Amino acid synthesis from glycolaldehyde and ammonia

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Introduction: Carbonaceous chondrites contain a diverse suite of extraterrestrial amino acids (AAs) [1]. We found 10 new AAs in the Murchison meteorite and 20 AAs including the new AAs were produced by the formose-type reaction with ammonia [2]. Since meteoritic AAs are known to exist as their “precursor” forms, the AA abundance increases after acid hydrolysis. In this study, we investigated the distribution of AAs and the precursors in the experiments using glycolaldehyde an ammonia in order to pursue their detailed pathways of abiotic AA synthesis in natural environments including the early Earth.

Materials and Methods: The aqueous solution (~3 mL) containing ammonia/glycolaldehyde (100/1 by mol) with H_2O/NH_3 (100/1) was heated at 60 °C for 6 days under a nitrogen or an air atmosphere. AAs in the unhydrolyzed and 6M HCl acid-hydrolyzed fraction of each sample were derivatized and analyzed by gas chromatography/ mass spectrometry (GC/MS). We also investigated the distribution of AA precursor(s) in each unhydrolyzed sample by high-performance liquid chromatography/ high-resolution mass spectrometry (HPLC/HRMS) using an Orbitrap® mass spectrometer.

Results and Discussion: Total 14 AAs were identified in the acid-hydrolyzed products by GC/MS. Glycine (Gly) is the most abundant and other amino acids are composed mainly of alanine, β-alanine, homoserine, serine, and isoserine. Gly in the products under an air atmosphere was ~13 times more abundant than that of products under a stream of nitrogen (~8400 ppm vs. 640 ppm relative to carbon amount of reactants, respectively). We observed the similar increase in a structure-unknown $C_4H_7N_2O^+$ detected by HPLC/HRMS. We consider the ion is a possible Gly precursor in the samples, called dihydropyrazinone. An ambient oxygen enhanced the yield of the Gly precursor. Therefore, we concluded that this glycine formation pathway includes intermidiate(s) affected by dissolved oxygen. This previously unreported pathway can be proceeded in oxic and anoxic natural envirionments.

References: [1] Burton A. S. et al. (2012) Chem. Soc. Rev., 41, 5459-5472. [2] Koga T. and Naraoka H. (2017) Sci. Rep., 1–8.