The formation of Amino acids and Organic acids from simulated mildly-reducing primitive atmosphere

*Miei Kinoshita[1], Ryohei Aoki[1], Junichi Ise[1], Hitoshi Fukuda[2], Yoshiyuki Oguri[2], Hiromi Shibata[3], Junichi Takahashi[1], Kimitaka Kawamura[4], Bhagawati Kunwar[4], Yoko Kebukawa[1], Kensei Kobayashi[1]

1. Yokohama National University, 2. Tokyo Institute of Technology, 3. Osaka University, 4. Chubu University

Since 1950s, a large number of laboratory experiments have been performed to examine possible formation of bioorganic compounds such as amino acids in primitive Earth atmosphere. Earlier experiments with strongly reducing gas mixtures containing large molar ratio of methane and ammonia, and it was reported that efficient production of amino acids and other important organics were formed in it by spark discharges and other energy sources. It is now estimated, however, that the early Earth atmosphere was only slightly reducing [1]: N_2 and CO_2 were the major atmospheric constituents, together with some small amount of reducing carbon species like CH_4 and/or CO. Simulation experiments suggested, however, that amino acid formation was restricted under these conditions [2]. We reported that cosmic rays could facilitate chemical reactions with less reducing model of primitive atmosphere such as a mixture of CO_2, CO, N_2 and H_2O [3]. However these energy sources have been ignored in experiments with initiation of prebiotic chemistry [4]. Here, we examine possible formation of amino acids from slightly reducing gas mixtures by applying high-energy protons to simulate the action of cosmic rays.

We conducted three sets of laboratory experiments using energetic particles, spark discharge and UV light as dominant energy sources. In these sets of experiments we used 400 mL of gas mixture of N_2, CO_2 and CH_4 introduced to a Pyrex tube together with 5 mL of pure water under 350 Torr of N2 and 350 Torr of mixtures with varied mixing ratios of CH_4 and CO_2. In order to simulate possible roles of cosmic rays, the gas mixture was irradiated with 2.5 MeV proton beam produced in the Tandem accelerator at Tokyo Tech, Japan. We also exposed the same composition of gas mixtures to spark discharges by using a Tesla coil to simulate lightning. The gas mixtures were also irradiated with UV light (λ > 190 nm) from a xenon lamp. Each product was acid-hydrolyzed and was subjected to amino acid analysis by HPLC and GC/MS, both after derivatization. Carboxylic acids were determined by GC/MS after derivatization. Starting and resulting gas mixtures were analyzed with a quadrupole mass spectrometer.

Amino acids were detected in the hydrolyzed products when gas mixtures of N_2, CO_2, CH_4 and H_2O were irradiated with 2.5 MeV protons at the initial the molar ratio of methane (r_{CH4}) in the starting gas mixture as low as 0.5 %. On the other hand, amino acids were detected only when r_{CH4} was greater than 15 % in the case of spark discharges. The experiments with UV irradiation source did not yield amino acids or their precursors even when r_{CH4} was 50 %. Very little amino acids were detected in all the products before hydrolysis. It was shown that not free amino acids but amino acid precursors were formed in selected experiments.

Carboxylic acids including formic acid, oxalic acid and glyoxylic acid were detected from unhydrolized products derived from N_2-CO_2 gas mixtures exposed to spark discharges and proton irradiation. We show that some free carboxylic acids could be formed in non-reducing atmospheres as well as slightly reducing atmospheres either by proton irradiation or by spark discharges. It was suggested that the mechanism of formation of amino acid precursors from N_2-CO_2-CH_4-H_2O mixtures was quite different from that of carboxylic acids.

Lightning and solar UV have been considered important energy sources for prebiotic synthesis in primitive Earth atmosphere. We here showed that lightning and solar UV could not singularly synthesize important N-containing organics such as amino acids from slightly reducing primitive Earth atmosphere. On the other hand, cosmic ray could have been an important energy source to synthesize amino acid precursors even if primitive Earth atmosphere was only slightly reducing. It would be of interest to examine whether there are synergetic effects among cosmic rays, UV and thundering.

References:

[1] H. Kuwahara and S. Sugita, *Icarus,* **257**, 290-301 (2015).

[2] H. Kuwahara *et al., Orig. Life Evol. Biosph.,* **42**, 533-541 (2012).

[3] K. Kobayashi *et al.*, *Orig. Life Evol. Biosph.* **28**, 155-165 (1998).

[4] S. L. Miller and H. C. Urey, *Science,* **130**, 245-251 (1957).

Keywords: Amino acid, Carboxylic acid, Early earth atmosphere, proton irradiation, spark discharge

