POSSIBLE FORMATION OF AMINO ACID PRECURSORS AND NUCLEIC ACID BASES IN INTERSTELLAR ENVIRONMENTS. K. Kobayashi[1], H. Tokimura[1], T. Matsuda[1], S. Enomoto[1], Y. Kebukawa[1], T. Kaneko[1], H. Fukuda[3] Y. Oguri[3], and S. Yoshida[1], Yokohama National University (Chemistry Department, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan; kkensei@ynu.ac.jp), [2]Tokyo Institute of Technology , [3]National Institute of Radiological Sciences

Introduction: It has been reported that a wide variety of complex organic compounds is present in carbonaceous chondrites (CCs) and comets. A great number of amino acids were detected in hot water extracts of CCs [1], and glycine was detected from a returned sample from comet [2] including amino acids and nucleic acid bases have been detected in carbonaceous chondrites and comets. There have been proposed a numbers of scenarios how such organic compounds were formed. One of the plausible scenarios is so-called the Greenberg model. In this model, interstellar media in molecular clouds were irradiated with cosmic rays and UV to form complex organics. We irradiated possible interstellar media with high-energy particles, and analyzed the products.

Experimental: Mixtures of carbon monoxide, methane, ammonia and/or water was irradiated with 2.5 MeV protons from a Tandem accelerator (TIT, Japan). In some experiments, ^{13}C-labelled carbon monoxide was used. Mixtures of methanol, ammonia and water with various mixing ratio were irradiated with high-energy heavy ions such as carbon ions (290 MeV/u) from HIMAC (NIRS, Japan). Products were subjected to analysis after or without acid-hydrolysis. Amino acids were analyzed by cation exchange HPLC and/or GC/MS with proper derivatization. Nucleic acid bases were first fractionated with reversed-phase HPLC, and then identified by LC/MS (negative mode) with a HILIC column. Products were characterized by FT-IR and other technics.

Results and Discussion:

Formation of amino acid precursors. From all the irradiation products after hydrolysis, a number of amino acids were detected, while only traces of amino acids were detected in unhydrolyzed products. Thus not free amino acids but amino acid precursors were formed by particle irradiation of mixtures having carbon monoxide (or methanol, ammonia) and ammonia. Proton irradiation product from a mixture of carbon monoxide, ammonia and water (hereafter referred to as CAW) gave glycine (precursors) at quite high-energy yield, whose G-value was as high as 0.3. When methane was added to the gas mixture (the product is referred to as CMAW), glycine yields were decreased but those of larger amino acids such as alanine and amino butyric acids were increased. Amino acid precursors were also formed even when the frozen mixtures (77 K) of methanol, ammonia and water were irradiated (the product: MeAW).

Formation of nucleic acid bases. Among purines and pyrimidines, adenine, guanine, xanthine, hypoxanthine, uracil and thymine were identified in CAW (unhydrolyzed) by LC/MS. Cytosine was not able to identified in the product by the present LC/MS method, but it was previously identified by GC/MS after TMS derivatization [3]. Uracil was most abundant (G-value: 7×10^{-5}) among purines and pyrimidines. Since these bases were identified in unhydrolyzed products, we can say that free nucleic acid bases can be synthesized from possible interstellar media.

Characterization of the products. An average molecular weight of CAW was estimated ca. 2900 by gel filtration. FT-IR spectra of both CAW and CMAW (before hydrolysis) showed peaks at 1670 cm^{-1} (amide C=O), and that of CMAW showed peaks at 1750 cm^{-1} (carboxylic acid or ester C=O). The amide C=O peaks were disappeared after hydrolysis. It is suggested that CAW contained sequences such as (-CO)–NH_2.CH_2-CO-(NH or O)- that could be released by hydrolysis to form glycine. If such sequence as –NH-CO-NH-CH_2-CH_2-CO- was formed by the irradiation, it would be stabilized by forming a ring to be uracil. The former sequence could have been appeared much more frequently than the latter, judging from the difference in G-values of glycine and uracil. When methane was added, CO/CH_2 ratio was decreased, which resulted in the decrease of the former sequences (glycine precursors).

Stability of amino acids and nucleic acid bases. Aqueous solution of amino acids, amino acid precursors (such as CAW) and nucleic acids were irradiated with heavy ions at HIMAC. Nucleic acid bases were most stable, followed by amino acid precursors. It was suggested that amino acid precursors and nucleic acid bases are robust molecules that can survive in space and could be delivered to the primitive Earth, while free amino acids are not robust. It will be confirmed by space exposure in the Tanpopo Mission [4].

References: [1] Kvenvolden K. A. et al. (1979) *Nature 228*, 923-926. [2] Elsila J. E. et al. (2009) *Meteoritics & Planet. Sci., 44,* 1323-1330. [3] Yamanashi H. et al. (2001) *Anal. Sci. 17 Suppl.,* i131–134. [4] Kobayashi et al. (2014) *Trans. Jpn. Soc. Aeronaut. Space Sci., 12 (ists29)*, Pp_1.