Exploring the Reactivity of Metabolically Relevant Precursors under Hydrothermal Analog Settings. J. M.
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Introduction: While mission work is challenging in terms of directly detecting the prebiotic/abiotic chemistry on distant worlds, many of these settings can be simulated in lab based settings. Astrobiologists and planetary scientists can use these analogs in order to test what to expect and plan for on future missions. Chemical gardens[1], which are inorganic precipitates, can be used as an analog for hydrothermal vent structures, which are important for origin of life theories on Earth and on other worlds [2][3]. Exploring what kinds of abiotic chemistry such structures are capable of will help inform the prebiotic chemistry available before the origin of life and on these other worlds. While the effect of amino acids on iron silicate chemical gardens have been explored [4], there have been few other examples of the effect of prebiotic organics on these compounds.

Herein, we explore the reactivity of two alpha keto acids: glyoxylic acid and pyruvic acid. These compounds are metabolically important – both for ancient protometabolisms as well as metabolic pathways today [5][6]. In the presence of iron oxyhydroxide minerals and ammonia, the corresponding alpha hydroxy acid and amino acid are formed via reduction and reductive amination, respectively [7]. We set out to explore if such transformations could be mediated by the chemical gardens. We explored these reactions with and without ammonia (NH_4Cl). We additionally wanted to explore what impact, if any, these additives would have on the chemical garden structure.

Impact on Chemical Garden Growth: We chose to explore iron silicate chemical gardens which are formed when Fe^{2+} is added to a solution of sodium silicate and water. The chemical garden precipitates were grown with 10 mM pyruvic acid (PA) or glyoxylic acid (GA) with no ammonia (NH_4Cl), low ammonia, and high ammonia concentrations (0, 20 and 100 mM respectively). Control chemical gardens with no additives were also synthesizes as well as chemical gardens with only 100 mM of ammonia and no organics. All chemical gardens were ran in duplicate.

In all cases, chemical gardens were successfully formed and the rate of growth was unaffected by the inorganic or organic additives. The only noticeable difference in morphology was in the high ammonia cases (Figure 1). Those chemical gardens only grew to 1-2 inches tall, whereas all other gardens grew to reach the top of the 50 mL Falcon tube.
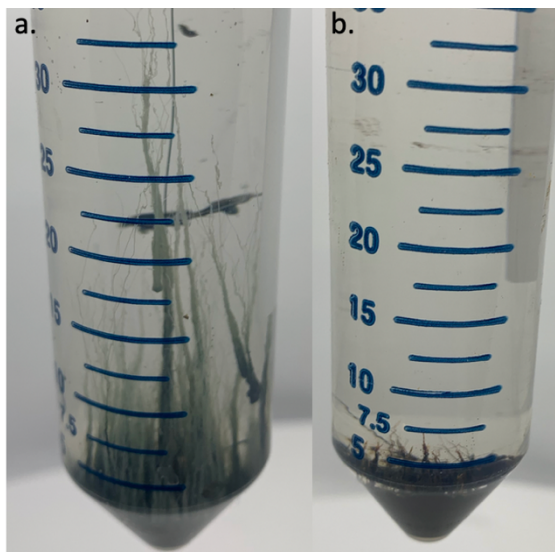

Figure 1. Comparison of chemical gardens grown with pyruvate (10 mM) and ammonia at 20 mM (a) and 100 mM (b) concentrations.

Additionally, over the course of 3 weeks, the chemical gardens containing additive were observed to turn red and oxidize faster than the control chemical gardens (Figure 2). The control structures were observed to maintain their green and white colors for weeks longer than the additive containing gardens, indicating that the additives were responsible for oxidation.
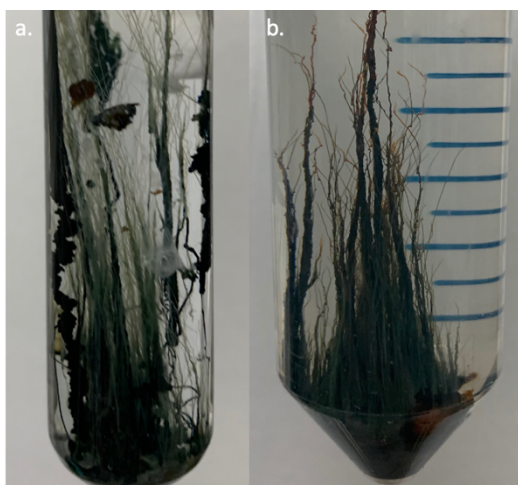

Figure 2. Comparison of chemical gardens grown with (a) no additives and (b) 10 mM glyoxylic acid and 20 mM ammonia after 3 weeks.

Reactivity of Alpha Keto Acids: The reaction products were determined by proton NMR. In the case of pyruvic acid, no productive reactivity to alanine of lactate was observed. With glyoxylic acid, glycolic acid was observed without ammonia present and glycolic acid, glycine, and other glycolic acid side products were detected. Interestingly, in the reaction network mediated by iron oxyhydroxide minerals [7], these additional side products were not observed.

To confirm that the reaction was being mediated by the chemical gardens, we explored the reaction in sodium silicate without iron present. In these cases, we observed nearly identical reactivity to what had been detected with the chemical gardens indicating that the primary reactivity did not occur within the iron-silicate gardens (Figure 3).

With silicate being able to catalyze such a reaction network, this opens up the possibility for multiple reaction pathways in the same setting – in particular, having homogeneous as well as heterogeneous reactions within sediments or hydrothermal chimneys – it is possible that more diverse arrays of organic products could have been available in geological hydrothermal settings. Having a diverse array of both organic building blocks as well as available reaction pathways could make settings comparable to these studies more habitable and more likely to have fostered origin of life type chemistry.
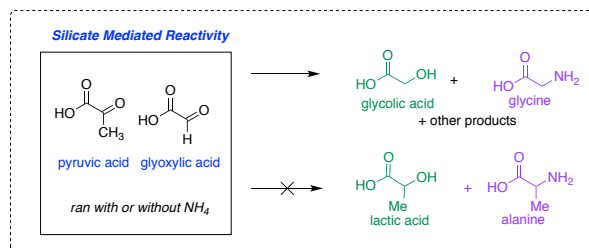

Figure 3. Silica Mediated Reaction Network of Alpha Keto Acids.

Conclusions: We determined the reactivity of two metabolically relevant alpha keto acids in the presence of iron-silicate chemical garden precipitates and their effects on the precipitation. High ammonia was observed to significantly decrease the height of the chemical garden structures. While pyruvic acid did not give productive reactivity, we observed significant reactivity in the case of glyoxylic acid. Interestingly, the iron-silicate precipitate was observe to not be the key reactant. The silicate in solution was observed to be primarily responsible for the reduction and reductive amination reactivity. This opens up additional reaction types and networks available for prebiotic chemistry in a hydrothermal setting both on earth and on ocean worlds including Enceladus. Further laboratory studies under specific analog conditions could allow for better constraints on the habitability of ocean worlds and give a basis for the chemical reactivity to expect upon a mission to such worlds.

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