Stability of Amino Acids and Amino Acid Precursors in Space: Approaches Through Space Experiments (Tanpopo and Tanpopo 2) and Ground Simulation Experiments

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Amino acids have been detected in water extracts of carbonaceous chondrites (CCs) [1], which suggests that extraterrestrial organics could be sources for the first life on the Earth. The fact that amino acids extracted from CCs increased after acid-hydrolysis [1] showed that not only free amino acids but also amino acid *precursors* were present in them. Experiments simulating interstellar environments showed that amino acid *precursors*, rather than free amino acids, were formed [2]. Though extraterrestrial *amino acid precursors* have not been well-identified, aminonitriles and hydantoins could be candidates. Beside such *simple* amino acid precursors, *complex* amino acid precursors were found in the product after proton irradiation of interstellar media analogue [3]. If extraterrestrial amino acids were delivered to the primitive Earth, they should survived in space environments against various types of energetic particles and photons. We investigated the stability of amino acids and their precursors against heavy ions, gamma-rays, UV, soft X-rays, etc. In addition to these laboratory simulations, we exposed amino acids and their precursors in the Exposed Facility of Kibo, ISS in the Tanpopo mission (2015-2019) [4] and the Tanpopo 2 mission (2019-2020).

Ground Experiments: Samples used were glycine (Gly), aminoacetonitrile (AAN), hydantoin (Hyd) and CAW (products of proton irradiation of a mixture of CO, NH_3 and H_2O [3]). *Heavy ions irradiation*: Aqueous solution of each molecule, frozen in liquid nitrogen, was irradiated with 290 MeV/u carbon ions from HIMAC (NIRS, Japan). *γ-Rays irradiation*: Aqueous solution of each target molecule was irradiated with γ-rays (5-15 kGy) from a ^{60}Co source (Tokyo Tech, Japan). *UV irradiation*: Each sample was UV irradiated from a xenon (Ushio), a deuterium (Hamamatsu Photonics) or an eximer lamp (Ushio) after dried in pits of an aluminum plate. *Soft X-rays irradiation*: Each sample was on the Al plate was irradiated with soft X-rays from a BL-6 of NewSUBARU. *Hydrothermal reaction*: Aquous solution of each sample was heated at 150℃ for 6-24 hours in an ETTAS Hightemp oven. Amino acid analysis: all the target materials were acid-hydrolyzed (6 M HCl, 110℃, 24 h), and were determined with an amino acid analyzer (Shimadzu UHPLC NEXERA).

The Tanpopo Mission: Alminum exposure panels with small pits were used. Gly, Hyd and CAW were put in the pits and covered with hexatriacontane (HTC). Five plates were prepaired: (i) The space-exposed with a MgF_2 window, (ii) the space-exposed with a SiO_2window, (iii) the dark control that was space-exposed behind other panels, (iv) the cabin control, stored in the ISS cabin and (v) stored in a ground laboratory (the ground control). Three sets of the plates were launched in 2015, and each set of the plates returned to the Earth in 2016, 2017 or 2018.

The Tanpopo 2 Mission: Gly, Hyd and CAW with different thickness of HTC were prepaird by using the same kind of aluminum plate. Besides them, Gly and CA (products of proton irradiation of a mixture of CO and NH_3) were directly evaporated onto silicon plates. The silicon plates with and without windows were prepared. Space exposure of the aluminum and the silicone plates with the target organics started in August 2019, and will returned to the Earth in 2020.

RESULTS AND DISCUSSION Recovery was discussed by glycine amount since glycine was major compound after acid-hydrolysis of the products (with the exception of Ival and EMHyd). Among Gly, Hyd, AAN and CAW, Gly showed the lowest recovery against gamma-rays, and AAN showed the lowest recovery in hydrothemal reaction, while Hyd showed the lowest recovery after space exposure of the Tanpopo Mission. In the case of UV irradiation, relative stability differed by the kinds of light sources: Gly was more stable than CAW in the Xe-lamp experiment, but CAW showed higher recovery than Gly in the D_2-lamp experiment and the soft X-ray experiment. Thus space experiments are importance to test stability in actual space environment. Overall, space UV would be fatal to all the organics tested, so that they should be protected by shielding with minerals or other materials to survive in space for a long period. CAW, complex precursor of amino acids, showed to be more stable against charged particles, soft X-rays, VUV and heat than free amino acids and simple precursors. The Tanpopo 2 would give further information on stability of organics in space.

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