Understanding abiotic organic chemistry driven by minerals in Ceres' and Enceladus' oceans

Background: Predicting abiotic carbon chemistry in a geochemical system such as the interiors of Enceladus or Ceres is not a simple matter, since the distribution of organic products can be very different depending on the specific geochemical parameters. The organics found in carbonaceous chondrites are a starting point for determining an "abiotic organic composition" to compare to. However, on an ocean world such as Enceladus or Ceres that has differentiated and possibly undergone hydrothermal heating, any organics already present would be further processed, and also new organics would be synthesized from geochemical CO_2/CO and H_2 . Entire organic reaction cycles that look "metabolic", and give product distributions different from those found in meteorites, can be driven abiotically in aqueous systems with reactive minerals. This is relevant for understanding how metabolism emerged from a geological system on Earth or perhaps on other worlds, but poses a problem for life detection since abiotic or prebiotic organic chemistry can drive life-like reactions.

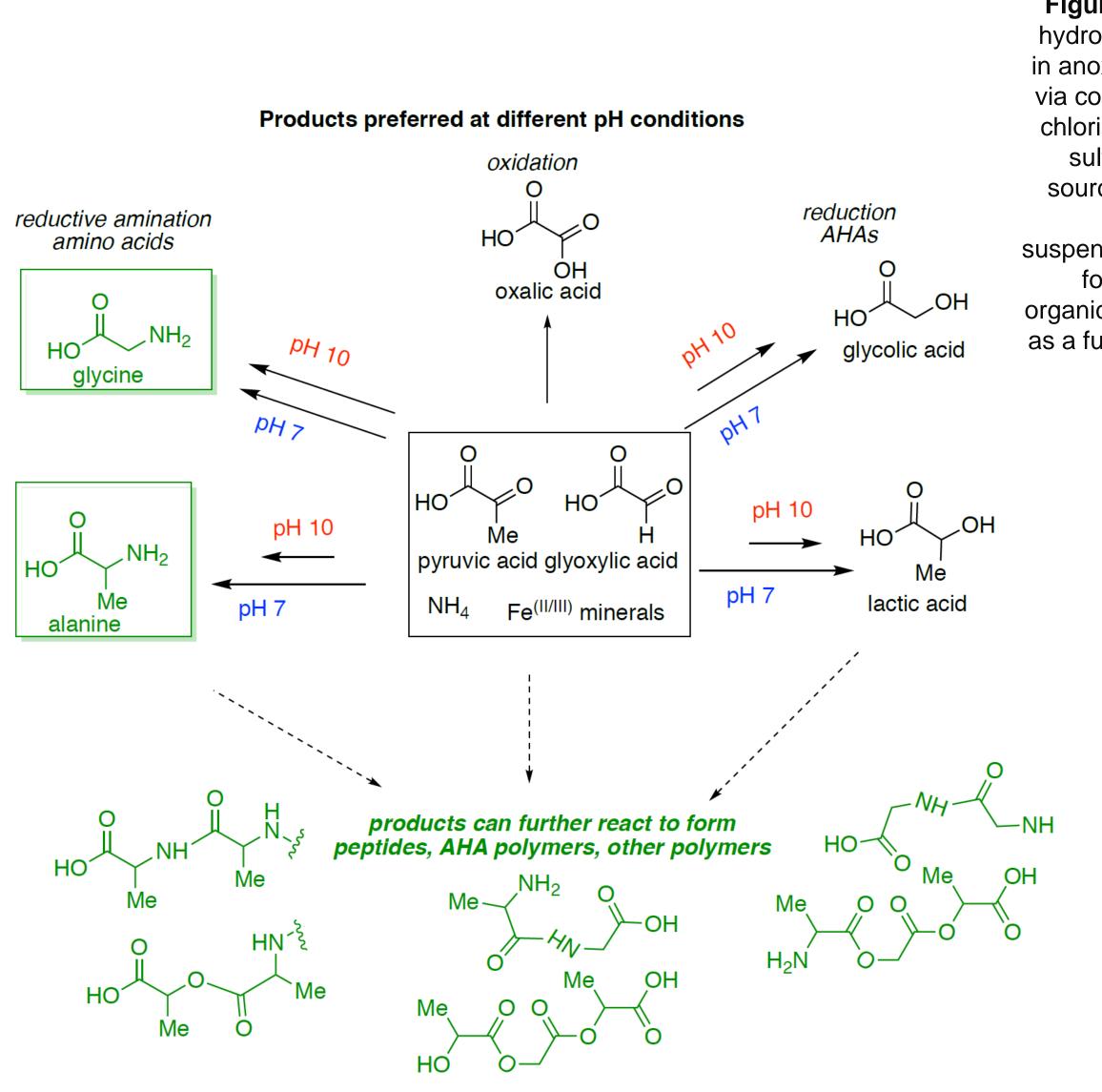


Figure 2: Organic reactions observed in iron hydroxide experiments with pyruvate and glyoxylate. Both amino acids (alanine and glycine) and hydroxy acids (lactate and glycolate) were observed, but the relative yield of each depended on both the pH (7 or 10) and the amount of reduced iron in the hydroxide mineral. (Barge et al. 2020, JGR-Planets)

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Figure 3: Organic distributions produced from reactions of pyruvate and glyoxylate with iron hydroxide minerals vary as a function of pH and the redox state of iron in the mineral. These results showed that the abiotic distribution pattern of organics is highly dependent on geochemical parameters. (Barge et al. 2020, JGR-Planets)

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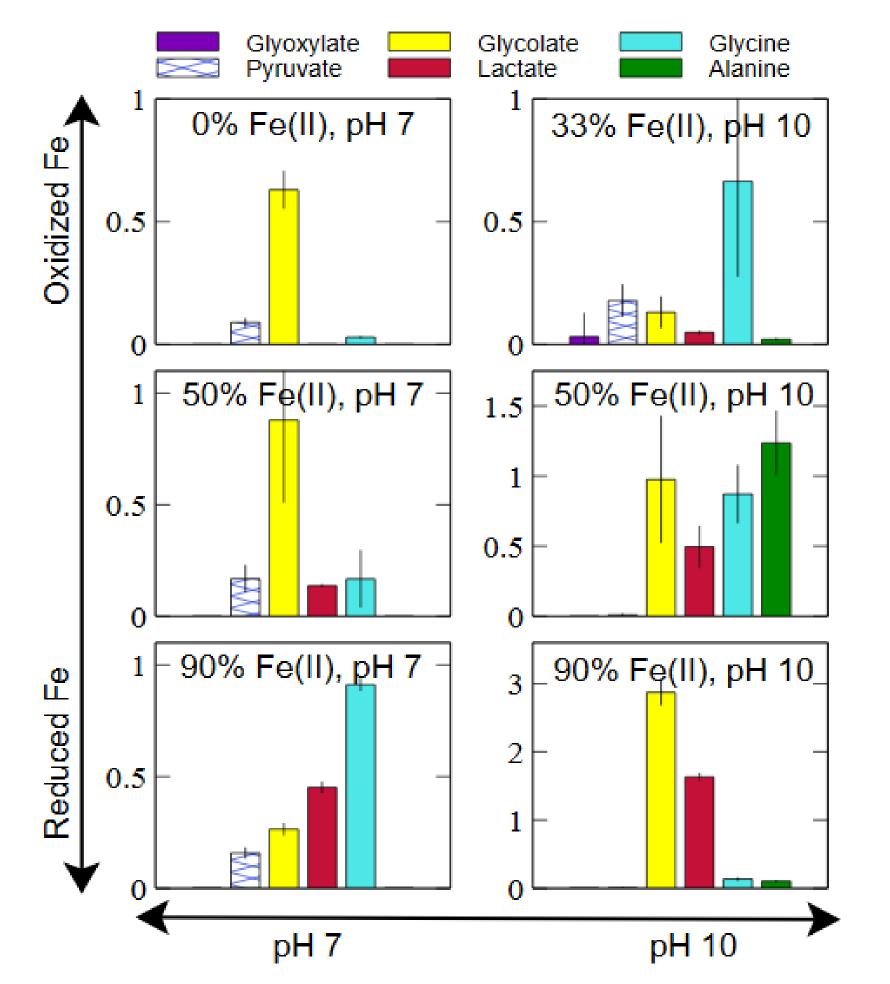
Objectives: The objectives of this work were to create a laboratory collection of Ceres / Enceladus surface and interior analog minerals from lab-synthesized minerals to be used in organic chemistry experiments, and then test organic synthesis from simple precursors under ocean world relevant conditions. We tested how abiotic organic reactions are affected by various geochemical parameters such as pH, concentration of ammonia or sulfide, and temperature, in order to determine how abiotic organic distributions are affected by environmental conditions. Another objective was to produce organic/mineral samples for delivery to Task 3 for analog organic detection studies.

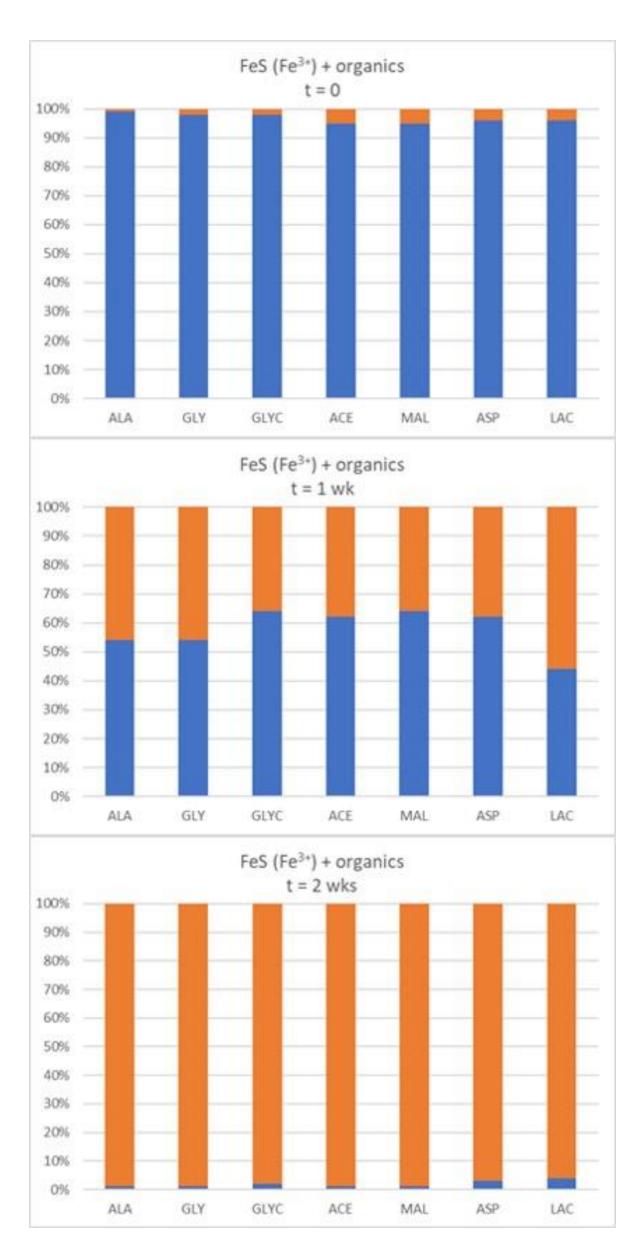
> Figure 1: Lab synthesized minerals (iron hydroxides shown) reacting with organics in anoxic vials. Minerals were synthesized via co-precipitation of ferrous and/or ferric chloride and sodium hydroxide or sodium sulfide; then organics and a reduced N source (in this case ammonium chloride) were added. The mineral/organic suspension was mixed and heated at 70°C for several days to one week, and the organics in the liquid phase were analyzed as a function of time. (Credit: Erika Flores)



Approach and Results: The chosen organic precursors for this work included pyruvate, glyoxylate, and oxaloacetic acid three carboxylic acids that are universal precursors to metabolism, detected in meteorites, and that can produce various organic molecules that might be detected by future missions. These are also of interest to prebiotic chemistry studies since they can react to form "proto-metabolic" cycles. Mineral reactants were chosen based on surface observations of Ceres, as well as hypothetical minerals in the interior "muddy oceans" that might be precursors to the minerals we see on the surface. Fe(II) / Fe(III)-containing minerals are important for organic reactions as seen in our previous work. Mineral mixtures are also important, even if one of the minerals does not have the Fe(II) reducing agent, since surfaces can impact binding of NH₄, or promote amino acid polymerization. All minerals were laboratory synthesized rather than field samples, in order to control the redox state of iron in the mineral and to ensure the samples are free of organic contamination. The minerals we focused on in this work were: ferrosaponites and nontronites, iron oxyhydroxides (including green rust), and iron sulfides.

Significance/Benefits to JPL and NASA: Ocean worlds are of significant interest for finding life in the solar system, since some dwarf planets or icy moons show clear evidence of water-rock chemistry, a past or present liquid water ocean, and geochemical disequilibria that may be able to support life through hydrothermal processes. Developing methods for detection of organic molecules that are also found in terrestrial biology is one method for trying to identify whether or not life is present on these worlds, and organics have already been detected on the surface of Ceres and in the plumes of Enceladus. However, organic detection – even detection of organics that are commonly found in Earth biology – does not necessarily mean life, because there are many processes that produce organics abiotically in geological systems. Thus we need to fully understand the range of abiotic / prebiotic organic chemistries that are plausible and favorable in these environments.





Publications: [1] Barge L. M., Flores E., Weber J., Baum M. M., VanderVelde D., Castonguay A.. (2020) Effects of Geochemical and Environmental Parameters on Abiotic Organic Chemistry Driven by Iron Hydroxide Minerals. JGR-Planets, 125, 11, e2020JE006423, https://doi.org/10.1029/2020JE006423. [2] 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 2021, in review.

Figure 4: Iron colorimetry data from experiments with organics and iron sulfide minerals (testing the adsorption of different organic products from the pyruvate/glyoxylate reactions to the minerals). In an experiment starting with only ferric iron, we observed that sulfide drives iron reduction within the first ~30 minutes, then slowly the iron oxidizes again over a ~2 week period. This shows how sulfur redox chemistry (by affecting iron redox state as shown in Fig 2-3) may be an important factor for abiotic organic reactions on ocean worlds. (Credit: Erika Flores)

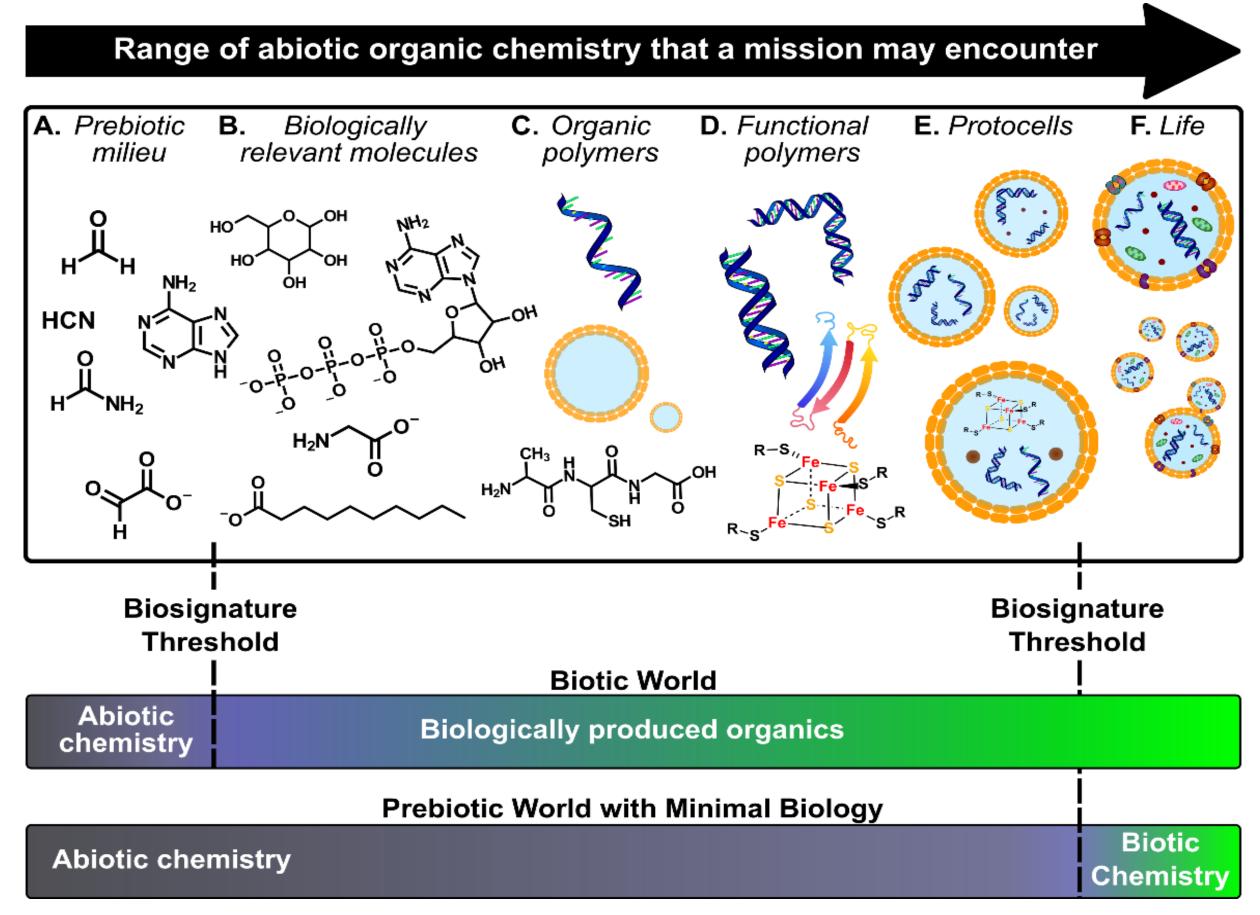


Figure 5: Abiotic chemistry can become very complex in planetary environments where life is excluded, including prebiotic chemistries that are no longer observable in Earth field samples. When interpreting organic signatures from another world (such as Enceladus or Ceres), we need a more complete understanding of where the abiotic -biotic boundary lies for the world or environment of interest. We argue that the biosignature threshold (boundary between "abiotic" and "biotic" organic chemistry) can shift depending on the geobiological state of the planet. On a biotic world, such as modern-day Earth, the threshold where an organic detection is likely to be from life is low since abiotic chemistry is suppressed. On a prebiotic world with advanced abiotic organic processes and minimal (if any) biology, the threshold to identify 'life' would be higher. (Barge, Rodriguez, Weber, Theiling; Astrobiology, in revision.)



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