## Prebiotic Formation of Amino Acid Precursors in Primitive Earth Atmosphere by Cosmic Rays and Solar Energetic Particles

\*Kensei Kobayashi<sup>1</sup>, Ryohei Aoki<sup>1</sup>, Yoko Kebukawa<sup>1</sup>, Hiromi Shibata<sup>2</sup>, Hitoshi Fukuda<sup>3</sup>, Kotaro Kondo<sup>3</sup>, Yoshiyuki Oguri<sup>3</sup>, Vladimir Airapetian<sup>4</sup>

1. Department of Chemistry, Yokohama National University, 2. Osaka University, 3. Tokyo Institute of Technology, 4. NASA Godard Space Flight Center

Since Miller's spark discharge experiment in 1953 [1], many experiments have been performed to see how bioorganic compounds such as amino acids were produced in primitive Earth atmosphere. In the earlier experiments, strongly reducing gas mixtures containing methane and ammonia were mainly used, and amino acids were detected after the applying such energies as spark discharges and ultraviolet light. In these days, however, it is estimated that the early Earth atmosphere were less reducing: its major constituents were  $CO_2$  and  $N_2$ , together with small amount of reducing carbon species like  $CH_4$  and/or CO [2]. Simulation experiments suggest, however, that amino acid formation is restricted under these conditions [3]. High-energy charged particles of galactic and solar origins are always penetrating into planetary atmosphere, which could facilitate reactions among atmospheric gases, but they have been ignored as prebiotic energy sources for their lower energy fluxes [4]. We examine possible formation of amino acids from slightly reducing gas mixtures by applying ionizing radiation to simulate the action of galactic and solar cosmic rays.

Gas mixture of  $N_2$ ,  $CO_2$  and  $CH_4$  of various mixing ratios were introduced to a Pyrex tube together with 5 mL of pure water. The gas mixture was irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Tech, Japan). The same composition of gas mixtures were subjected to spark discharges by using a Tesla coil to simulate thudering. Each product was acid-hydrolyzed and was subjected to amino acid analysis by HPLC and GC/MS.

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, even if the molar ratio of methane ( $r_{CH4}$ ) in the starting gas mixture was as low as 0.5 %. In the case of spark discharges, however, amino acids were not detected when  $r_{CH4}$  was lower than 15 %. Considering fluxes of various energies on the primitive Earth [5], galactic cosmic rays appear to be an efficient factor to produce N-containing organics than any other conventional energy sources like thundering or solar UV emission irradiated the early Earth atmosphere.

Besides galactic cosmic rays, frequent solar energetic particles (SEPs) associated with solar explosive events could have served as energy sources for prebiotic chemistry in the atmosphere of early Earth. Frequent superflares have been observed in young sun-like stars [6], which suggests that high energy SEPs produced during solar magnetic storms could have been efficient in supplying energy for efficient production of HCN and  $N_2O$  [7]. Solar energetic particle events could have enhanced production of bioorganic compounds in primitive Earth atmosphere. Further experimental studies on such effects are in progress.

References: [1] S. L. Miller, *Science*, **117**, 528-529 (1953). [2] H. Kuwahara and S. Sugita S., *Icarus*, **257**, 290-301 (2015). [3] H. Kuwahara *et al. Orig. Life Evol. Biosph.*, **42**, 533-541 (2012). [4] S. L. Miller and H. C. Urey *Science*, **130**, 245-251 (1957). [5] K. Kobayashi *et al.*, *Orig. Life Evol. Biosph.* **28**, 155-165 (1998).
[6] H. Maehara *et al. Nature* **485**, 478-481 (2012). [7] V. S. Airapetian *et al.*, *Nat. Geosci.* **9**, 452-455 (2016).

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