

## SURFACE-CATALYZED PEPTIDE FORMATION ON SULFIDE MINERALS

S. Ohara<sup>1</sup> and G. D. Cody<sup>1</sup><sup>1</sup>Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

**Introduction:** The formation of peptides from amino acids in dilute solutions on the early Earth remains an enigma for the origins of life. Spontaneous peptide formation under moderately dilute conditions can only occur at very low levels due to unfavorable thermodynamics. In biological systems, peptide formation in the ribosome occurs through group activation and amino acid transfer at the expense of ATP and GTP. Presumably the ribosome was innovated at some time after the origins of life, therefore, it appears reasonable to consider simpler origins for peptides via abiological pathways.

Many enzymes that are integral to the formation of organic molecules from small components contain transition metal sulfide clusters at their active sites [1]. The important role of metal sulfide clusters in extant microbial biosynthesis inspired two distinct hypotheses by Wächtershäuser [2, 3] and Russell and Hall [4] wherein sulfide mineral surfaces catalyzed the production of the first biomolecules in the absence of enzymes. Cody et al. [5, 6] showed that many common transition metal sulfides have the capacity to convert simple molecules (e.g. CO<sub>2</sub>, CO and H<sub>2</sub>) into carboxylic acids. Interestingly Huber and Wächtershäuser [7] reported that dipeptides were formed via reactions of amino acids in the presence of a (Ni,Fe)S precipitate with CO and H<sub>2</sub>S (or CH<sub>3</sub>SH) at 100°C. In these later experiments, however, it was subsequently shown that COS may have been the condensation reagent [8] and a special role of the metal sulfide for this reaction is not required. We present here results where peptide formation is significantly enhanced in presence of pyrite and sphalerite and in the absence of COS.

**Experimental:** Pyrite (Huanzala, Peru) and sphalerite (New York, USA) were crushed, sieved (diameter <210 μm) and acid-washed in 0.5 M HCl and rinsed several times with deionized water. The sulfides were then dried under a N<sub>2</sub> atmosphere and sealed into glass capillaries filled with N<sub>2</sub>-purged glycine solution. The capillaries were reacted at 100°C for 6-24 hours under the vapor pressure of the solution.

Quantitative analysis of glycine and its peptides was performed by electron spray ionization-liquid chromatography-mass spectrometry (ESI-LC-MS), using ACQUITY UPLC System (Waters) with a BEH C18, 1.7 μm, 2.1 x 50 mm column (Waters) and a mobile phase of 5 mM undecafluorohexanoic acid and methanol (99:1). L-aspartic acid was added to the reac-

tion mixture before LC-MS analysis as the internal concentration standard.

**Results and Discussion:** It is well known that glycylglycine (Gly<sub>2</sub>) and 2,5-diketopiperazine (DKP) will form at 100°C at low concentrations consistent with thermodynamic expectation. In the presence of sulfide minerals, peptide formation is considerably enhanced up to the formation of 4-mers. That the peptization reaction is surface catalyzed is suggested by the fact that the yield strongly correlates with mineral surface area. Recent computer simulations suggest that Lewis acid catalysts dramatically lower the activation barrier for the peptide formation [9]. An element's ionization potential is a rough guide to Lewis acid strength and both iron and zinc act as strong Lewis acids. Accordingly, the formation of Gly<sub>2</sub> and longer peptides could be catalyzed on the iron and zinc sites of pyrite and sphalerite surfaces, respectively.

It is interesting to note that the yield of Gly<sub>2</sub> with sphalerite was much higher than with pyrite under the same surface-area condition. It is known that the oxidation of surface iron and reaction with water forms hydroxyl radicals (·OH) [10]. Zinc is incapable of oxidation and, thus peptides formed on the surface of ZnS would not be subjected to decomposition as may occur with pyrite. It appears possible that on the early Earth sphalerite might have acted as a catalyst to promote prebiotic peptide formation.

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