AMINO ACID SYNTHESIS UNDER ALKALINE HYDROTHERMAL CHIMNEY CONDITIONS. E. Flores[1,2], D. VanderVelde[2,3], K. Kallas[1,2], M. J. Russell[1,2] M. M. Baum[2,4], L. M. Barge[1,2], [1]NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109, [2] NASA Astrobiology Institute Icy Worlds team. [3]California Institute of Technology, Dept. of Chemistry and Chemical Engineering, 1200 E California Blvd, Pasadena, CA 91125, [4]Oak Crest Institute of Science, 132 W Chestnut Ave, Monrovia, CA 91016.

Introduction: Synthesis of biomolecules, particularly amino acids and peptides, from geochemical carbon sources is an important issue for assessing the potential of alkaline hydrothermal environments for the origin of life. Hydrothermal chimneys formed from alkaline vent fluid feeding into the early iron-rich (Fe^{2+} and minor Fe^{3+}) ocean may have contained a large fraction of iron hydroxides / oxyhydroxides [1,2]. It has been shown that pyruvate, a key intermediate in various metabolic pathways, can be produced under simulated hydrothermal vent conditions [3], and that pyruvate and other α-keto acids can react in the presence of transition metal sulfide minerals to form a variety of products including lactate, aldols, thiols, and alanine (in the presence of ammonia) [4,5]. In this work we tested the synthesis of alanine from pyruvate catalyzed by iron oxyhydroxides instead of sulfides, focusing on the effect of gradients of pH, Fe^{2+}/Fe^{3+}, and temperature that would be likely to be encountered in an alkaline vent system. Preliminary results suggest that alanine is synthesized under hydrothermal conditions at particular points within the gradient, and that it can be concentrated and preserved in the mineral interlayers.

Methods: Experiments were conducted under anaerobic early Earth conditions. Iron (Fe^{2+} and Fe^{3+}) was added along with pyruvate, ammonia, and hydroxide to form an iron mineral precipitate and pyruvate reactions were driven by this mineral catalyst. Samples were taken at 24 hour intervals and organics were analyzed with ^{1}H NMR. Several conditions were varied to optimize alanine synthesis: Fe^{2+}/Fe^{3+} ratio, pH, and temperature.

Results/Discussion: The iron oxidation state in the mineral catalyst had a great impact on how much, if any, alanine was produced. When only oxidized iron Fe^{3+} was added to produce a ferric hydroxide, pyruvate did not react. When ferrous hydroxide was used, only lactate was produced. However, when Fe^{2+}/Fe^{3+} was added in ratios between 30-90% Fe^{2+}, alanine was produced. Focusing on these experiments, we were then able to take a look at the effect of pH on the reaction; at more acidic pH, no alanine was produced, but at more alkaline conditions, alanine production greatly increased. This is likely related to the pK_a of ammonia at 9.25. Increased temperature also favored the synthesis of alanine. A control experiment was also performed to test whether the soluble iron in the "ocean" or iron mineral precipitate was actually driving the reaction. We found that the reaction only occurs when the mineral precipitate is present; therefore, the iron mineral catalyst is what drives the alanine synthesis suggesting that amino acids would form within chimneys and precipitates in hydrothermal vent systems. We also tested the propensity of the mineral to adsorb and concentrate amino acids once produced; aspartate was more readily adsorbed into synthetic iron hydroxides than alanine, though both were incorporated and preserved in the solid phase.

Discussion: In mildly acidic, iron-rich oceans of the early Earth, the interface of seawater with alkaline hydrothermal fluid would have produced a mix of mineral precipitates including iron oxyhydroxides at various ratios of Fe^{2+}/Fe^{3+}. These could have reacted with pyruvate or other α-keto acids, along with ammonia (perhaps sourced from mineral-catalyzed reduction of atmospheric N_2 and/or NO_x species), to produce amino acids. This mechanism provides a plausible source of alanine and other amino acids in moderate temperature vent chimney systems; our work shows that there is a particular "position" in the chemical gradients between vent fluid / seawater where amino acid synthesis would be most favored compared to other products of pyruvate. Since the yield and type of organic product is highly dependent on pH and temperature, it is important to understand the specifics of hydrothermal gradients on early Earth and ocean worlds to determine their potential for synthesizing building blocks of life. The suite of amino acids that is most likely to form in a given vent condition must also be considered in the context of the suite of amino acids most likely to adsorb / concentrate in the minerals that catalyzed their formation; even though alanine readily is synthesized in these systems, its abundance for peptide formation and other reactions would depend on the mineral's adsorption capacity, which may favor a different combination of products.

References: [1] Russell, et. al. (2014) *Astrobiology* 14, 308-43. [2] Barge et al. (2015) *JoVE* DOI:10.3791/53015 [3] Cody et al (2000) *Science* 289, 5483:1337–1340 [4] Novikov and Copley (2013) *PNAS* 110, 33, 13283-13288. [5] Huber and Wächtershäuser (2003) *Tetrahedron Letters* 44, 1695-1697.