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Redox and pH Gradients Drive Amino Acid Synthesis at Hydrothermal Vents

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Alkaline hydrothermal environments have been proposed as sites for the emergence of metabolism, and thereby life, on the early Earth. In these environments, iron oxyhydroxides (includeing green rust) and sulfides would have comprised hydrothermal sediments and chimney precipitates where alkaline vent fluids interfaced with the early iron-rich ocean [1,2]. These reactive iron minerals could have stoichiometrically, and perhaps catalytically, driven organic chemical reactions such as amino acid synthesis. A step toward such an outcome is through the hydrothermal carbonylation of iron sulfides – a reaction which produces the carboxylic acid, pyruvate [3]. In the presence of metal sulfides and in similar conditions this, and other carbonic acids, can undergo reductive amination to amino acids [4]. We conducted experiments to test if amino acids could also be synthesized from pyruvate in the presence of the redox-sensitive iron oxyhydroxides (precipitated with Cl^- counter ion). Reactions were carried out in an anoxic glove box to simulate early Earth conditions, and the synthesis of alanine was investigated by focusing on the effects of the various gradients likely to be encountered at alkaline submarine hydrothermal vents. These include varying the pH, temperature and also mineral composition. Products were analyzed with ^{1}H liquid NMR. Our preliminary results showed that while no amino acids were produced at more acidic conditions, high yields of alanine were produced as the pH approached the pK_a of ammonia at ~9.3 and beyond. But it was found that alanine synthesis also depended upon the Fe^{2+}:Fe^{3+} ratios of the iron hydroxide mineral. There was no reaction at all in cases where the iron hydroxide was completely oxidized, whilst only lactate formed in cases where it was completely reduced. Thus, the redox and pH gradients obtaining at the vent must be considered in gauging the likelihood of amino acid synthesis from simple precursors as a first step in assessing the conditions likely to have driven life to emerge on this, and other, wet and rocky worlds.

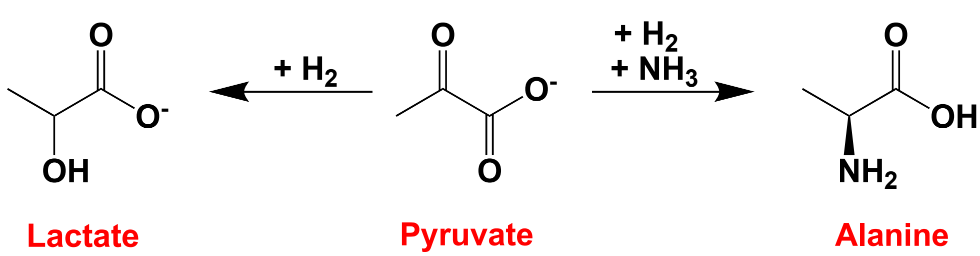

Figure 1 – Reaction of pyruvate reacting with ammonia to produce alanine and/or lactate.

[1] Russell, et. al. (2014) *Astrobiology* 14, 308-43. [2] Barge et al. (2015) *Journal of Visualized Experiments* DOI:10.3791/53015 [3] Cody et al (2000) *Science* 289, 5483:1337–1340 [4] Novikov and Copley (2013) *Proceedings of the National Academy of Sciences* 110, 33, 13283-13288.