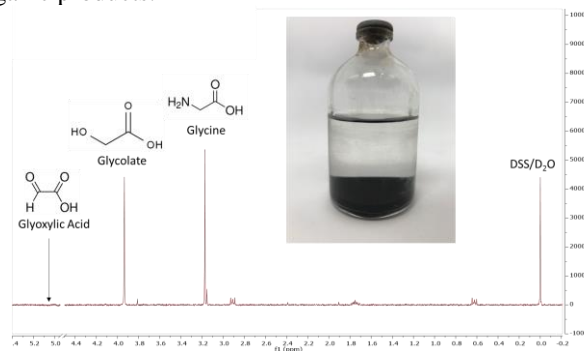


**ABIOTIC ORGANIC SYNTHESIS AND PRODUCT DISTRIBUTIONS IN MARS ANALOGUE IRON MINERAL SYSTEMS.** L. M. Barge<sup>1</sup>, E. Flores<sup>1</sup>, S. M. Perl<sup>1,2</sup>, D. VanderVelde<sup>3</sup>, M. M. Baum<sup>4</sup>. <sup>1</sup>NASA Jet Propulsion Laboratory, California Institute of Technology (laura.m.barge@jpl.nasa.gov), <sup>2</sup>Los Angeles Natural History Museum, <sup>3</sup>California Institute of Technology, <sup>4</sup>Oak Crest Institute of Science.

**Introduction:** Detection of organic compounds in Mars soils remains a high priority for future instruments and missions, especially those organics that may serve as signs of extant life or past biosignatures in the near subsurface. However even with robust chemical detection, identifying actual biosignatures is challenging since many pathways can synthesize organics abiotically in geochemical systems [1-4]. Amino acids are significant since they form proteins and are a fundamental component of terrestrial biology, but can also be synthesized abiotically and are found in meteorites and other geochemical systems without apparent biological precursors or biogenic activity. Other molecules of significance include alpha-hydroxy-acids (AHA's, e.g. lactate or glycolate), many of which are central to metabolism and can be formed by related pathways to amino acids [2]; as well as carboxylic acids (e.g. pyruvate, a common metabolic intermediate). Previous studies have indicated that various carboxylic acid precursors can react with a  $\text{NH}_3$  source to form amino acids [2,4] as well as various thiols if sulfide is present [2]; these reactions are greatly affected by the presence of minerals, specifically Fe and sulfide-rich mineral components. We have previously focused on the effects of iron minerals on pyruvate reactions [5]; here we examine the effects of other precursors and gradients including  $\text{NH}_3$  concentration, in experiments containing iron (oxy)hydroxides similar to what may be found in the Mars subsurface. We find that: amino acids and AHA's are abiotically synthesized from carboxylic acid precursors in iron mineral systems over several days; the liquid phase products are stable and detectable; a fraction of the organics are incorporated into mineral solid phase and are challenging to detect / analyze; the distributions of amino acids and AHA's produced in a system are related to the relative concentration of precursors and also are a function of the particular geochemical conditions. In a system containing partially oxidized iron (oxy)hydroxide or sulfide minerals, organic precursors and an ammonia source, it is likely that amino acids (and AHA's) will be formed in detectable amounts, with distributions that do not appear random but that are related to the geochemistry of the environment.

**Methods:** Iron hydroxides at various oxidation states were synthesized anaerobically via coprecipitation of Fe(II) and Fe(III) chloride salts with NaOH; carboxylic acids were added as pyruvate sodium salt or glyoxylic acid (GA) hydrate; ammonia was added as

$\text{NH}_4\text{Cl}$ . The vials were either left at room temperature or placed in a hot water bath programmed to maintain temperature of 50 – 80°C. After samples were taken, the liquid phase was analyzed with  $^1\text{H}$  NMR to detect organic products.



**Figure 1:**  $^1\text{H}$  NMR spectrum showing reactions of GA with partially oxidized iron hydroxides at 70°C in the presence of ammonia (and no oxygen); glycine and glycolate are synthesized abiotically within 1-3 days.

**Results and Discussion:** The presence of minerals affects carboxylic acid precursors differently: in aqueous solution GA forms glycine whereas pyruvate does not react; but the presence of Fe-oxyhydroxide minerals lead GA to form glycolate as well as glycine. The ratio of Fe(II)/Fe(III) in the oxide/hydroxide mineral is also significant: in the presence of more reduced minerals, synthesis of AHA's relative to amino acids increases. The yield of amino acid is also related to the concentration of  $\text{NH}_3$  in the system. Even though these organic molecules are readily synthesized abiotically, only some products are more likely to remain in the liquid phase; in a typical experiment a substantial fraction of the carbon remained in the solid phase (detectable only at trace levels). Reduced Fe minerals are highly reactive in their initially precipitated form, but are extremely unstable and difficult to analyze when exposed to oxygen / oxidants; on Mars this may affect exposure of subsurface material, and mineral oxidation / other chemical perturbations may induce further reactions of any organics within the system.

**References:** [1] Cody G. D. et al. (2000) *Science* 289 (5483):1337-1340. [2] Novikov Y. and Copley S. D. (2013) *PNAS* 110 (33):13283-13288. [3] Huber C., Wächtershäuser G. (1997) *Science* 276 (5310):245-247. [4] Huber C., Wächtershäuser G. (2003) *Tetrahedron Letters* 44(8):1695-1697. [5] Flores E. et al. (2017) XVIIIth Intl Conf on Origin of Life [#4178].