Evolution of Interstellar Organics to Meteoritic and Cometary Organics: Approaches by Laboratory Simulations. K. Kobayashi[1,2], Y. Kawamoto[1], W. El-Masry[1], M. Eto[1], H. Tokimura[1], T. Kaneko[1], Y. Obayashi[1], H. Mita[3], K. Kanda[4], S. Yoshida[5], H. Fukuda[6] and Y. Oguri[6], [1]Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, kkensei@ynu.ac.jp, [2]National Institutes of Natural Sciences, 4-3-13 Toranomon, Minato-ku, Tokyo 105-0001, Japan, [3]Fukuoka Institute of Technology, [4]University of Hyogo, LASTI, 3-1-2 Koto, Kamigori-cho, Ako-gun 678-1205, Japan, [5]National Institute of Radiological Sciences, 4-9-1 Anagawa, Inage-ku, Chiba 263-8555, Japan, [6]Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

Introduction: Wide variety of organic compounds including amino acid precursors have been detected in such extraterrestrial bodies as carbonaceous chondrites and comets, and their relevance to the origin of life on the Earth is discussed. Isotopic ratios of meteoritic and cometary organics has suggested that these organics were formed in extremely cold environments such as dense clouds. Laboratory experiments simulating possible reactions in ice mantles of interstellar dust particles (ISDs) indicated that amino acid precursors were easily formed in them [1]. Organic compounds formed in ISDs should have been altered after introduced to proto-solar nebula by high-energy photons and particles and/or thermal / hydrothermal reactions in parent bodies of meteorites. Here we examined possible formation of amino acids and nucleic acid bases (or their precursors) from possible interstellar media, and alteration with high-energy photons, particles and hydrothermal reactions.

Experimental: *Synthesis of possible interstellar organics.* Carbon monoxide (350 Torr), ammonia (350 Torr) and liquid water (5 mL) was put in a Pyrex tube, and the gas mixture was irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Institute of Technology). Total electric quantity irradiated was 1 - 4 mC, and the products were hereafter referred to as CAW. Gas mixtures of carbon monoxide (350 Torr) and ammonia (87.5 – 350 Torr) were also irradiated with 2 mC of 2.5 MeV protons, and the products were referred to as CA. A mixture of methanol, ammonia and water (molar ratio was 1:1:2.8) was irradiated with heavy ions (290 MeV/u carbon ions, or 500 MeV/u argon ions) from HIMAC, NIRS, Japan. Total irradiation dose was 1.5 – 15 kGy, and the products were referred to as MeAW. All the irradiated products were acid-hydrolyzed and then were subjected to amino acid analysis by HPLC and/or GC/MS.

Alteration of amino acids and their precursors by high-energy photons. Five amino acid-related samples - Glycine (Gly), hydantoin (Hyd: precursor of glycine), isovaline (Ival), 5-Ethyl-5-methylhydantoin (EMHyd: precursor of isovaline) and complex organic compounds synthesized by proton irradiation of a mixture of CO, NH_3 and H_2O (referred to as CAW) - were irradiated with continuous light from soft X-rays to IR (hereafter referred as to soft X-rays) at NewSUBARU BL-06 (University of Hyogo) under high vacuum condition. After collecting the irradiated sample with pure water, we measured the recovery ratio of each compound by using ion exchange or reversed-phase HPLC systems. In some cases, CaF_2 window was used to cut soft X-rays and EUV (referred as to VUV irradiation; cut-off wavelength is ca. 130 nm). Vacuum ultraviolet light at 172 nm from an eximer lamp (Ushio, Japan) was also used to test stability of amino acids and related compounds against VUV irradiation.

Alteration of amino acids and their precursors by high-energy particles. Amino acids, their precursors and nucleic acid bases were irradiated with high-energy heavy ions (*eg.,* carbon ion of 290 MeV/u) at HIMAC BIO, NIRS, Japan. The target molecules were irradiated either in aqueous solution or in dried phase.

Hydrothermal alteration. Aqueous solution of CAW in Pyrex glass tube was heated at 200 – 300°C for 2 hours in an autoclave after pressurized with a gas mixture of hydrogen (1%) and nitrogen (balance).

Analysis of the products. Amino acids were determined by ion-exchange HPLC and/or GC/MS after acid-hydrolysis. Nucleic acid bases were identified by HPLC and LC/MS after or without acid-hydrolysis. XANES spectra were measured at BL-5 of NewSUBARU, University of Hyogo, Japan.

Results and Discussion: *Formation of amino acid precursors and nucleic acid bases*. Wide variety of amino acids was detected in the hydrolysates of CAW, CA and MeAW. Glycine was always predominant among resulting amino acids, whose G-value was as high as 0.4 in the case of CAW. CAW was quite complex organic molecules whose molecular weights were thousands [2]. Several purines and pyrimidines were identified in unhydrolyzed portions of CAW and CA, though their G-values were much less than those of amino acids. It was suggested that amino acids were mainly formed in the forms of complex precursors in ISD environments, while free nucleic acid bases could be formed there.

Alteration of bioorganic compounds with high-energy particles and photons. Amino acid precursors were more stable against soft X-rays than free amino acids. Water-insoluble products were formed after soft X-rays irradiation. XANES spectra before and after soft X-ray irradiation showed increase of C=C and decrease of C=O in the target molecules. Nucleic acid bases were more stable than amino acids and their precursors against the irradiation. Heavy ions were generally less effective than soft X-rays for decomposition or alteration of the molecules examined.

Suggested scenario of evolution of organic compounds in the proto-solar nebula and in the solar system. Most of meteoritic organics are so-called IOM (insoluble organic matter), and are quite hydrophobic. Cometary dusts sampled in the STARDUST mission were analyzed by XANES: Some of the particles were as hydrophobic as meteoritic organics while some others were much less hydrophobic. Laboratory simulation experiments suggested that ISD organics could be quite hydrophilic. Soft X-rays flax from young sun was much stronger than the present sun. Soft X-rays irradiation from young sun could hydrophobize organic compounds of interstellar origin. Formation of amphiphilic compounds from hydrophilic compounds by soft X-rays irradiation would have been important for the formation of organic structure or aggregates in prior to the generation of the first cell in primordial sea.

Alteration of organic compounds in parent bodies of meteorites. Differences in characteristics of meteoritic and cometary organics might be due to hydrothermal and thermal alteration in parent bodies of meteorites. Preliminary experiments suggested that hydrothermal reactions made organic compounds more hydrophobic. Further experiments are now in progress.

Delivery of extraterrestrial organics to the primitive Earth. It was suggested that more organic carbons were delivered to the early Earth by interplanetary dust particles (IDPs) than by meteorites or comets [3]. A demerit of IDPs for the carriers of extraterrestrial organics is that IDPs are so small that they are directly exposed to solar radiation that might decompose organics. Thus the presence of bioorganics in IDPs is expected, but it is difficult to judge it since IDPs (or micrometeorites) are so small and they have been collected in the terrestrial biosphere. Thus it would be of importance to study possible alteration of IDP organics in space environments, and to collect pristine IDPs out of the terrestrial biosphere. We are planning a novel astrobiology mission named *Tanpopo* by utilizing the Exposed Facility of Japan Experimental Module (JEM/EF) of the International Space Station (ISS). Two types of experiments will be done in the Tanpopo Mission: Capture experiments and exposure experiments [4].

References: [1] Kobayashi K. et al. (1995) *Adv. Space Res., 16,* 20–26. [2] Takano, Y. (2004), *Appl.. Phys. Lett., 84*, 1410-1412, [3] Chyba C. and Sagan C. (1992) *Nature, 355*, 125-132. [4] Yamagishi A. et al. (2009) *Trans. JSASS Space Tech. Jpn 7, No. ists26, Tk_49-55*.