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宇宙環境下でのアミノ酸関連分子の安定性：宇宙実験たんぽぽ・たんぽぽ２での検証

Stability of Amino Acid-Related Molecules in Space Verified by Space Experiments Tanpopo and Tanpopo2

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1. Introduction

Wide variety of organic compounds have been detected in extraterrestrial bodies. Carbonaceous chondrites (CCs), especially, contain a wide variety of organics including bioorganic compounds like amino acid precursors[1], suggesting that exogenous organic compounds could be important sources for the first life on the Earth. Concentration of Amino acids in CCs increased after acid-hydrolysis[2], which showed that not only free amino acids but also amino acid *precursors* were present in them. Amino acids found in CCs might have been formed from interstellar ices in molecular clouds[3] or in meteorite parent bodies[4], and experiments simulating such extraterrestrial environments showed that amino acid *precursors*, rather than *free* amino acids, were formed. As candidates for extraterrestrial amino acid precursors, aminonitriles[5] and hydantoins[6] were proposed. In addition to such simple amino acid precursors, *complex amino acid precursors* were found in the product after proton irradiation of interstellar media analogue[7]. If amino acids or their precursors formed in extraterrestrial environments were delivered to the primitive Earth, they should survive in space environments against energetic particles and photons. We performed space experiments, where amino acids and their precursors were exposed to space in the Exposed Facility of Kibo, ISS in the Tanpopo mission (2015-2019)[8] and the Tanpopo 2 mission (2019-2020).

2. The Tanpopo Mission

2.1 The Mission Description

The Tanpopo Mission is the first Japanese astrobiology space experiments by utilizing Kibo (Japanese Experimental Module) Exposed Facility (JEM-EF) of the International Space Station. The objectives of the mission were to examine possible interplanetary transfer of microbes and possible delivery of bioorganics by cosmic dusts. The mission was composed of the capture experiment and the exposure experiment. Several 10 cm x 10 cm (or 20 cm) x 2 cm panels were used for both experiments, which were attached to ExHAM (the Exposed Experiment Handrail Attachment Mechanism) and ExHAM was placed at JEM-EF.

In the capture experiment, panels with ultra-low-density silica aerogel were placed in JEM-EF for about 1 year to collect dusts that were moving in space at high speed. In the exposure experiment, panels with aluminum plates having small pits were used. Microbes or organic compounds were put in the pits, covered with quartz or MgF2 windows, and exposed to space for 1-3 years. The mission started in 2015, and samples returned to Earth in 2016, 2017, 2018 and 2019.

2.2 The Organic Exposure Experiment[9)]

The following amino acids and their precursors were used: Glycine (Gly), Isovaline (Ival), hydantoin (Hyd; precursor of Gly), 5-Ethyl-5-methylhydantoin (EMHyd), and complex organics synthesized from CO, NH_3 and H_2O by proton irradiation (CAW). Target molecules were put in the pits and covered with hexatriacontane (HTC) to avoid sublimation in space. Five plates were prepared: (i) The space-exposed with a MgF_2 window, (ii) the space-exposed with a SiO_2 window, (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. UV dose was monitored with the alanine dosimeter newly developed.

2.3 Results and Discussion on the Tanpopo Organic Exposure Experiment.

The recoveries of Gly, Hyd and CAW were evaluated by glycine amount by HPLC since glycine was major compound after acid-hydrolysis of the products. In the case of Ival and EMHyd, the recoveries were calculated as isovaline yields after acid-hydrolysis by HPLC. Recoveries of Gly, Ival, Hyd and EMHyd were also obtained without hydrolysis by GC/MS or LC/MS.

After 1-3 years space exposure, each of the target molecules showed pseudo first-order kinetics for decomposition. Gly and CAW showed higher recoveries than the other three after space exposure of the Tanpopo Mission. In the case of UV irradiation on ground, 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. In the Tanpopo Mission, every sample was covered with HTC so that short-wavelength VUV ($\lambda < 160$ nm) was mostly cut. Thus, Gly's high recovery was due to its low absorbance at $\lambda > 160$ nm. On the other hand, CAW had quite high absorbance at $\lambda > 160$ nm, but still showed almost the same stability as Gly.

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, γ-rays and heat than free amino acids and simple precursors, which suggested that complex amino acid precursors are robust in molecular clouds and meteorite parent bodies .

3. The Tanpopo2 Mission

In the Tanpopo mission, the use of HTC and windows (MgF_2 or quartz) cut short-wavelength VUV from the Sun. It is of important to test the stability of molecules against full spectrum of solar radiation. We started the succession mission of the Tanpopo, Tanpopo2 from 2019. In this mission, Gly, Hyd and CAW was exposed to space with different thickness of HTC by using the same kind of aluminum plate as the Tanpopo Mission. Besides them, Gly and CA (products of proton irradiation of a mixture of CO and NH_3 [10]) 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 autumn of 2020.

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