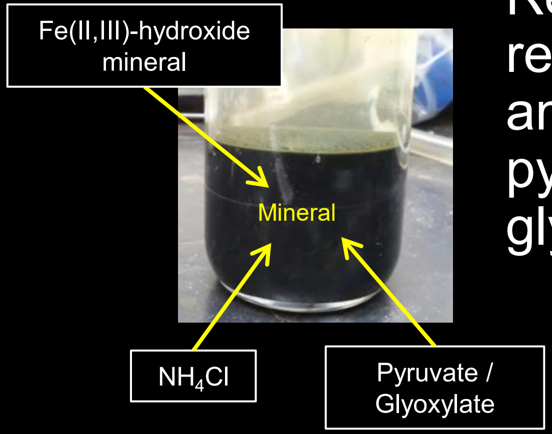
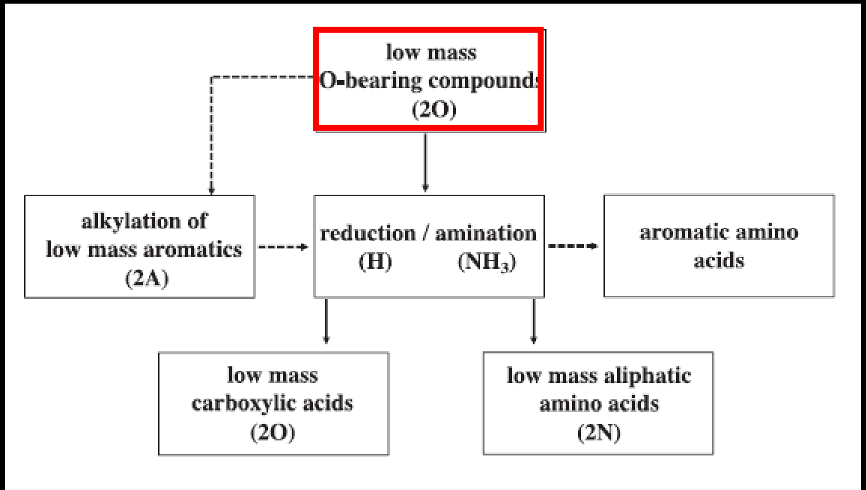
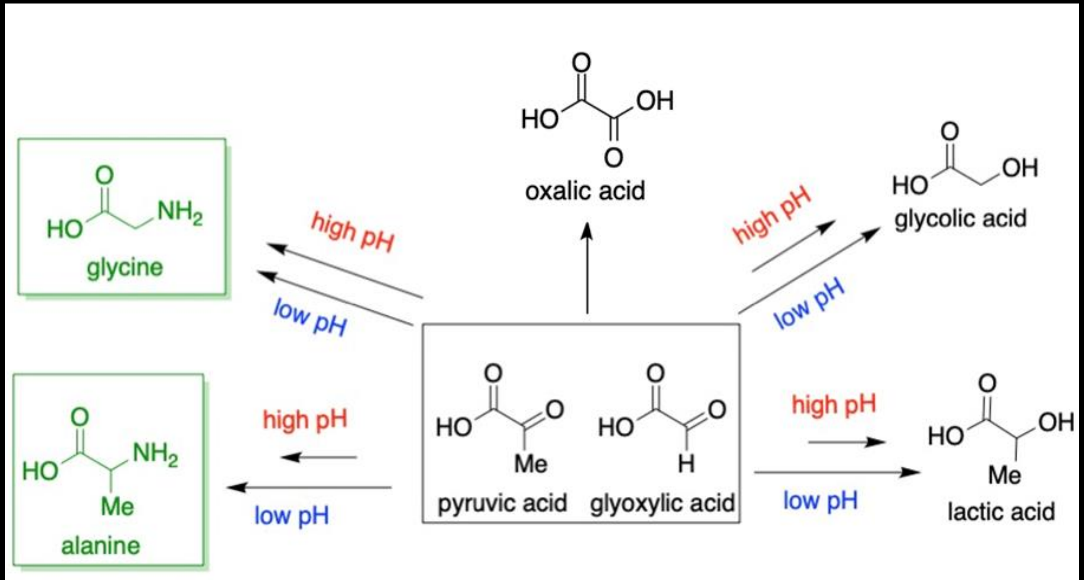


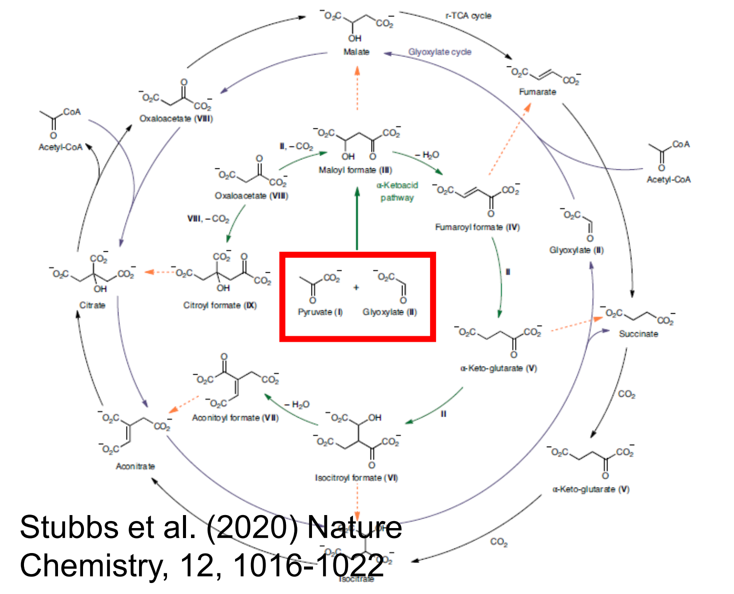
Reduction / reductive amination of pyruvate & glyoxylate



Khawaja et al. 2019, MNRAS 489, 5231–5243



Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833



Stubbs et al. (2020) Nature Chemistry, 12, 1016-1022

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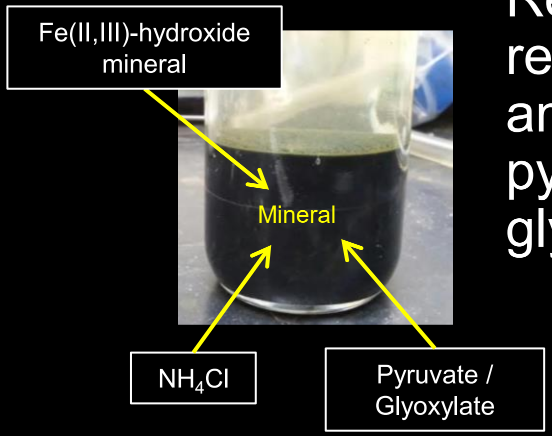

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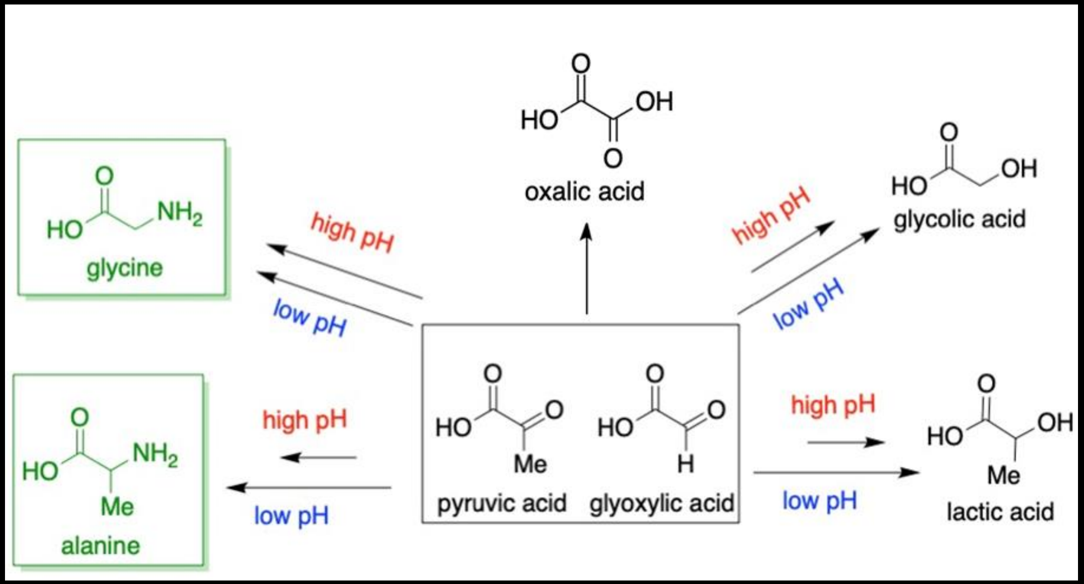


A simple abiotic organic reaction with known products – but, geochemical conditions can affect the reaction outcome:

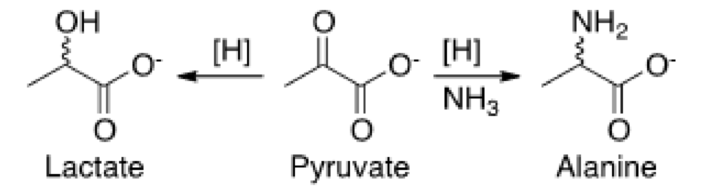
- Fe(II)/Fe(III) ratio
- pH
- N species and concentration
- Temperature
- Presence of competing ions (e.g. phosphate)

Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833

Effect of iron hydroxide mineral Fe(II)/Fe(III) ratio

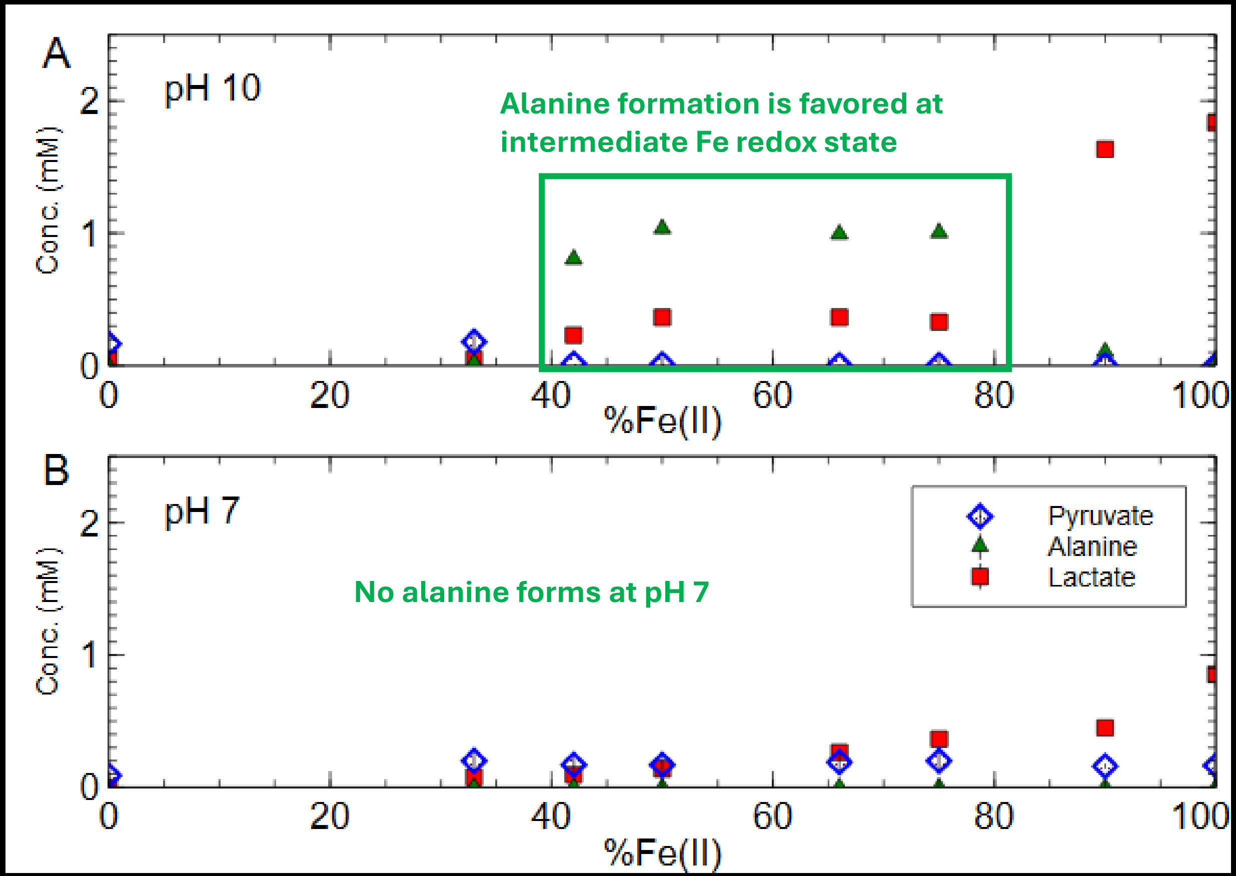
Effect of iron hydroxide mineral Fe(II)/Fe(III) ratio

Pyruvate reacts to form alanine and lactate in the presence of minerals, but the Fe redox state determines which product is favored



T = 70°C

100% Fe(III)



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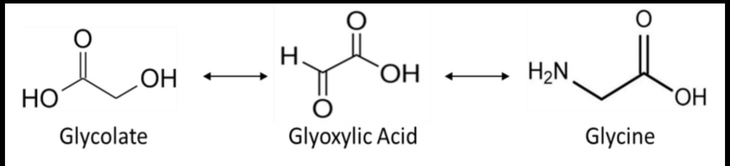
Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833

Effect of iron hydroxide mineral Fe(II)/Fe(III) ratio

Glyoxylic Acid forms glycine under many conditions; but the ratio of products depends on Fe redox state



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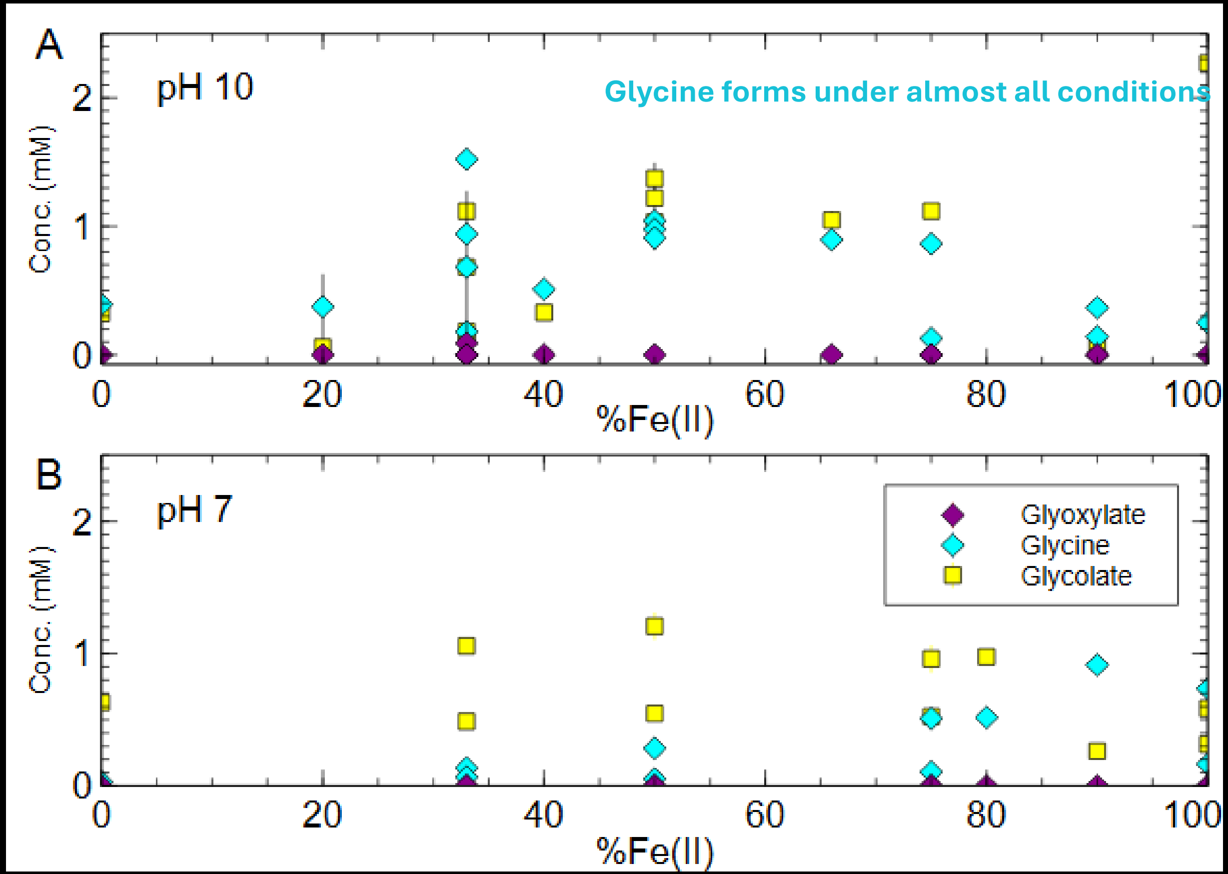

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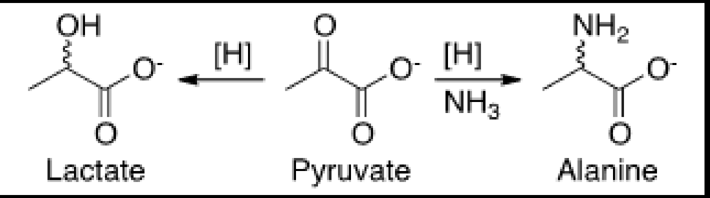
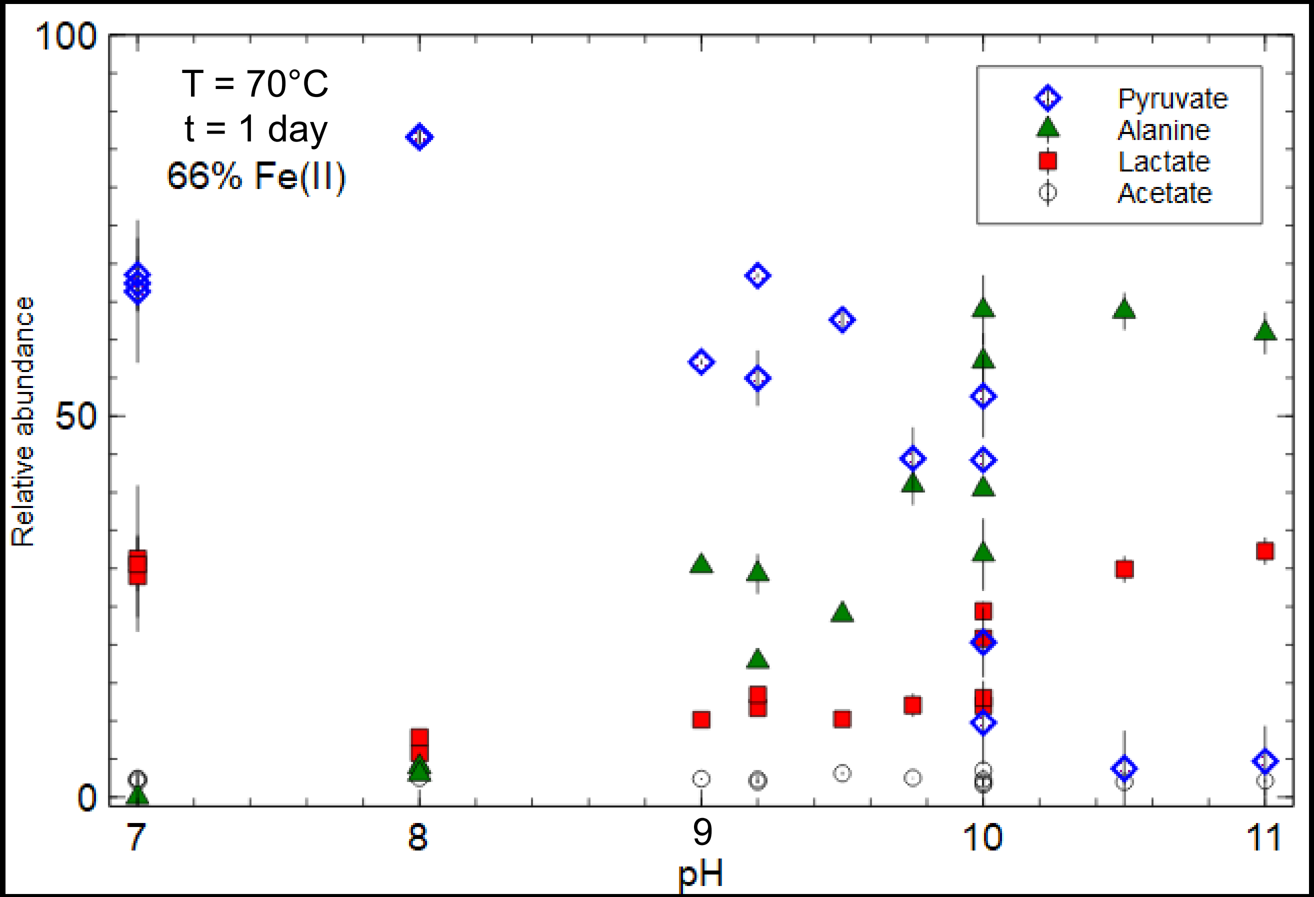
Barge et al. 2019, *PNAS* 116 (11) 4828-4833

Effect of pH

Effect of pH

Pyruvate reduction to form lactate is favored at low pH
Reductive amination to alanine is accelerated above the pK_a of ammonia





$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

$pK_a = 9.25$

Barge et al. (2019) *PNAS* 116 (11) 4828-4833

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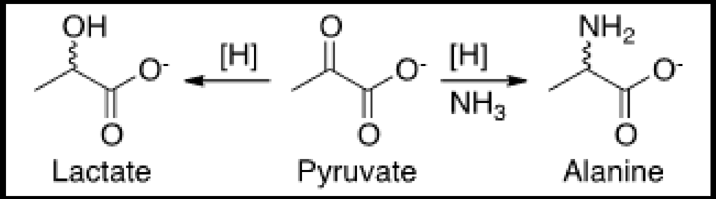

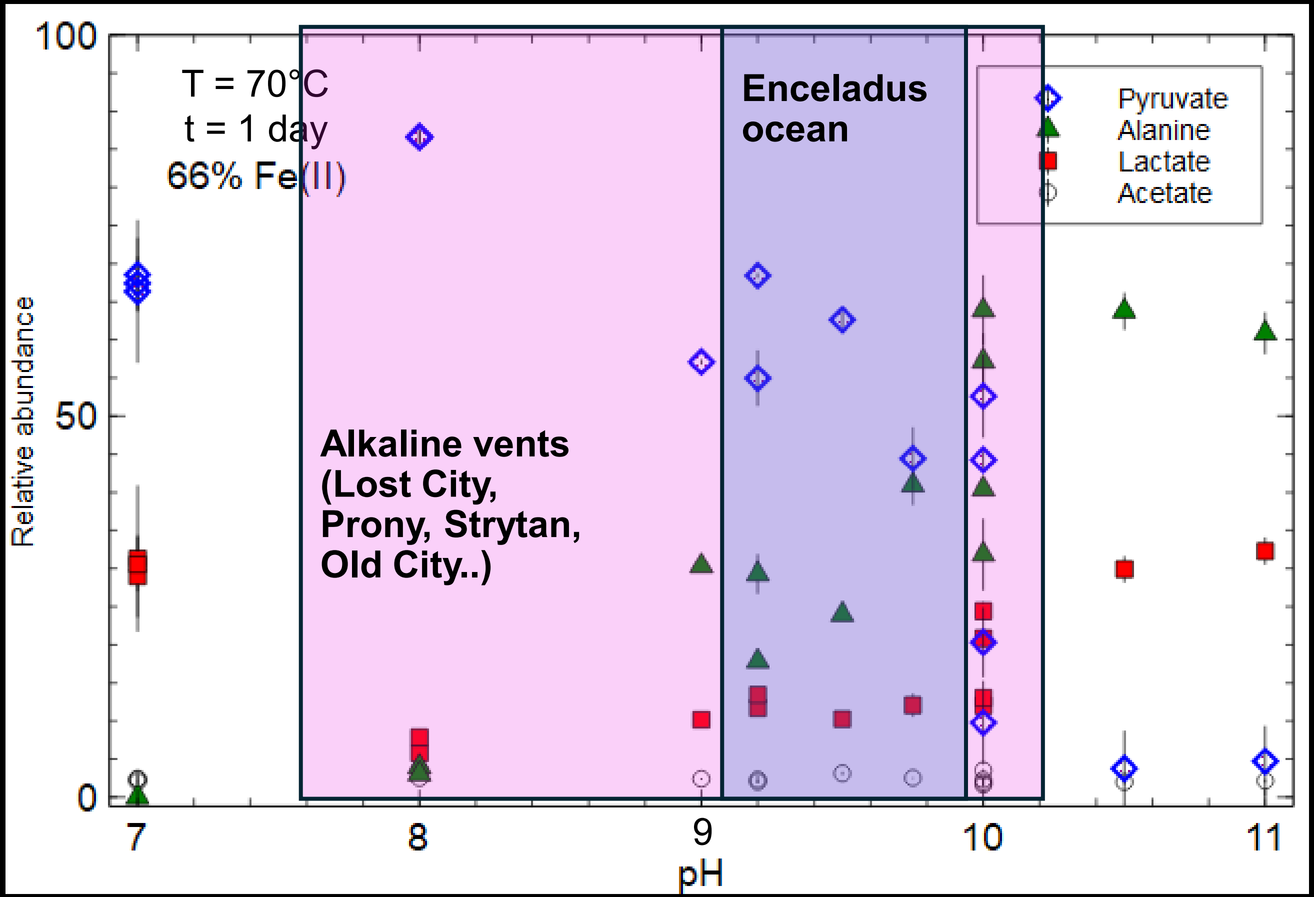

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Effect of Minerals and Temperature

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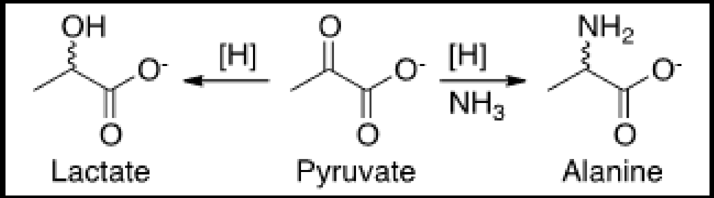
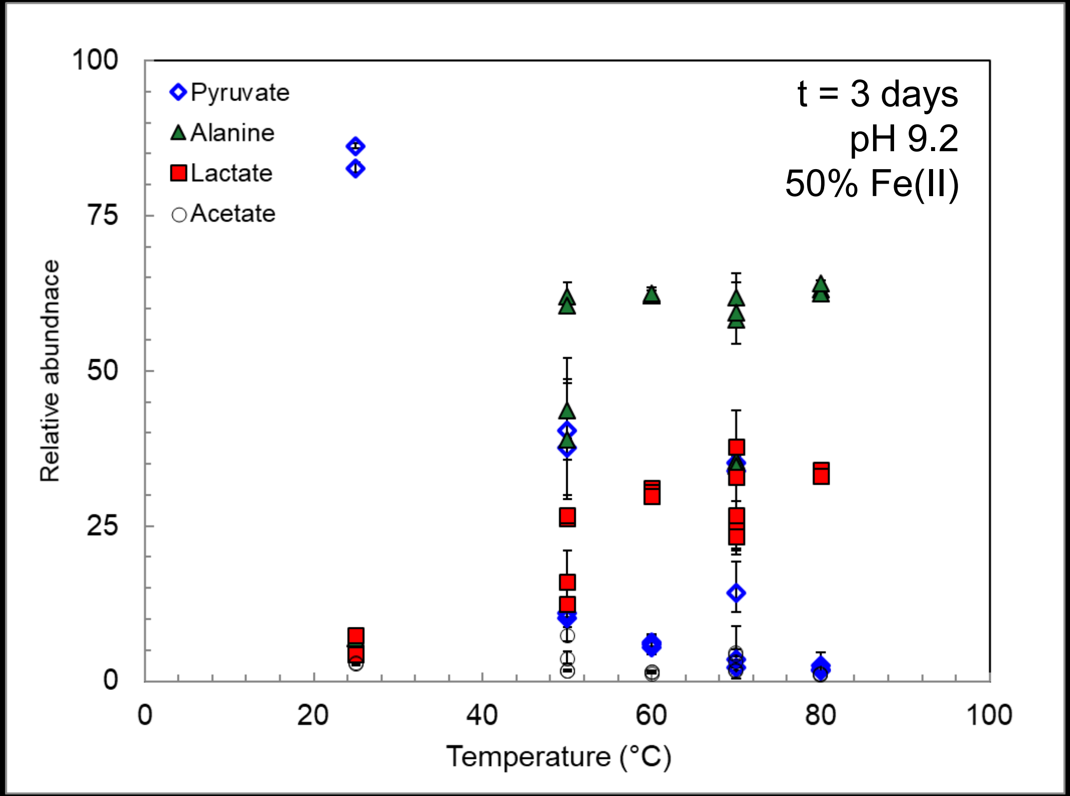


Temperature speeds up the reaction between 25 – 50 °C



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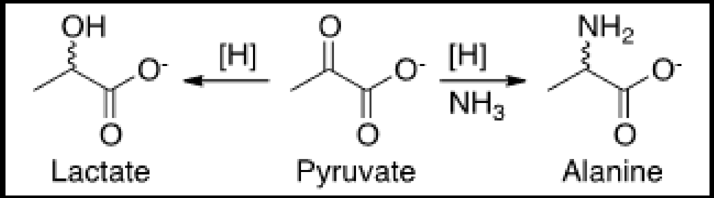

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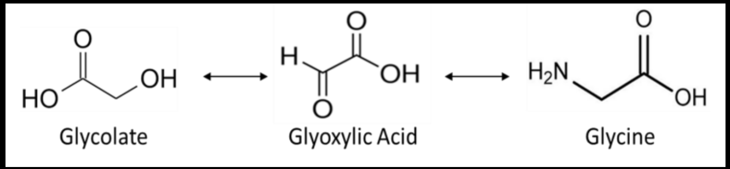
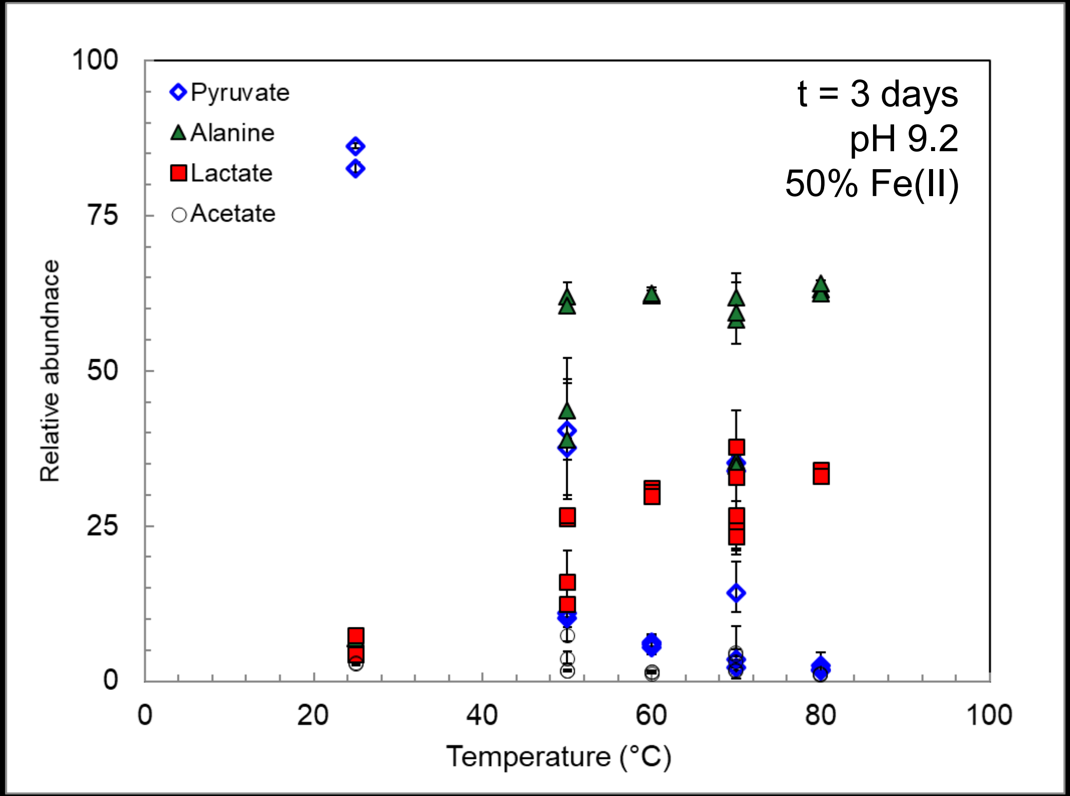
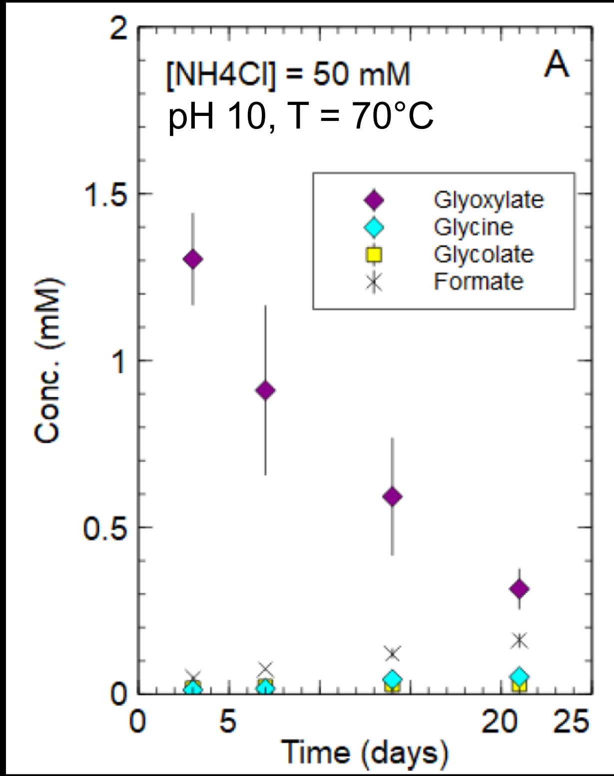


With no mineral, the reaction occurs but slowly





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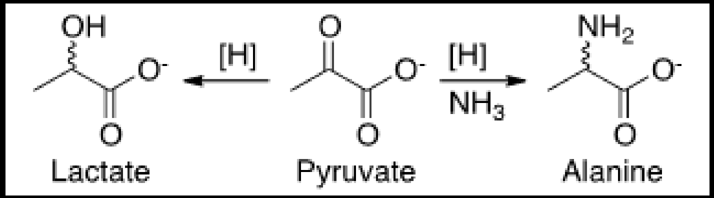

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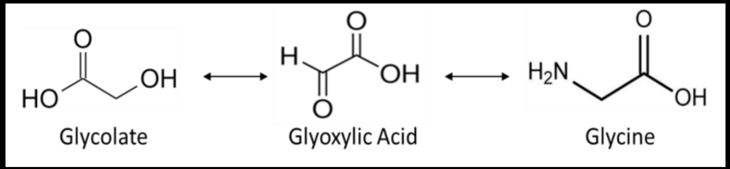

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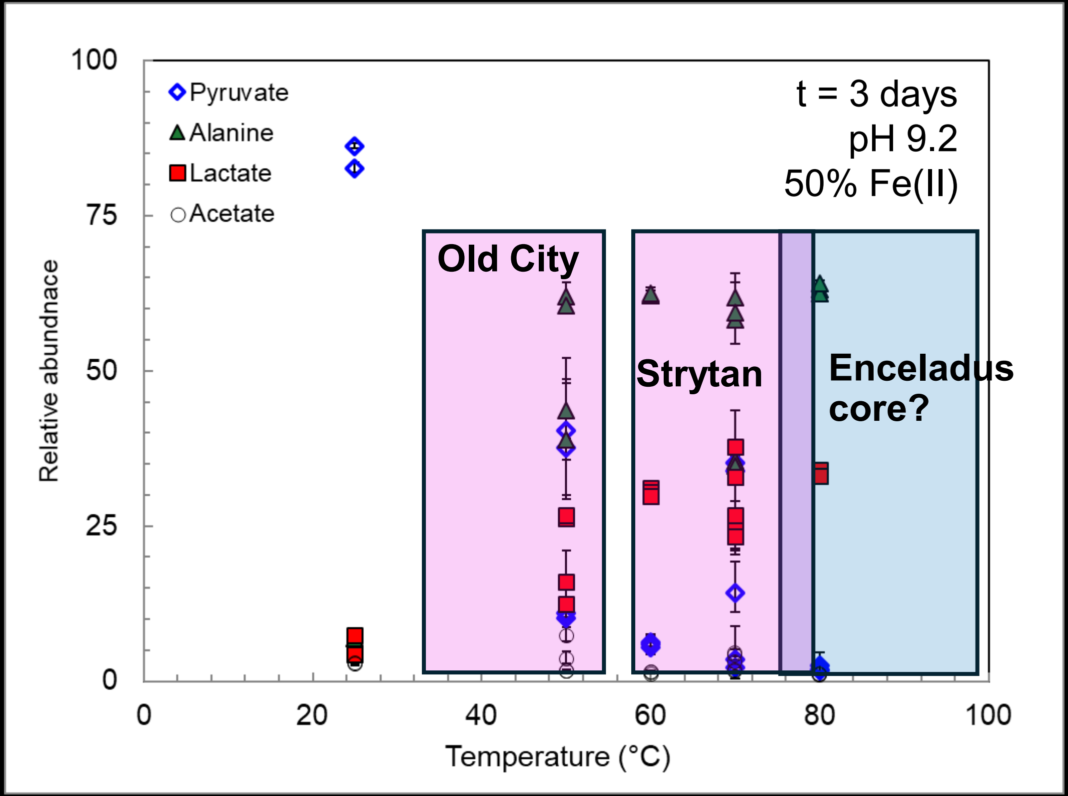

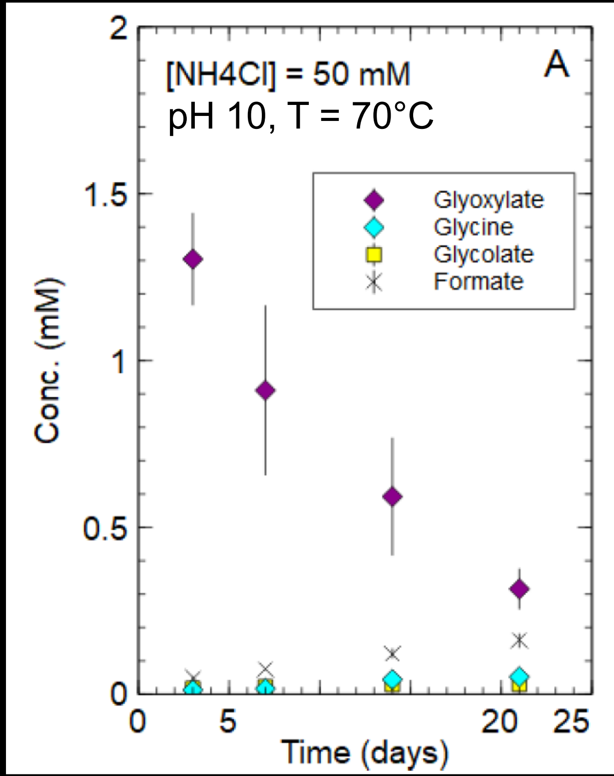

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Barge et al. 2019, *PNAS* 116 (11) 4828-4833

Effect of ammonia concentration

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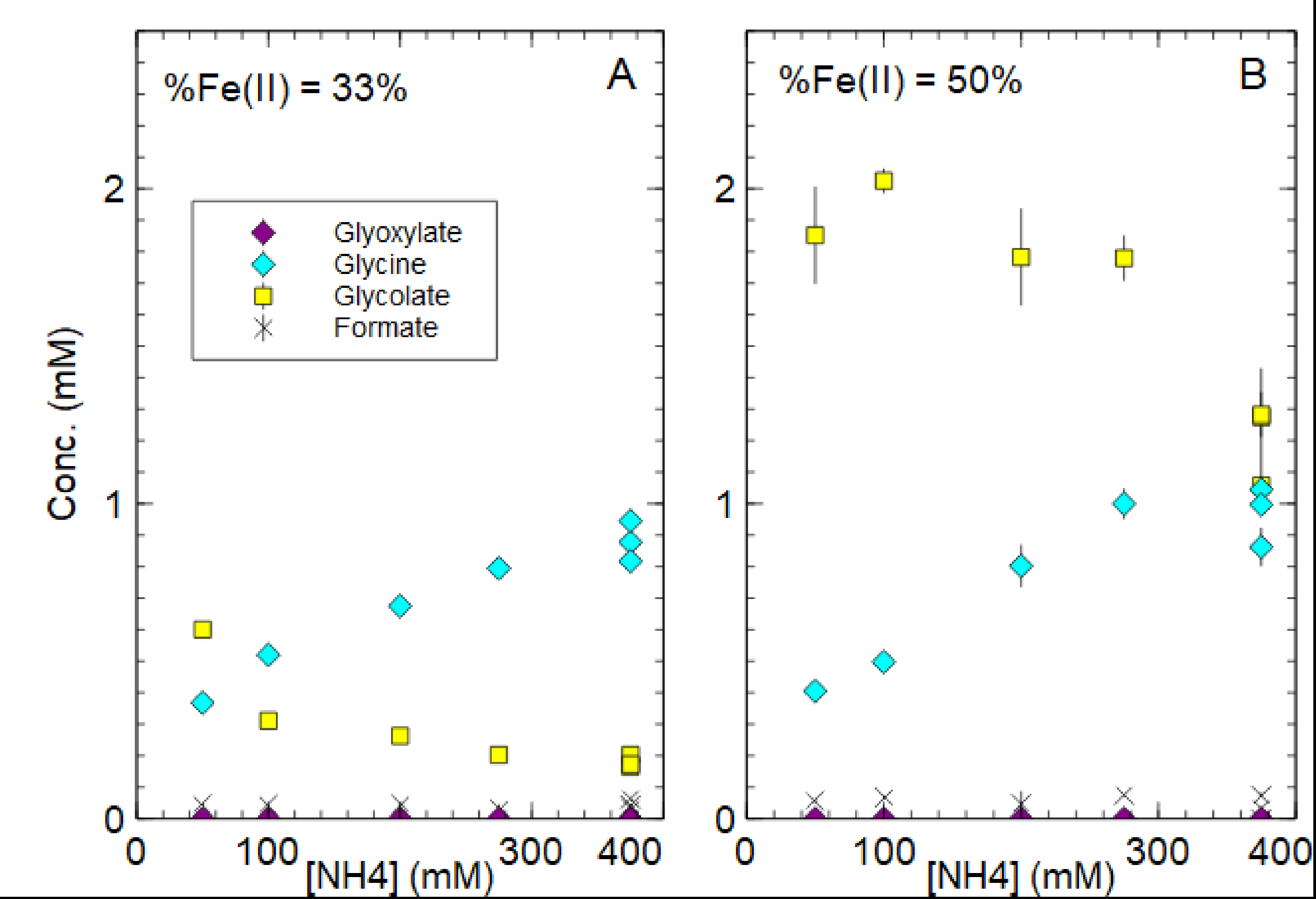
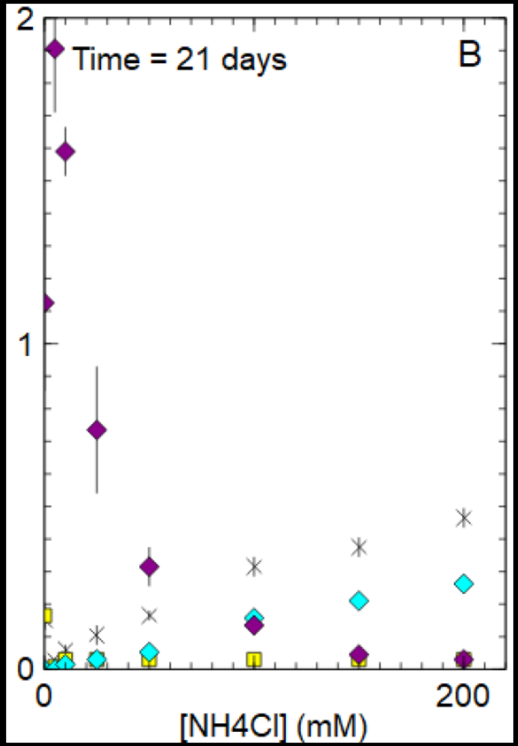
Increasing [NH_4] increases glycine yield at a given %Fe(II).

pH 10

t = 3 days



With no mineral



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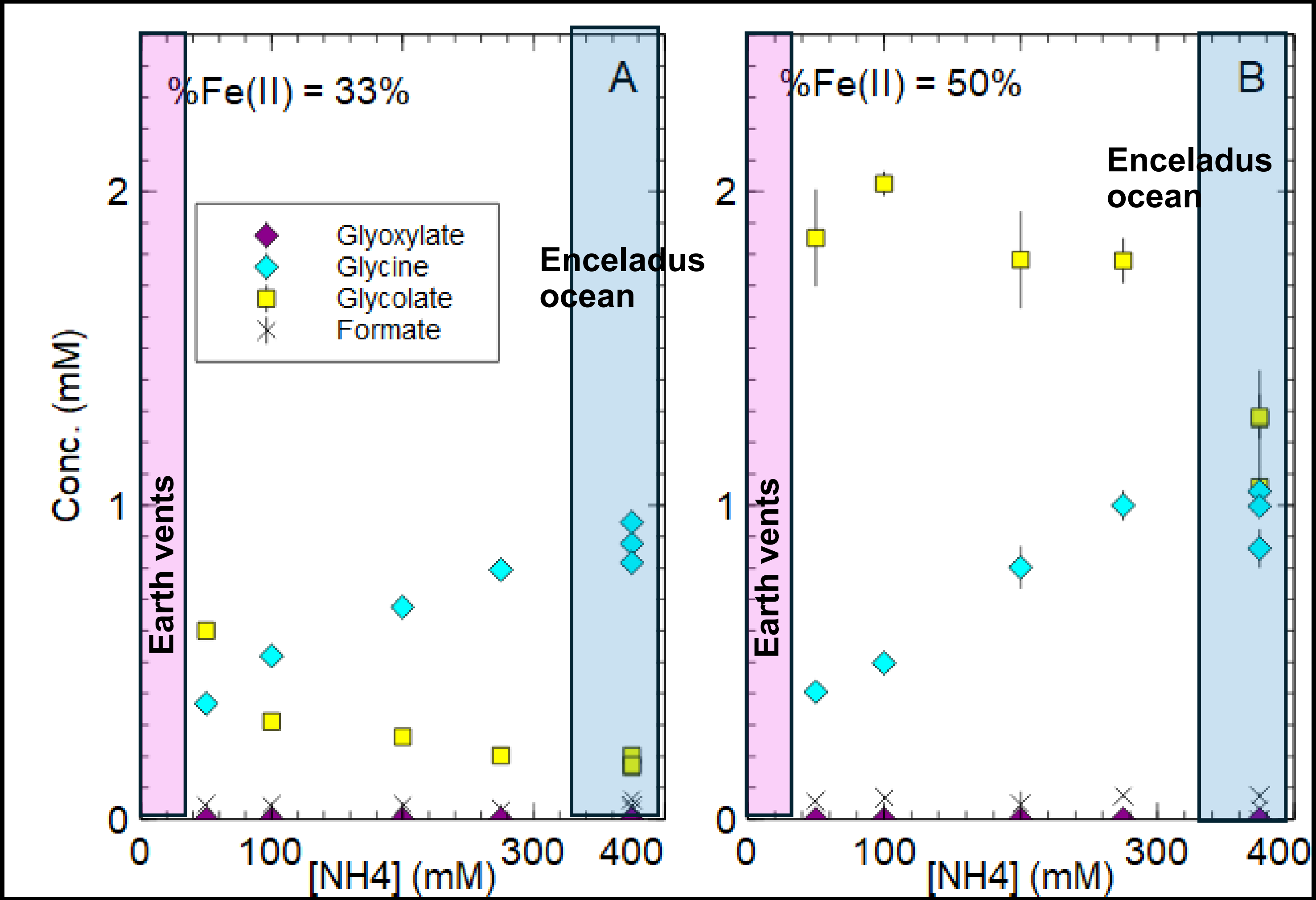

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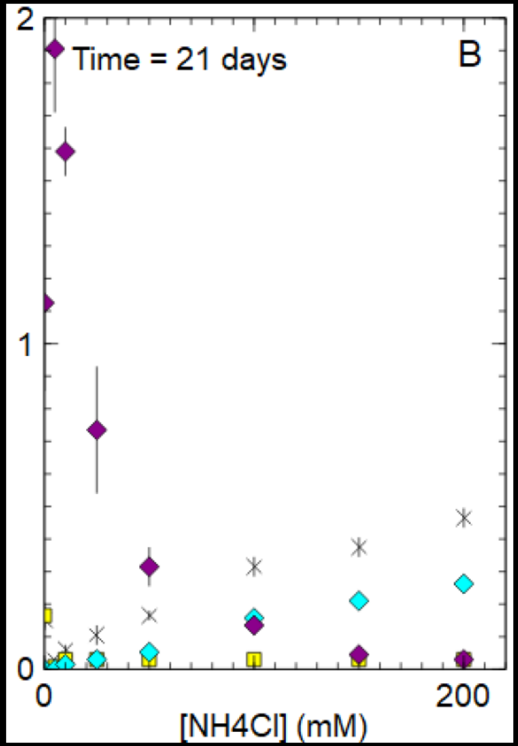

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Prebiotic conditions produce reactive species and radicals

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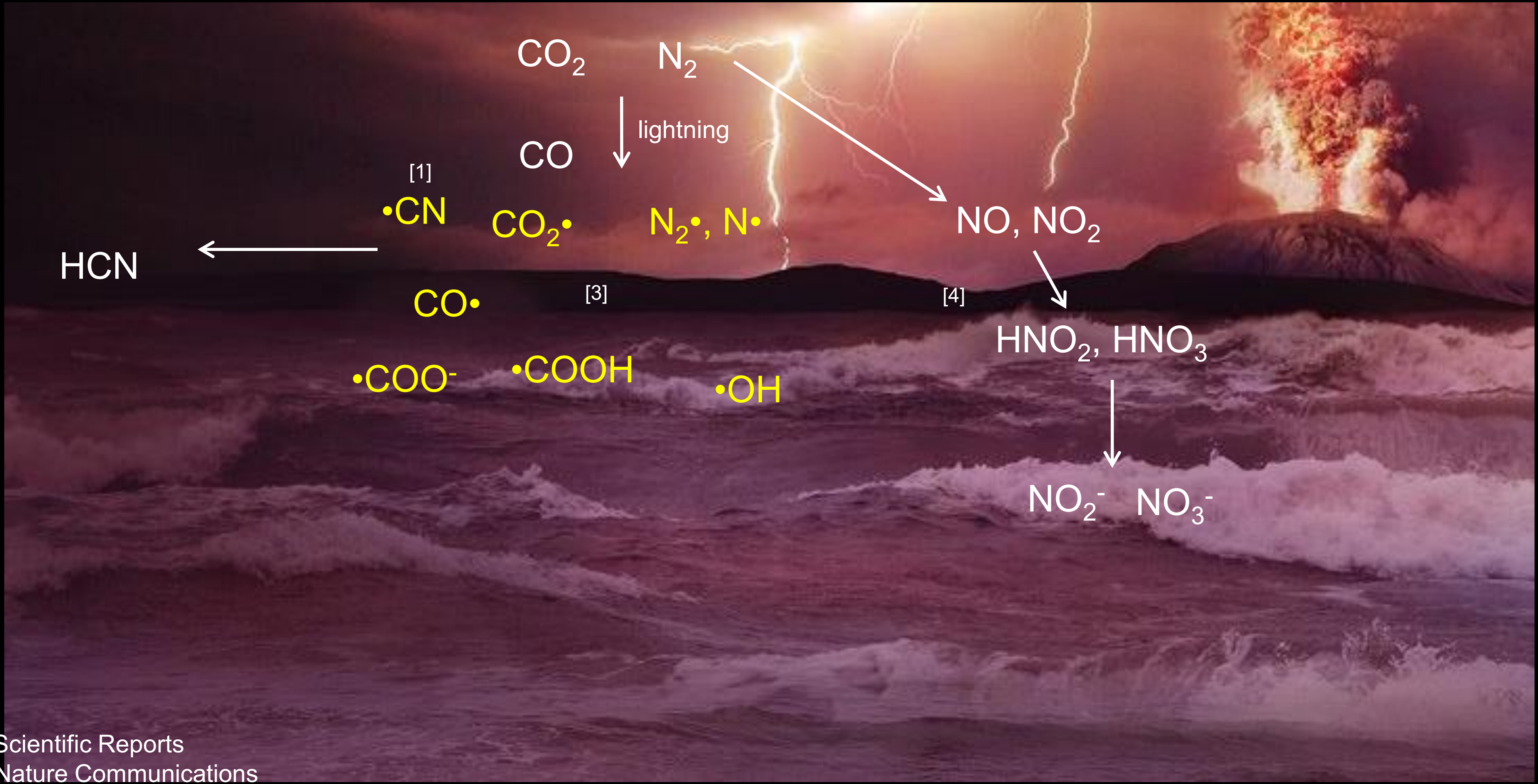

[1] Ferus et al 2017, Scientific Reports
[2] Ernst et al. 2023, Nature Communications
[3] Jiang et al. 2024, PNAS
[4] Adams et al. 2024, GRL
[5] Sauvage et al. 2021, Nature Communications
[6] Sherwood Lollar et al. 2021, GCA
[7] He et al. 2023, PNAS

Image: Gregoire Cirade, Science Photo Library

Image: NASA

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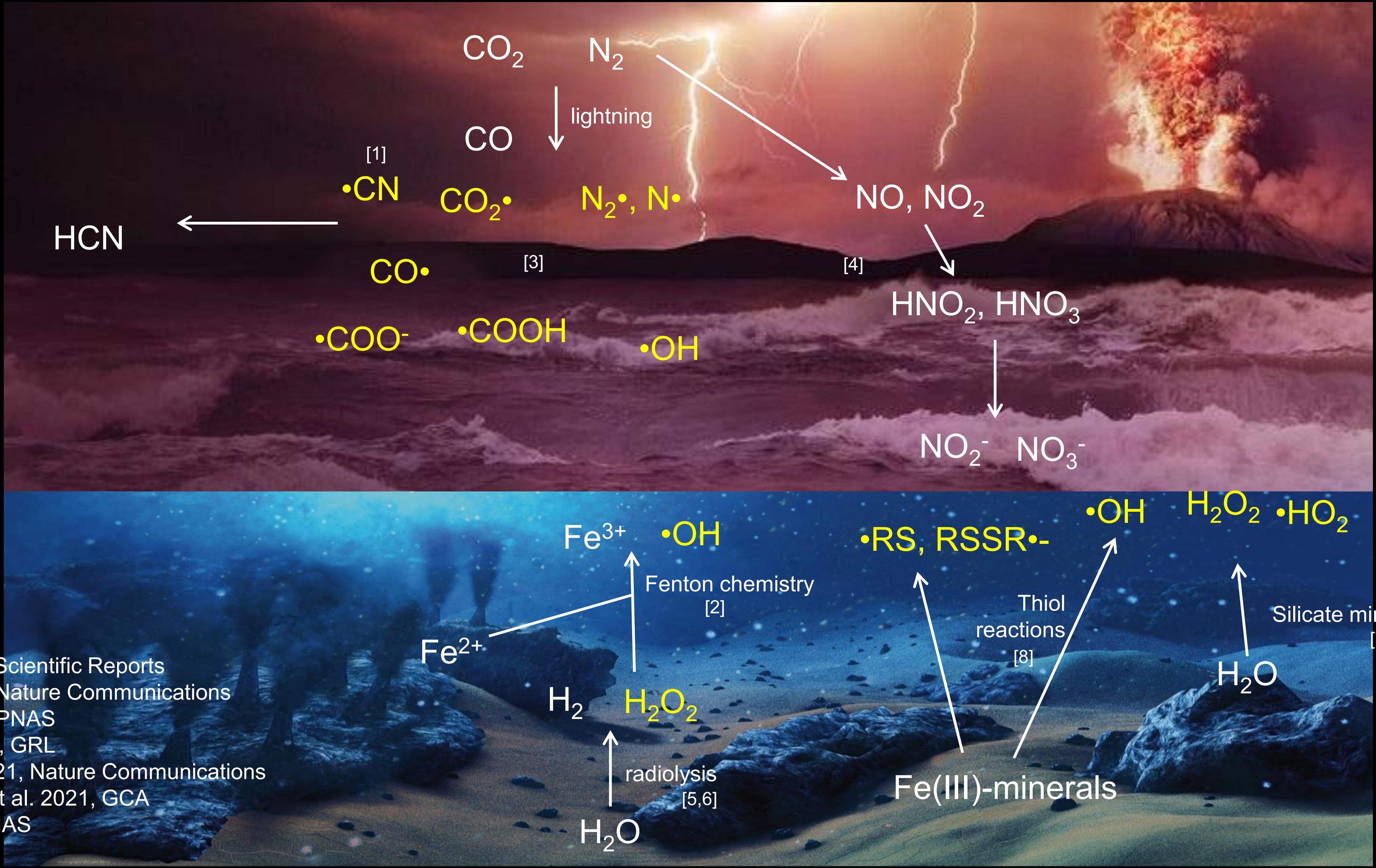

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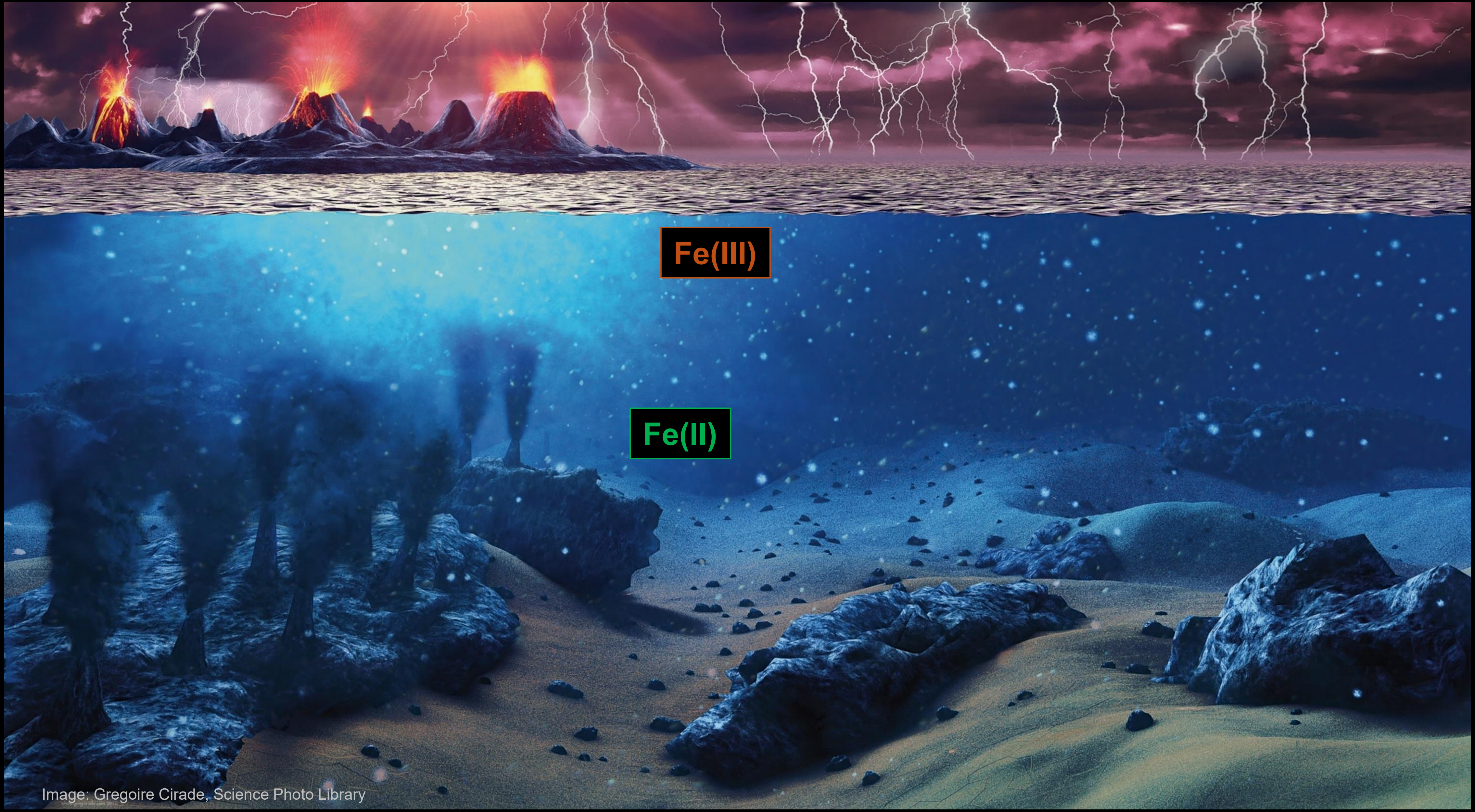
Image: Gregoire Cirade, Science Photo Library

Image: NASA

Other chemical species can affect key parameters for organic chemistry



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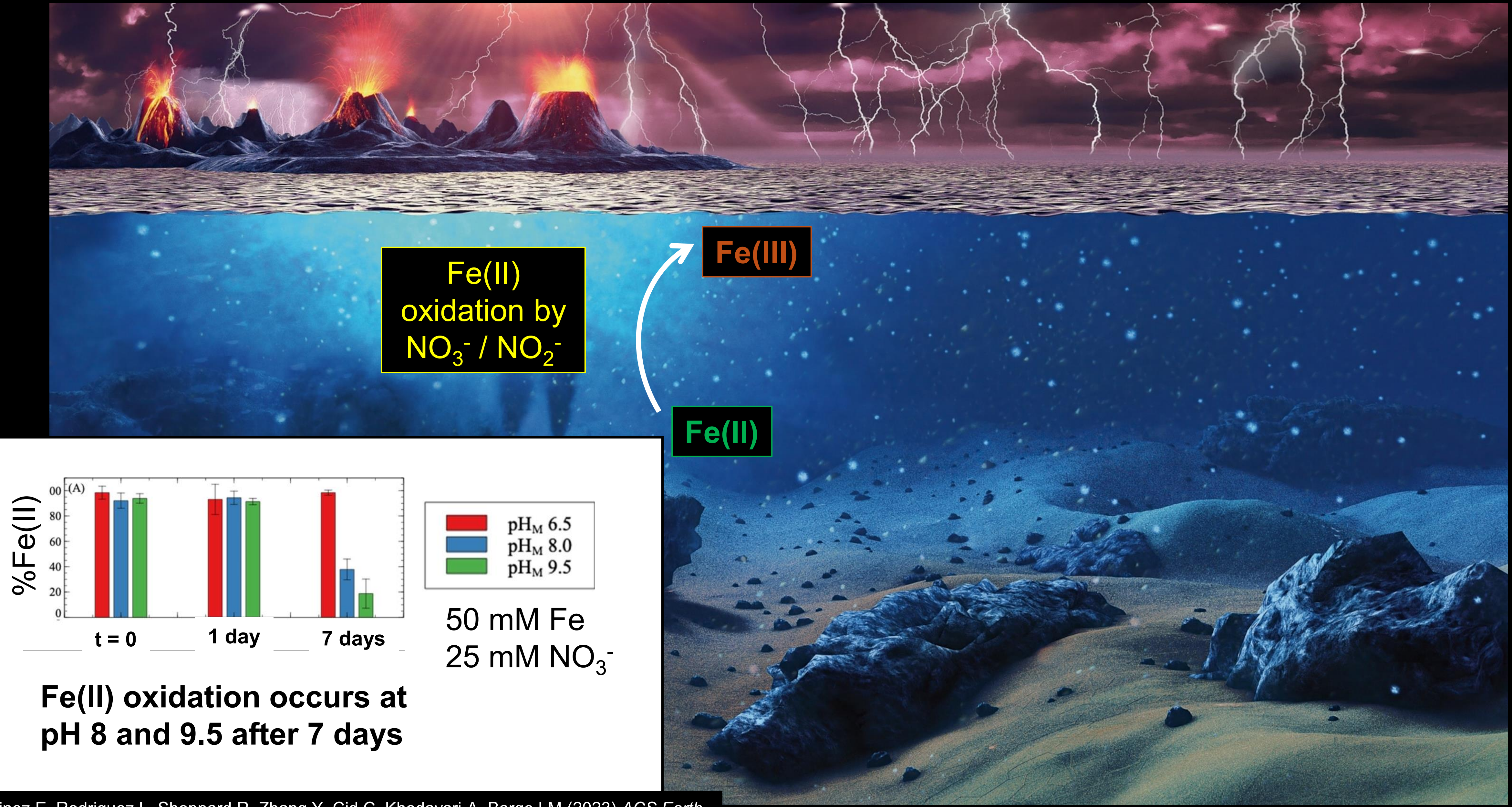

50 mM Fe
25 mM NO_3^-

Fe(II) oxidation occurs at pH 8 and 9.5 after 7 days

Martinez E, Rodriguez L, Sheppard R, Zhang Y, Cid C, Khodayari A, Barge LM (2023) *ACS Earth Space Chem*, 7, 11, 2287–2297.

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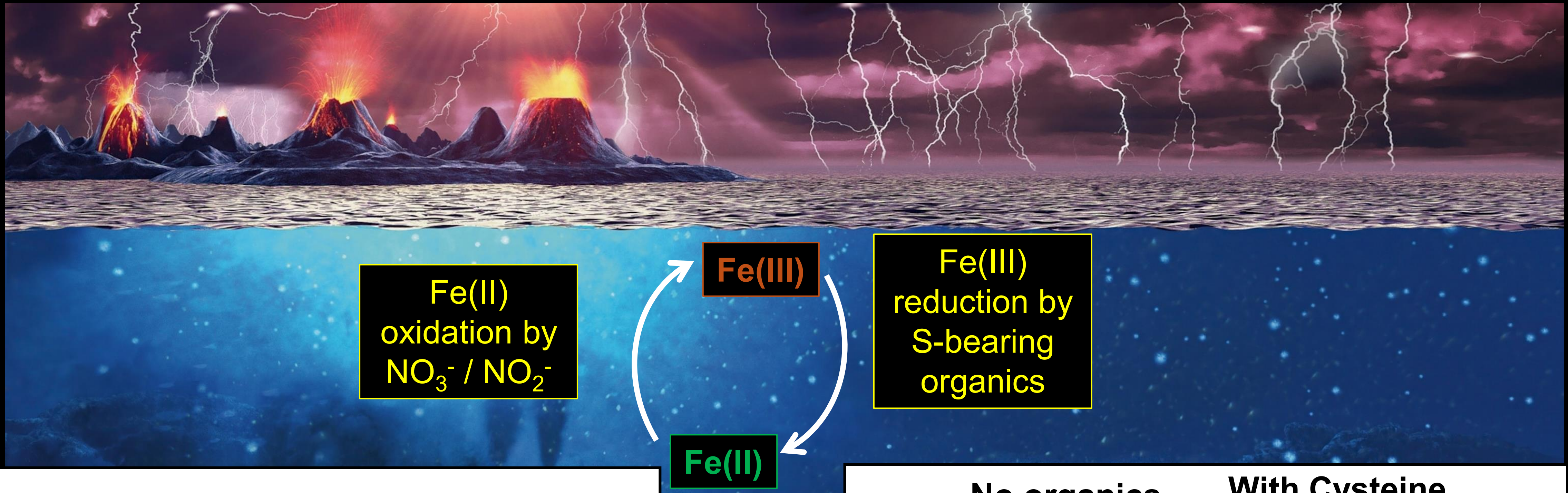

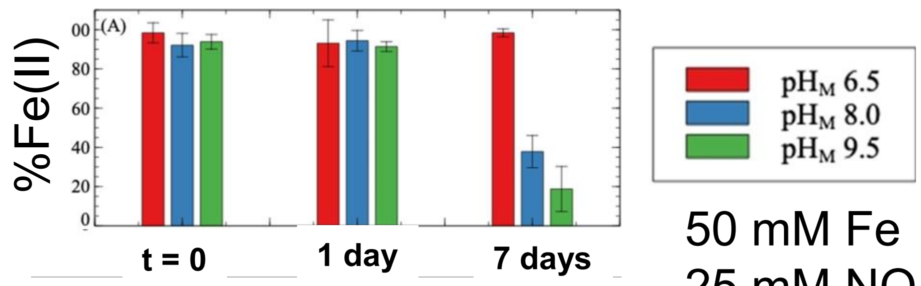

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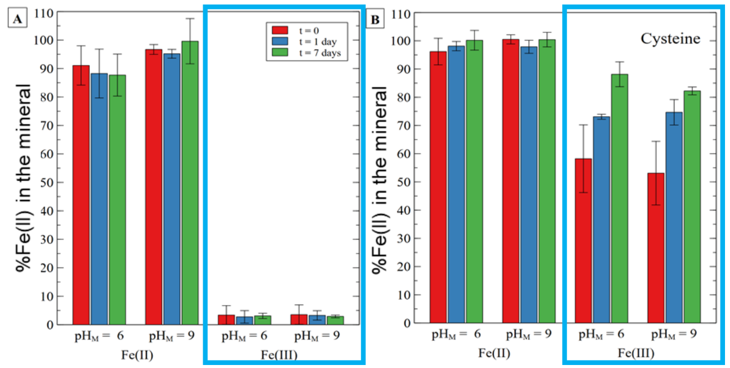
No organics **With Cysteine**



Fe(III) reduction occurs over 7 days in the presence of S-bearing organics

Martinez E, Rodriguez L, Sheppard R, Zhang Y, Cid C, Khodayari A, Barge LM (2023) *ACS Earth Space Chem*, 7, 11, 2287–2297.

Flores E, Martinez E, Rodriguez LE, Weber JM, Khodayari A, Barge LM (2021) *ACS Earth Space Chem,* 5, 5, 1048–1057

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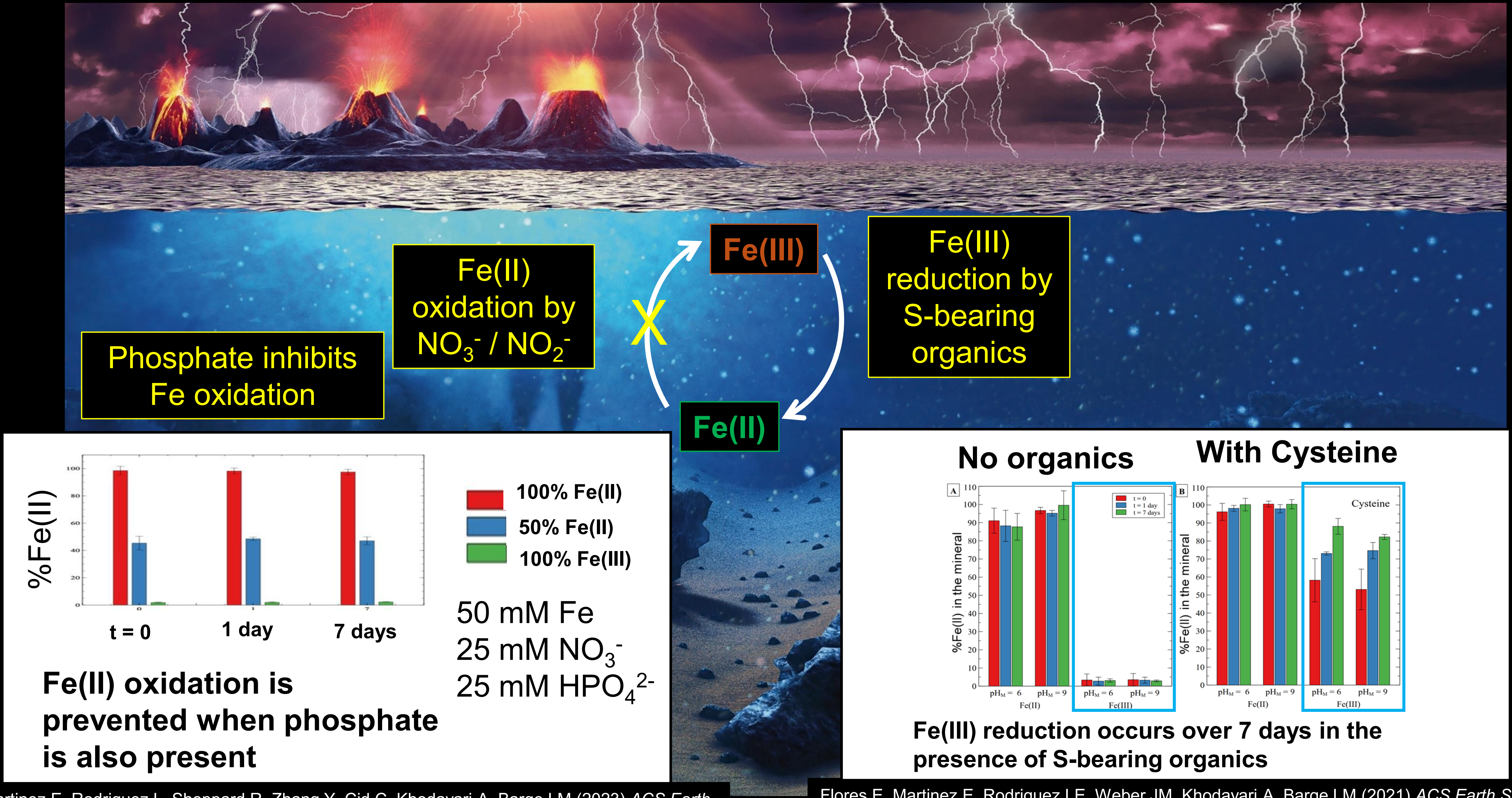

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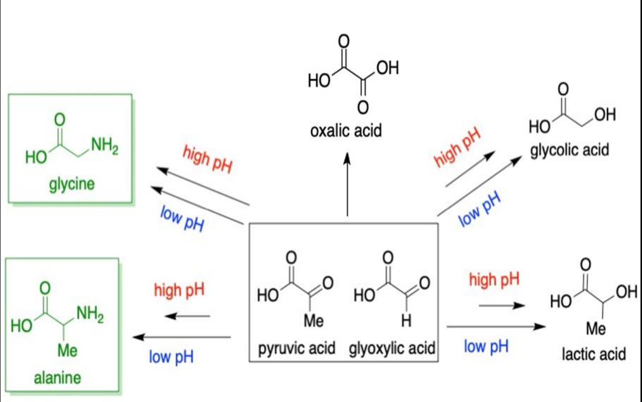
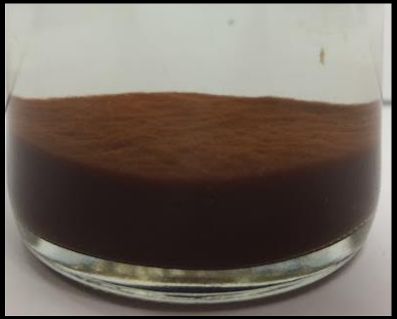
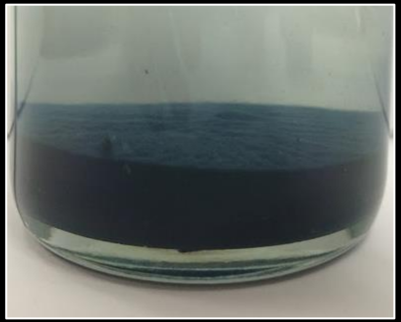
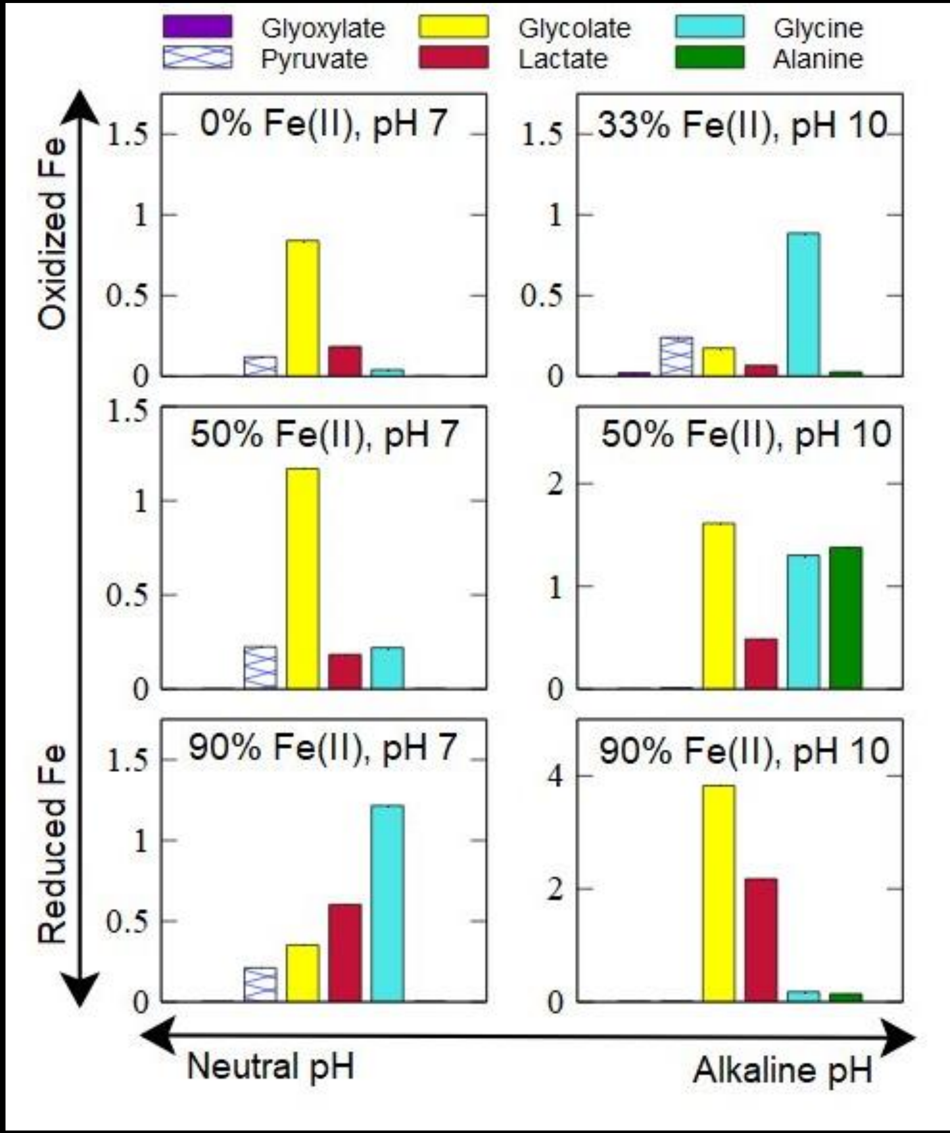


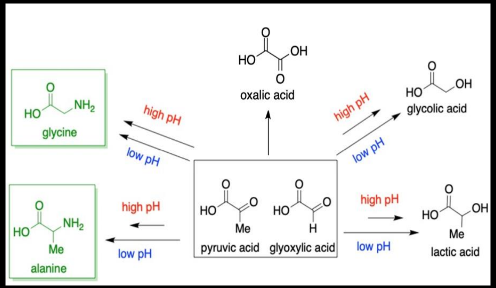


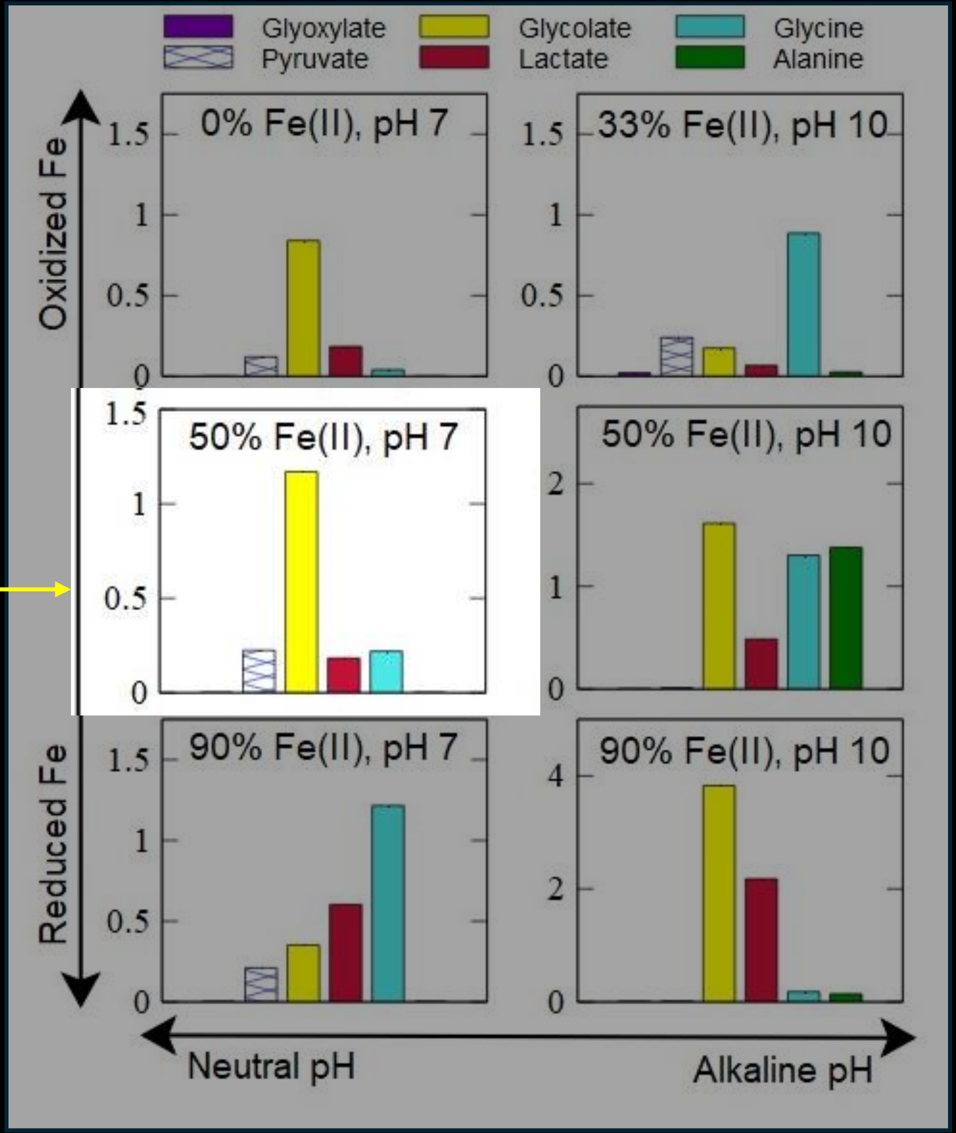




Environmentally driven organic distributions are produced in abiotic systems

Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833





Initial products (anoxic ocean, netural pH vent)

Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
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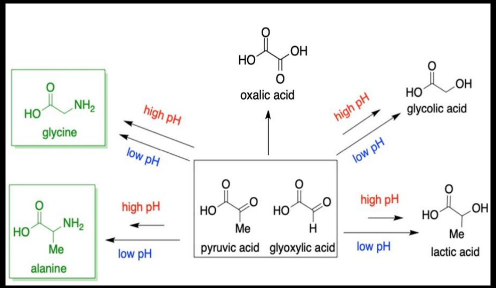

Shallow waters with increased Fe(II) photo-ox.

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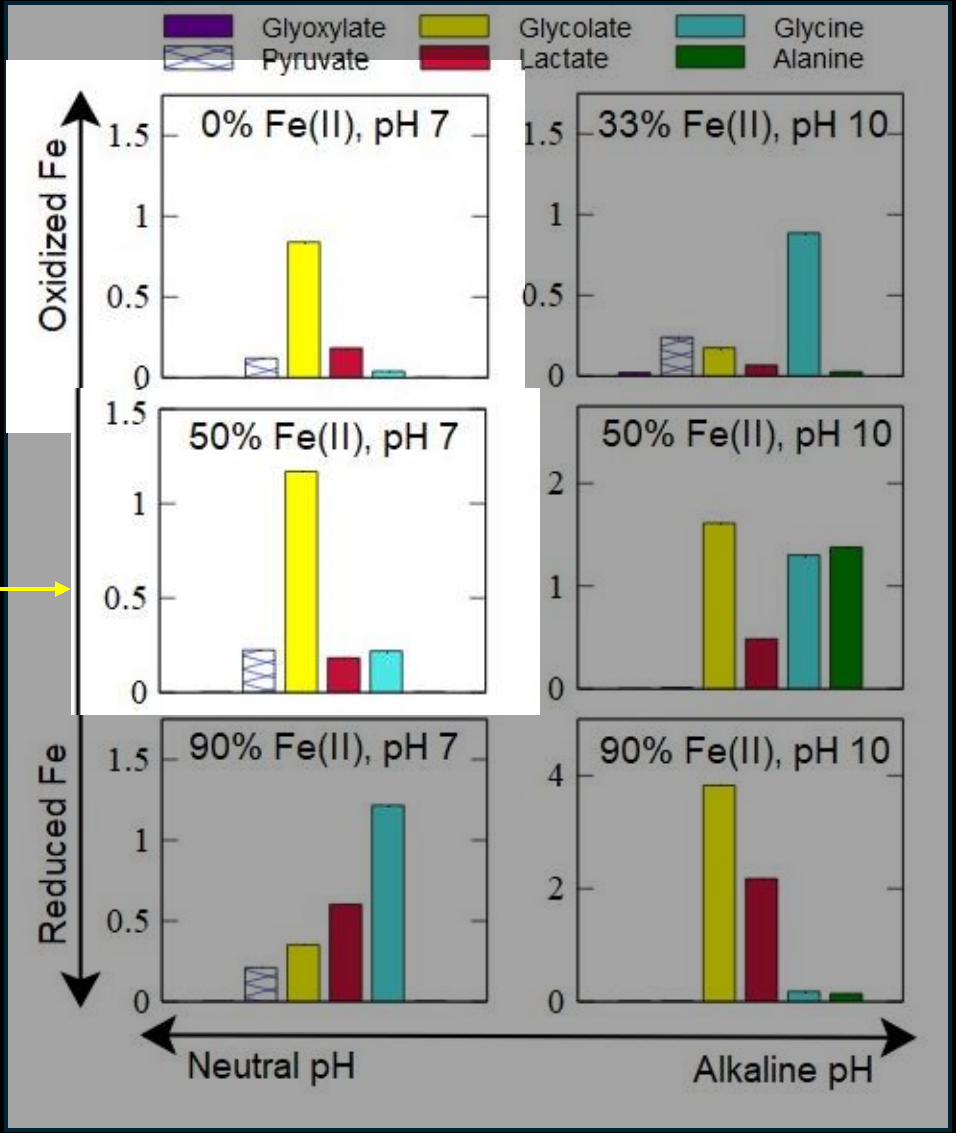

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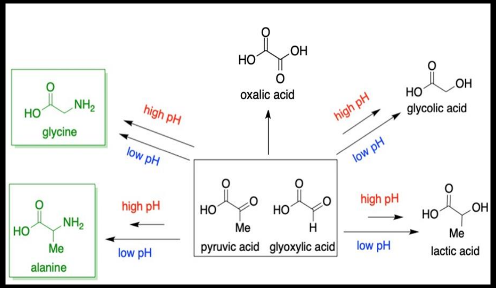

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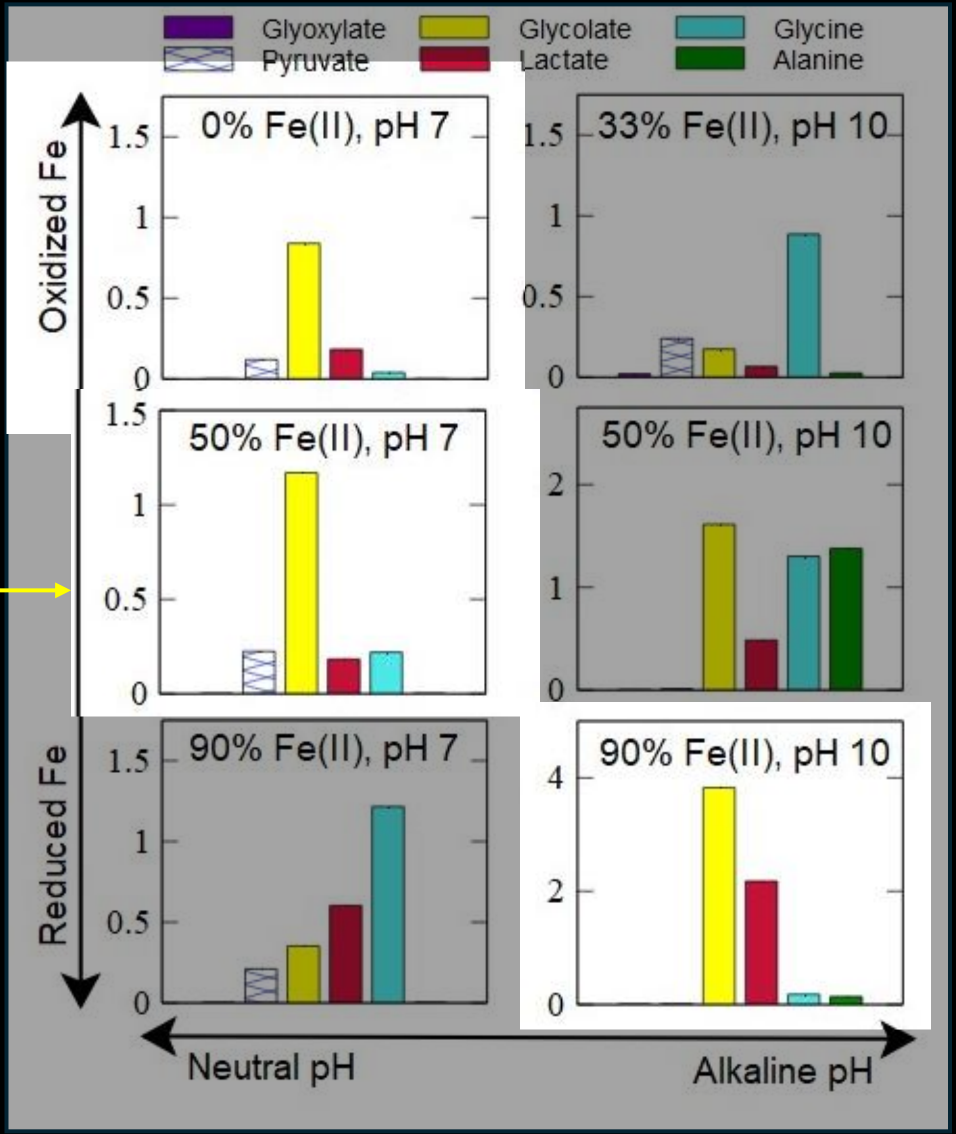
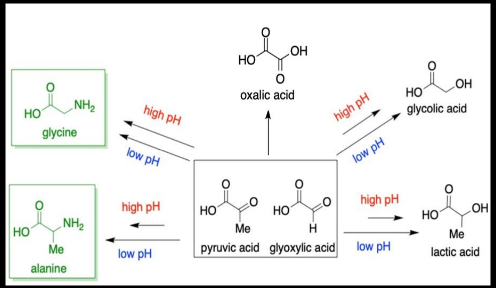


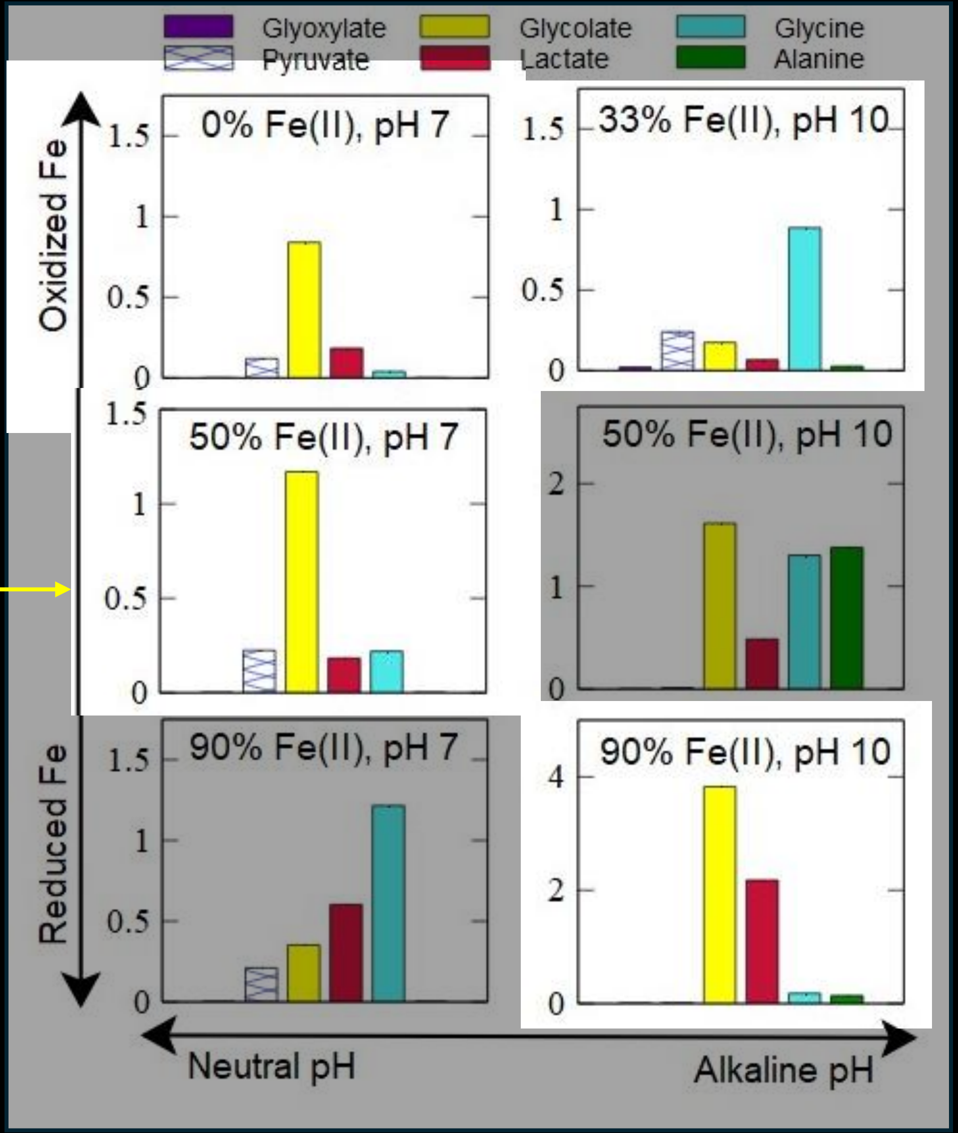
Thiols/sulfide reduces Fe(III); inc. pH from alkaline vent plume

Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833



Shallow waters with increased Fe(II) photo-ox.

Initial products (anoxic ocean, netural pH vent)



Surface exposed alkaline vent; Fe(II) ox. from nitrate/nitrite

Thiols/sulfide reduces Fe(III); inc. pH from alkaline vent plume

Barge et al. 2020, *JGR-Planets* 125, 11 e2020JE006423
Barge et al. 2019, *PNAS* 116 (11) 4828-4833

Images: NASA

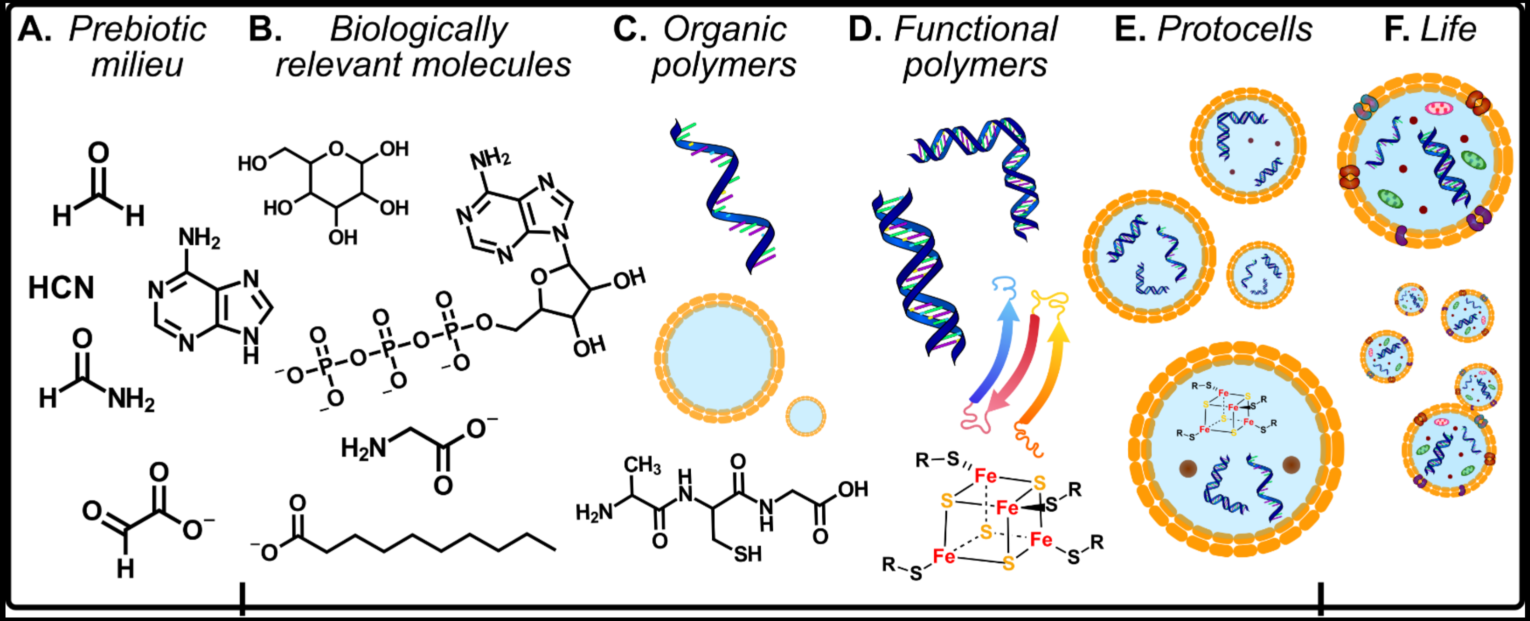
Even if life is not present, remnant abiotic / prebiotic chemistry might exist on other solar system bodies

Images: NASA

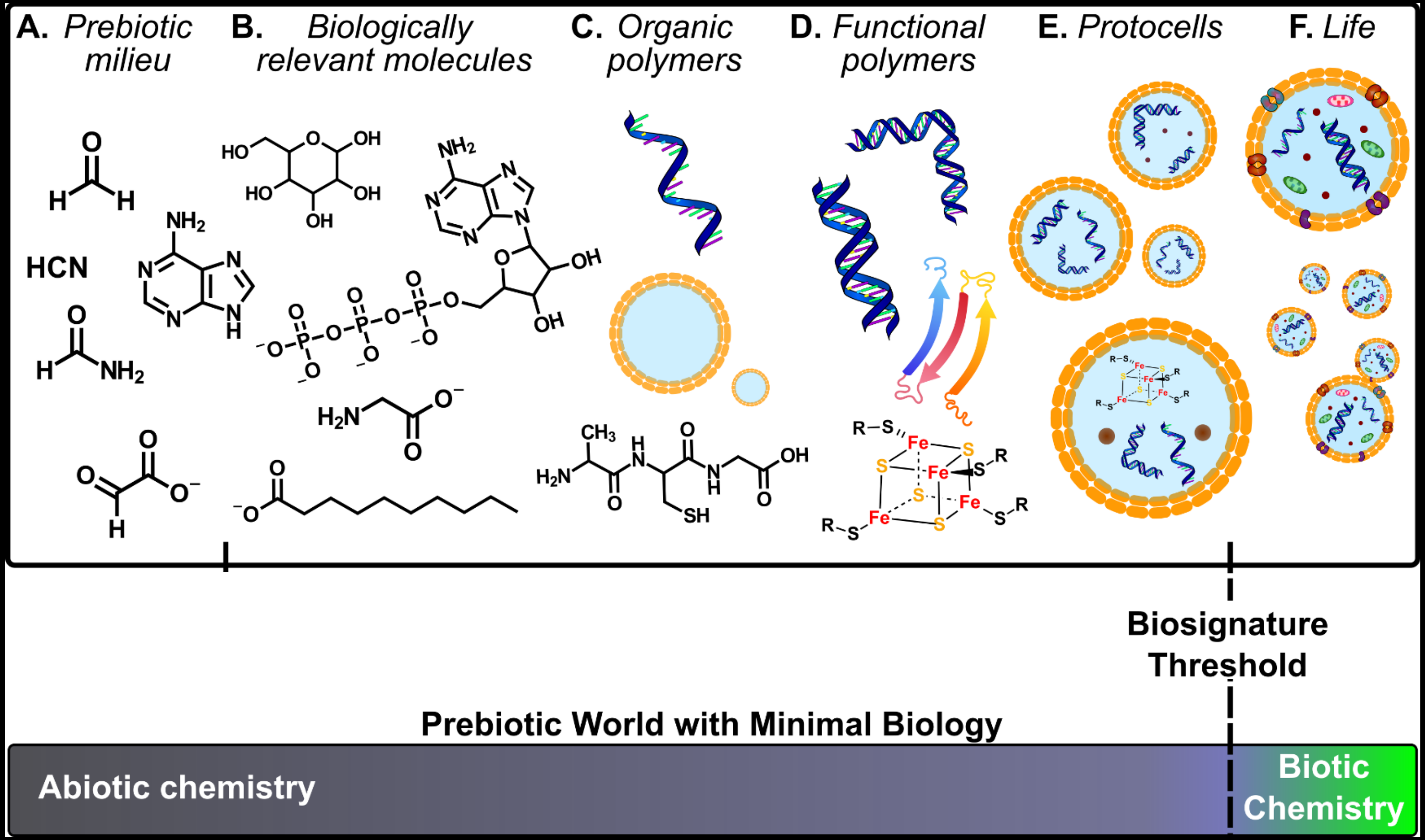
Even if life is not present, remnant abiotic / prebiotic chemistry might exist on other solar system bodies

The threshold for biosignature identification changes depending on the organic chemical state of the planet

Images: NASA



Barge L.M., Rodriguez L.E., Weber J.M., Theiling B.P. Determining the “Biosignature Threshold” for Life Detection on Biotic, Abiotic, or Prebiotic Worlds. Astrobiology 2022, 22,4,481-493, http://doi.org/10.1089/ast.2021.0079.



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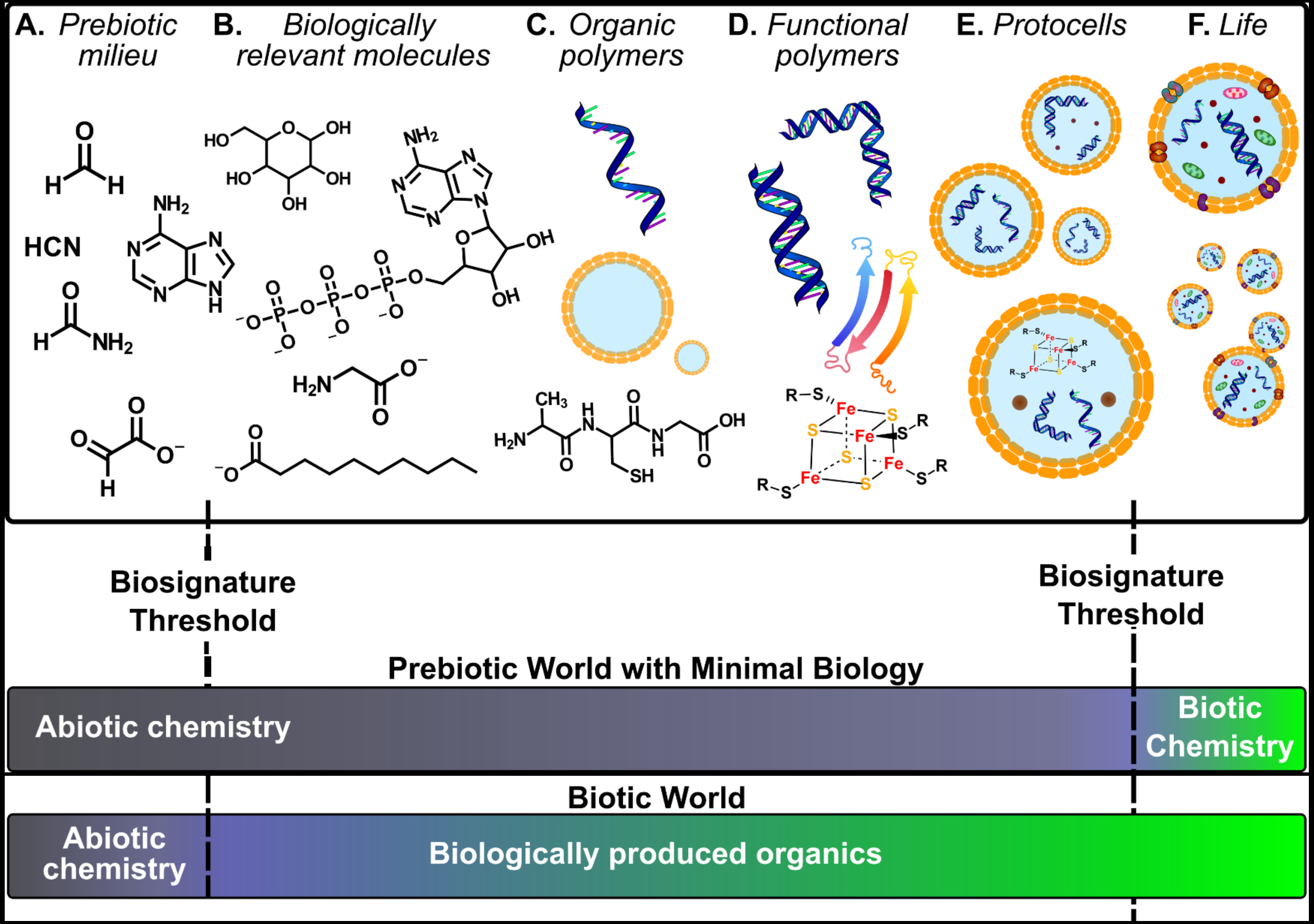

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Takeaways / Future directions

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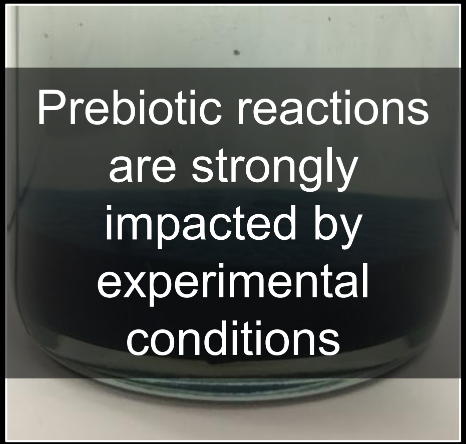

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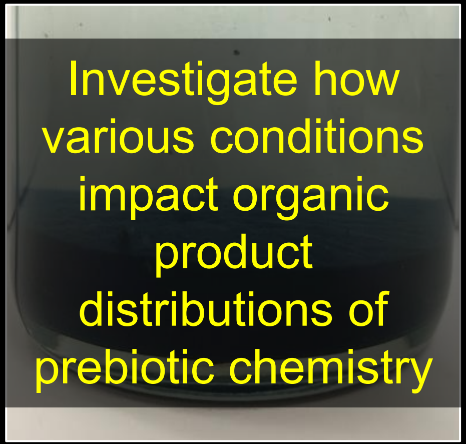

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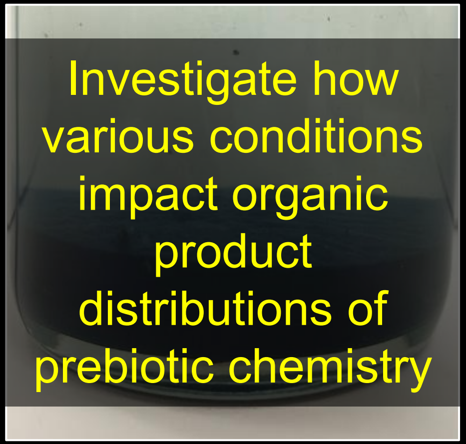

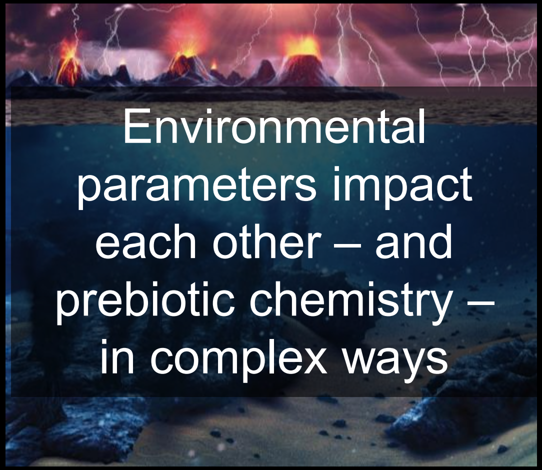

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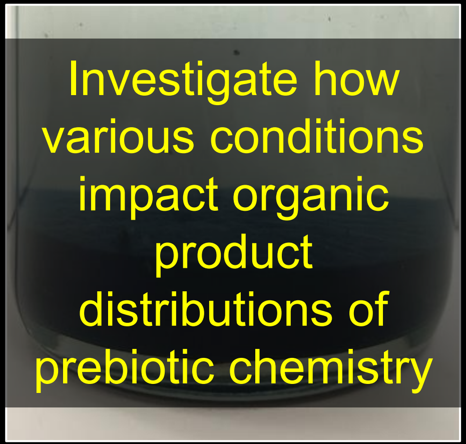

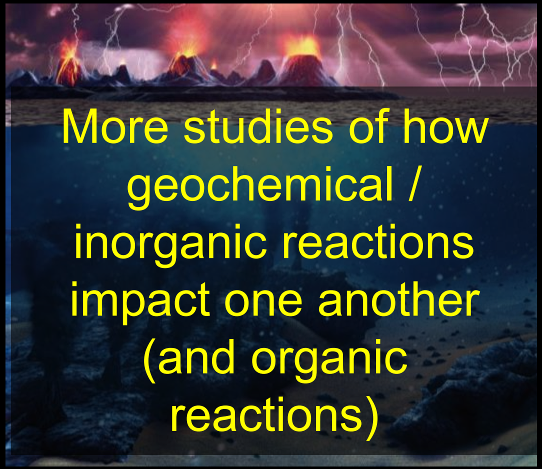

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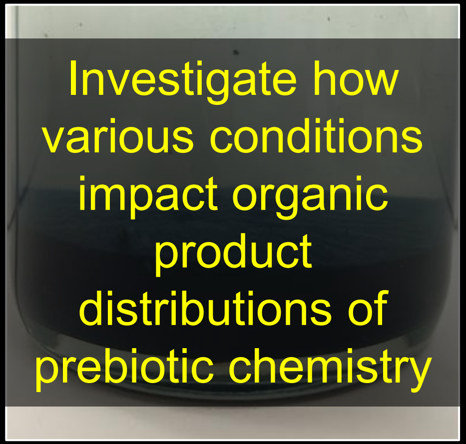

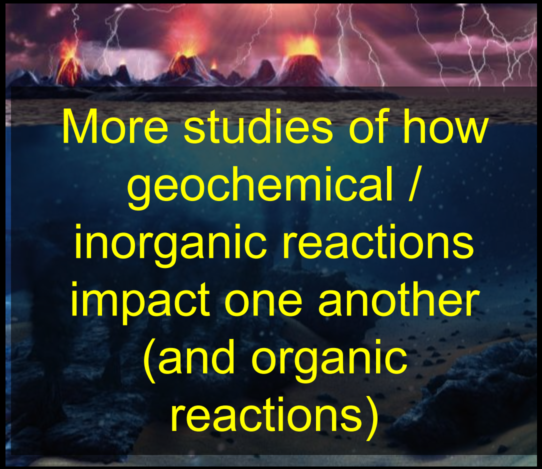

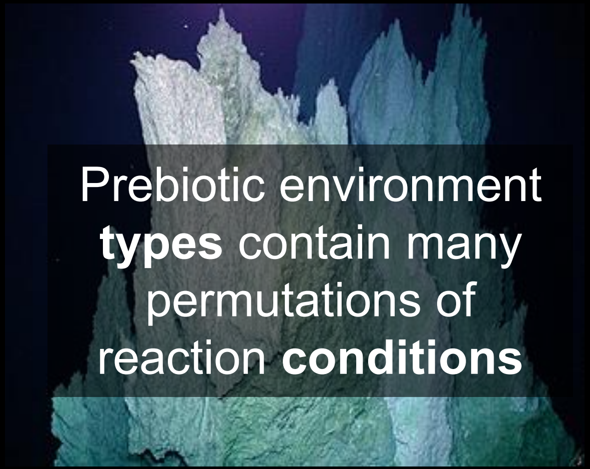

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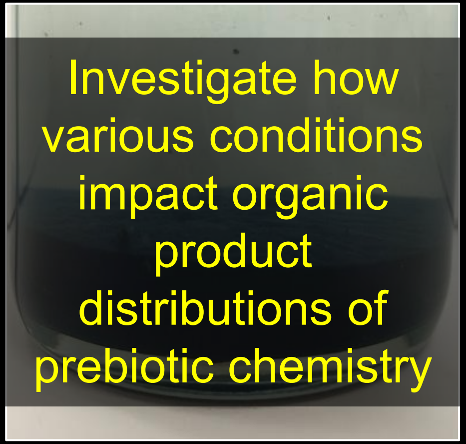

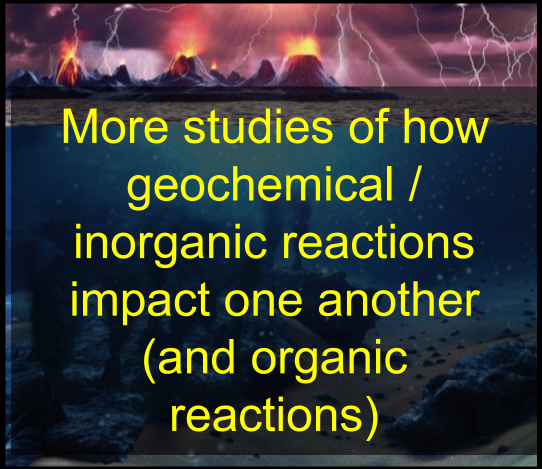

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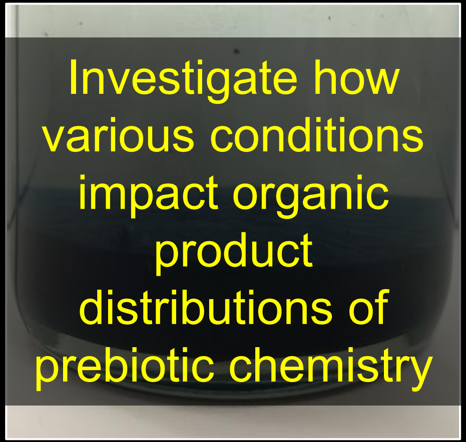
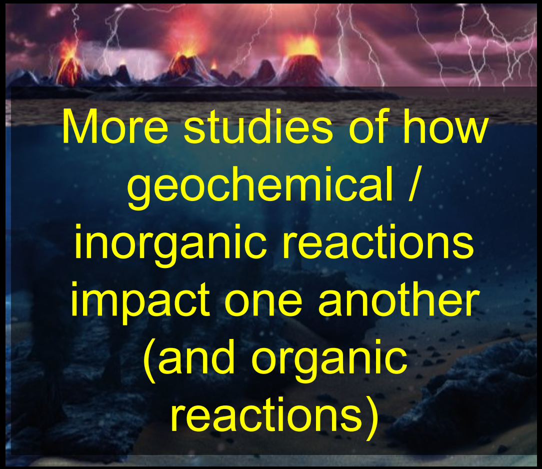
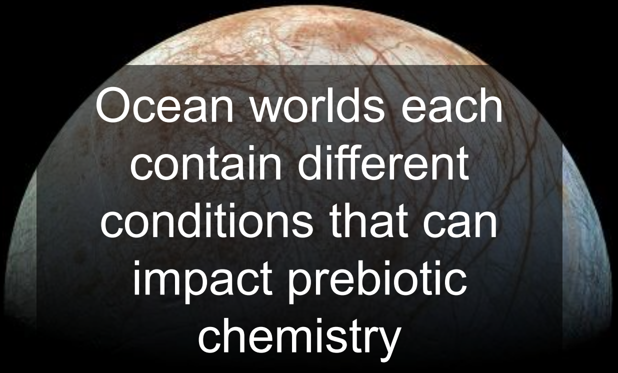


Investigate how various conditions impact organic product distributions of prebiotic chemistry



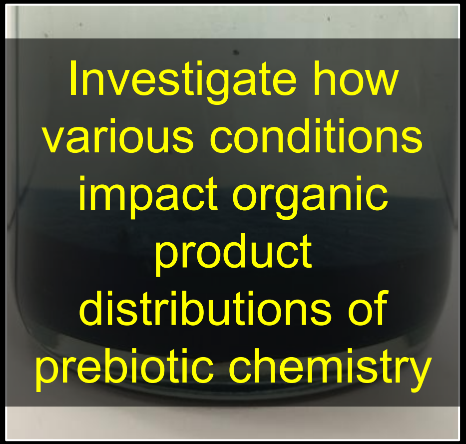
More studies of how geochemical / inorganic reactions impact one another (and organic reactions)

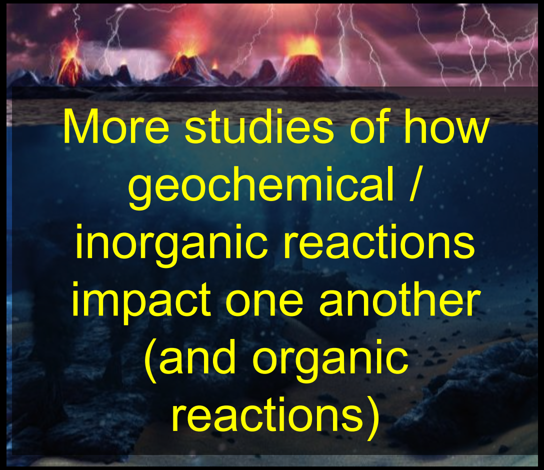
Studies of planetary environments to determine what sets of conditions they may contain

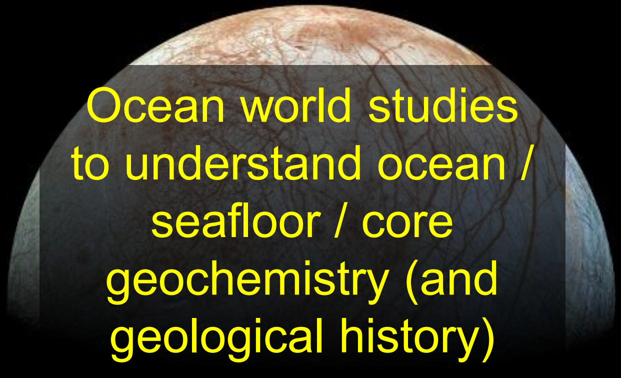


Ocean worlds each contain different conditions that can impact prebiotic chemistry

Takeaways / Future directions







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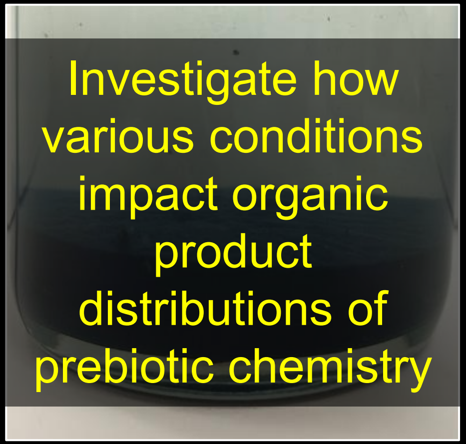

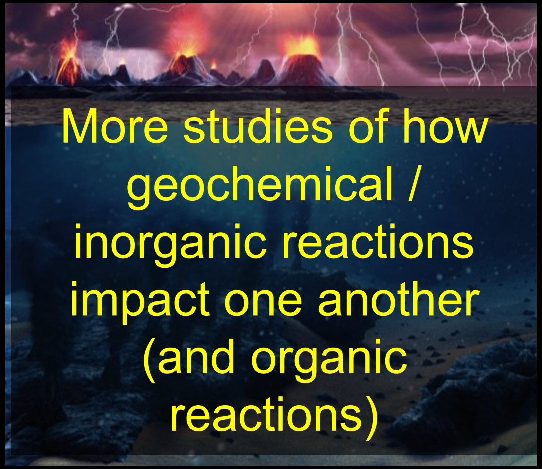

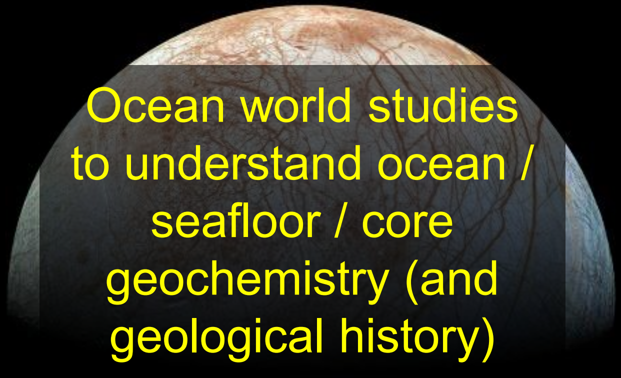

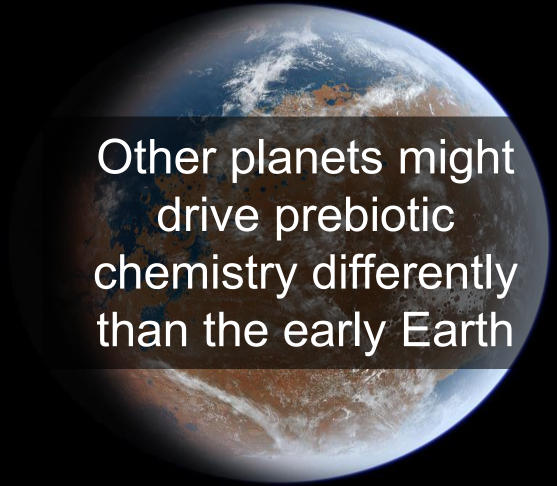

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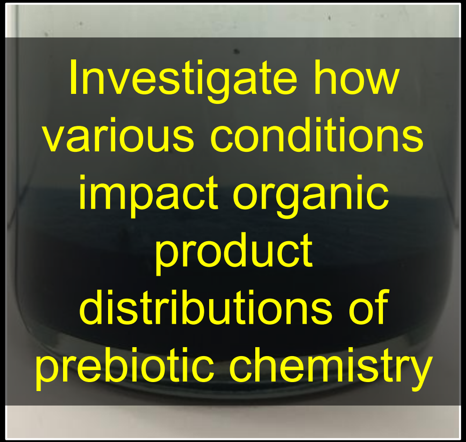
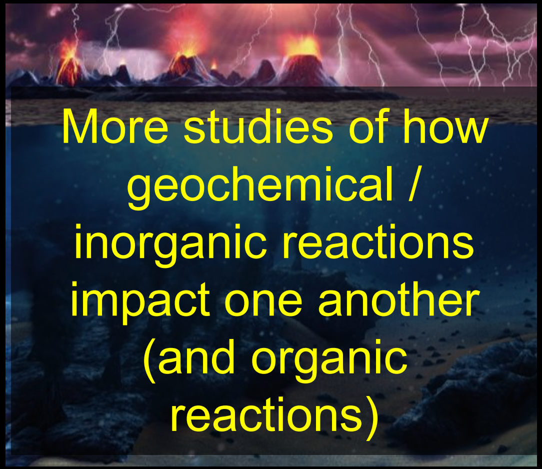
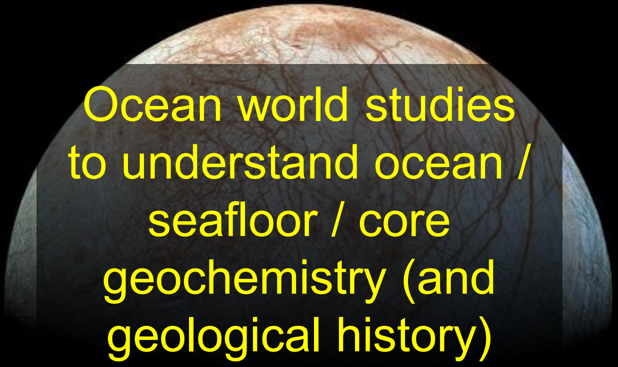
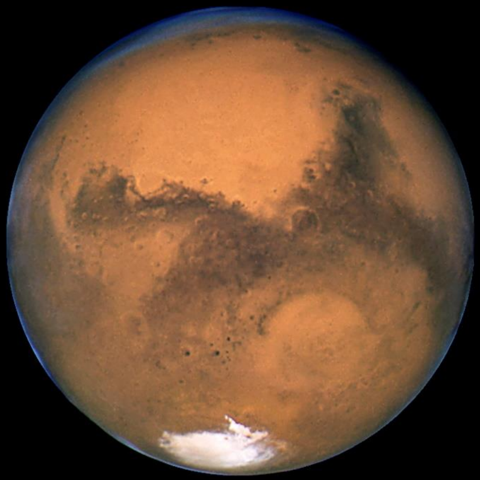
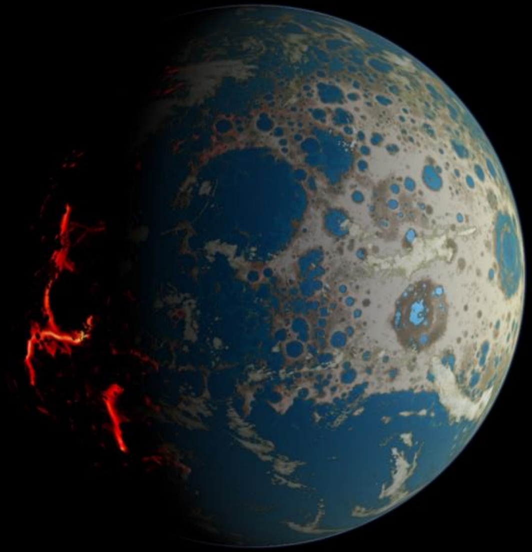
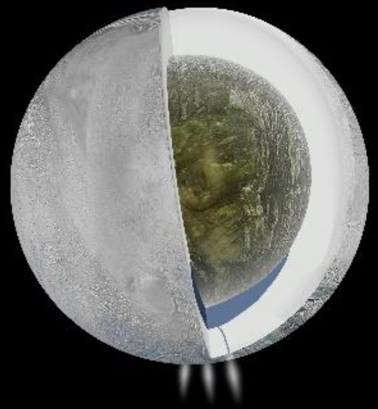
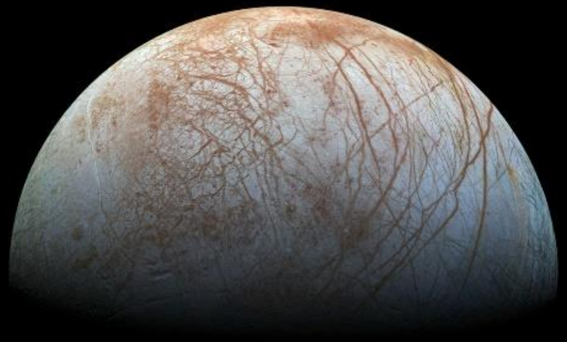






Questions?

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