

# Virtual Research Presentation Conference

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

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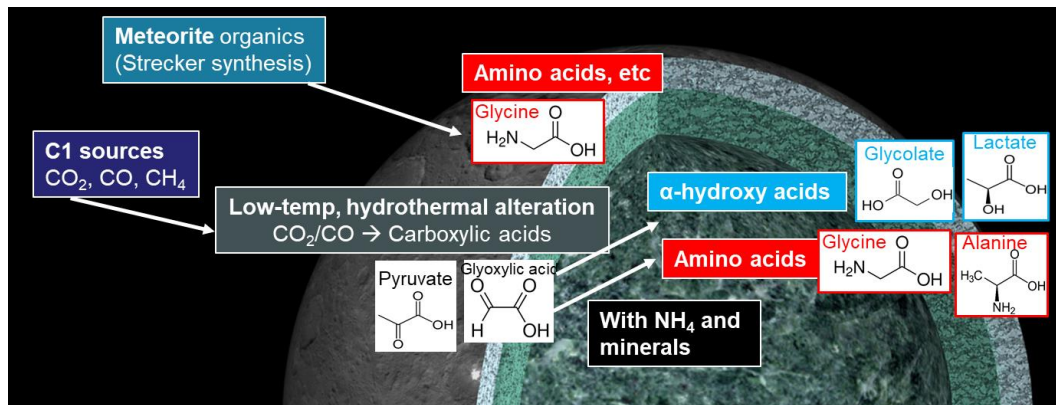
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**Program: Strategic Initiative**



**Jet Propulsion Laboratory**  
California Institute of Technology

# Tutorial Introduction



## Abstract

A variety of organics produced abiotically could be present in ocean worlds. Ceres and Enceladus in particular have environments that are very favorable for abiotic organic (prebiotic) chemistry. In order to understand whether future organic detections on the ocean worlds are convincingly suggestive of an extant biosphere, we must be able to distinguish from abiotic organic signatures. Thus we need to fully understand the range of abiotic / prebiotic organic chemistries that are plausible and favorable in these environments; many of which produce varying organic distributions and organic reaction cycles that look “metabolic”. Through the work proposed here, we will experimentally investigate realistic chemical pathways in ocean world analog systems and determine which distributions of organics or biomarkers are reliable indicators (and which are not) to support habitability and life-detection efforts on these bodies.



# Problem Description

## a) Context (Why this problem and why now)

- a) Organics have been detected on Ceres and Enceladus; ocean worlds are of significant interest for searching for life elsewhere. **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.** Advances in prebiotic chemistry / origin of life have shown how entire organic reaction cycles that look “metabolic”, and give product distributions entirely different from those found in meteorites, can be driven abiotically in aqueous systems with reactive minerals. Complex abiotic organic chemistry has not been well studied in the context of other worlds besides early Earth, and in order to interpret any future organic detections on Ceres or Enceladus, we need to investigate these organic chemical pathways.

## b) SOA (Comparison or advancement over current state-of-the-art)

- a) **Current state of the art:** Previous work with these abiotic organic reactions has focused on yields. There is a large body of work about CO<sub>2</sub> reduction on iron sulfides to produce simple organics [1-5]; and some studies have been done with the goal of trying to produce yields of certain “prebiotic” compounds from these precursors to lead into origin of life scenarios [e.g. 6]. **However, these studies focus on early Earth contexts and yields of individual products; for planetary organic detections we need to explore networks and organic distribution patterns as they are affected by planetary conditions.**
- b) **Advancement on state of the art:** In a planetary science context we have to look at these organic systems in the context of biosignatures, not the yields of single components but the **organic distributions** which are not meteoritic, but are also not biological, and vary greatly depending on the geochemical context. This Task is the first investigation of how organic distribution patterns are affected by geochemical conditions on other planets, and has implications for life detection and also origin of life on those worlds.

## c) Relevance to NASA and JPL (Impact on current or future programs)

- a) This Strategic Initiative builds on the recent detection of organics by Dawn and Cassini at Ceres and Enceladus (key habitability targets in NASA/JPL Strategic Plans). At the end of this work, we will identify high-fidelity organic indicators of geological conditions and conditions under which they may be preserved to identify science technologies for future investment.



# Methodology

Synthetic mineral reactants are chosen to approximate the range of reactive minerals that may be present on Ceres / Enceladus, focusing on Fe-bearing redox active minerals:

- Ferrous / ferric clays
- Iron sulfides
- Iron hydroxides & green rust

Organic precursors (carboxylic acids pyruvate, glyoxylate, oxaloacetic acid; and carbamate) are reacted with ammonia ( $\text{NH}_4^+$ ) and the reactive minerals. Conditions:

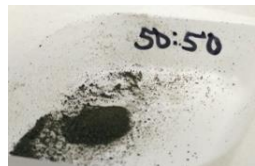
- Titrated to alkaline pH (10), 70°C
- Vary environmental parameters: Fe(II)/Fe(III) ratio, reactant concentrations,  $[\text{NH}_4^+]$

Samples of mineral and supernatant are taken at time points (up to ~3 weeks).

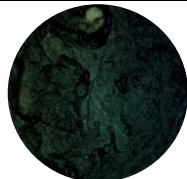
Organic products are analyzed with  $^1\text{H}$  Nuclear Magnetic Resonance (NMR)

Minerals are dissolved to analyze Fe(II)/Fe(III) content after reactions

Other mineralogy: XRD, Raman



Synthetic Fe/Mg saponite clay (UNLV)



Synthetic green rust (Oak Crest)



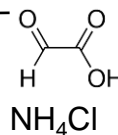
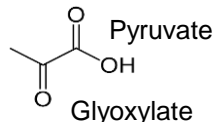
Synthetic iron hydroxides, JPL

Add mineral reactants



Sample solid/liquid

Add organics

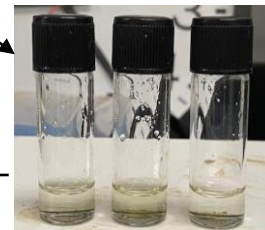


$^1\text{H}$  NMR samples

Remove iron

+ HCl & heat

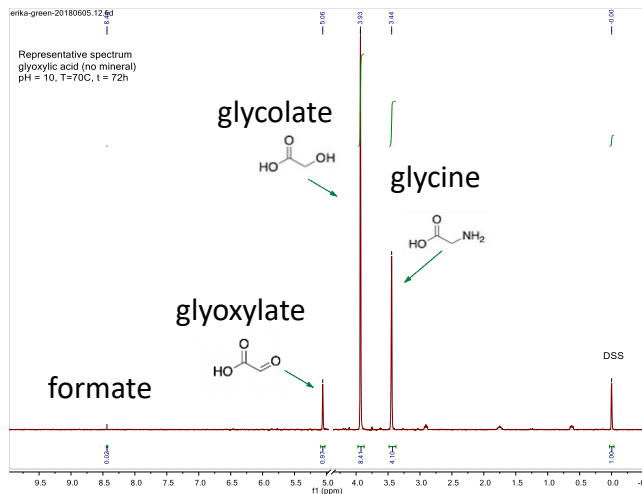
Colorimetry for  $[\text{Fe}^{2+}]$





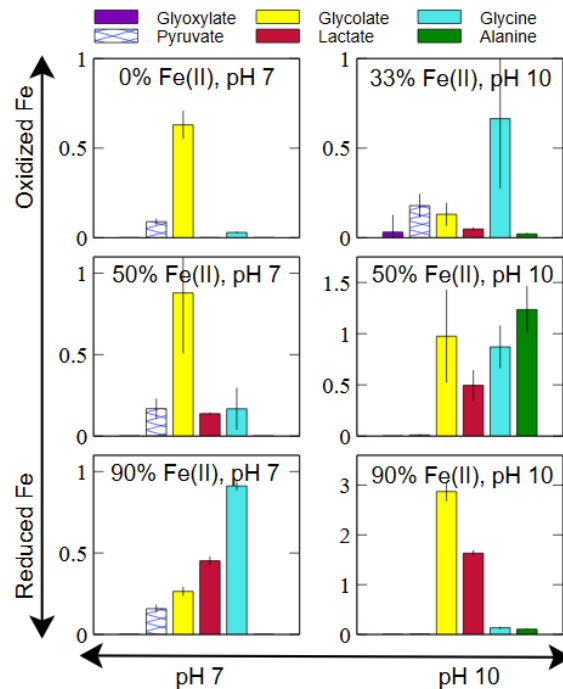
# Results

Example NMR data; concentration of organic products (mM) is proportional to peak area



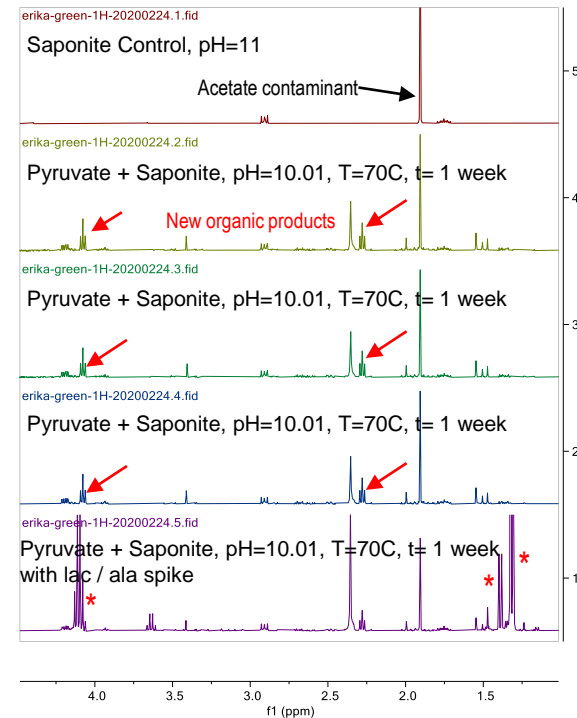
Most major reactants / products can be seen with <sup>1</sup>H NMR; however some are not visible with this technique and require QTOF/MS

Data from Fe-hydroxide experiments



Organic distribution patterns vary as a function of geochemical conditions (mineral %Fe(II) and pH)

Preliminary data from Fe-bearing clay (saponite) experiments



In clay experiments, **new organic products** are formed (to be identified); and the expected products\* do not form

## Results

### Accomplishments versus goals

- 1. Milestone completed:** We completed Objective 1 in this project (test how all the organic precursors react with iron hydroxides) for pH and  $[\text{NH}_4^+]$  and a manuscript is in revision [1].
- 2. Milestone partially completed (descoped due to budget cuts):** The clay synthesis was completed and delivered to JPL in 2019, and experiments have begun. The data shows that new organic products are produced in the presence of saponite clay that are different from organics produced in the presence of our other minerals (hydroxides and sulfides).
- 3. Milestone partially completed (descoped due to budget cuts):** We have begun experiments with iron sulfide. Results of sulfide experiments also show new products that are likely reactive thiols capable of forming polymers.

### Significance

Results so far show that 1) the type of mineral has a significant effect on the organic reactions in an abiotic system; 2) specific geochemical parameters (e.g. pH, Fe redox state, chemical concentrations) drive the organic distribution patterns produced (there is no one “abiotic distribution pattern”); 3) A significant amount of the organics are trapped in the solid phase. These are all significant for understanding how to interpret an organic detection on an ocean world, and (3) means that we need to also understand adsorption characteristics of these organics and minerals.

### Next steps

Continue to test organic reactions with sulfide and identify products; Identify products in clay experiments and characterize effect of parameters; Conduct experiments with green rust (which is more redox active); Test organic adsorption.

# Publications and References



## Publications:

[1] L. M. Barge, E. Flores, J. Weber, M. M. Baum, D. VanderVelde, A. Castonguay. Effects of Geochemical and Environmental Parameters on Abiotic Organic Chemistry Driven by Iron Hydroxide Minerals. Submitted to *JGR-Planets*, 2020

[2] L. M. Barge, L. Rodriguez, J. Weber, B. Theiling (2020) Beyond “Biosignatures”: Importance of Applying Abiotic / Prebiotic Chemistry to the Search for Life on Other Planets. White paper submitted to the Planetary Science / Astrobiology Decadal Survey.

## References:

[1] Huber & Wächtershäuser, 1997 *Science*, 276, 245-247.

[2] Huber & Wächtershäuser: 1998, *Science* 281, 670–672.

[3] Huber & Wächtershäuser 2003, *Tetrahedron Letters*, 44(8), 1695-1697.

[4] Cody et al 2000, *Science* 289:1337–1340.

[5] Yamaguchi et al. 2014, *Electrochimica Acta*, 141, 311–318.

[6] Muchowska et al. 2019, *Nature* 569, 104–107.