Reductive Amination Driven by Iron Hydroxides in Hydrothermal Systems

L. M. BARGE[1,2], E. FLORES[1,2], D. VANDERVELDE[2,3], M. M. BAUM[2,4]

[1]NASA Jet Propulsion Laboratory, California Institute of Technology (laura.m.barge@jpl.nasa.gov)
[2]NASA Astrobiology Institute, Icy Worlds
[3]Department of Chemistry, California Institute of Technology
[4]Oak Crest Institute of Science

The synthesis of biomolecules from geochemical carbon sources, particularly amino acids and their condensation into peptides, is an important research topic for assessing the potential role of hydrothermal environments in the origin of life. Iron sulfides as well as iron hydroxides have been shown to be capable of driving reductive amination of α-keto acids to form amino acids [1,2]; this reaction is thought to proceed through an imine intermediate followed by reduction to form the amine [3]. Pyruvate is of particular relevance for the emergence of metabolism since it is a key intermediate in various metabolic pathways; other relevant precursors include oxaloacetate and glyoxylic acid, which can be reductively aminated to form aspartic acid and glycine, respectively. We attempted reductive amination reactions in the presence of the precursor carbonyl compound and ammonia, driven by mixed valence iron hydroxides similar to those likely to be found in an early Earth alkaline hydrothermal environment. For the synthesis of alanine, we found that the reactivity of pyruvate varied depending on both pH of the reaction mixture and the overall oxidation state of the mineral. Alkaline conditions along with partially oxidized iron hydroxides strongly favored the formation of alanine along with lactate (a reduction product of pyruvate), whereas neutral conditions favored only lactate production. In the case of glycine, the same conditions that resulted in the highest alanine yield (and lactate) seemed to promote the synthesis of glycine and glycolate from glyoxylic acid and ammonia. However, when oxaloacetate was used, aspartic acid was not obtained and the starting material was converted to pyruvate and, subsequently, afforded alanine and lactate. These experiments provide a basis for how reductive amination may be driven in seafloor systems by minerals, and how the ambient geochemical gradients can drive selectivity for various products.

[1] Novikov Y. and Copley S. D. (2013) PNAS 110, 33, 13283-13288. [2] Huber, C., Wächtershäuser, G. (2003). 44(8), 1695-1697. [3] Gomez S., et al. (2002) Adv. Synth. Catal., 344, 10: 1037-1057.