Formation and Solubility of Organic Aerosols in the Atmoshperes of Titan and Early Earth. H. Tabata[1], Y. Sekine[1], H. Suga[2], N.O. Ogawa[2], Y. Takano[2], N. Ohkouchi[2], [1]Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, (sekine@eps.s.u-tokyo.ac.jp), [2]Department of Biogeochemistry, JAMSTEC, 2-15 Natsushima-cho, Yokosuka-city, Kanagawa, 237-0061, Japan.

Introduction: Titan has a thick atmosphere mainly composed of N_2 and CH_4, which might resemble that of early Earth [1]. In the upper atmosphere of Titan, complex photochemistry driven by sloar UV irradiation and Saturn's magnetospheric particles bombardments is producing various hydrocarbons and N-bearing organic compounds. Previous studies have performed irradiations of cold plasma or UV light to the gas mixtures of N_2 and CH_4 simulating organic chemistry in Titan's atmosphere [2][3]. Recent studies have studied the chemical and optical properties of organic materials, called tholin, formed in laboratory experiments; however, the formation mechanisms of early Earth tholin are still poorly understood. Moreover, organic aerosols produced in the atmospheres of both Titan and early Earth would have undergone further chemical reactions with liquids on the surfaces. Yet, solubility of early Earth tholin to the solovent has not been studied.

Methods: Laboratory experiments were conducted by irradiating cold plasma onto three types of gas mixtures simulating the atmospheric compositions of Titan and early Earth; N_2-CH_4 (N_2 : CH_4 = 9 : 1), N_2-CH_4-CO (N_2 : CH_4 : CO = 89 : 9.9 : 1 and N_2 : CH_4 : CO = 63 : 7 : 30), and N_2-CH_4-CO_2 (N_2 : CH_4 : CO_2 = 87 : 9.7 : 3.5). Mass spectrometry and emission spectroscopy were performed during the irradiation in order to identify intermidiate products in the gas phase. Chemical structures of produced tholins were analyzed with infrared and UV-VIS spectroscopy. The production rates of tholins were examined by measuring the time evolution of thicknesses of tholins with ellipsometry. Solvent extraction of tholins were performed. The chemical structure of dissolved fractions were analyzed by UV-VIS spectroscopy.

Results and Discussion: The results of emission spectroscopy of Titan tholins show that CN radicals are produced by plasma irradiation in the gas phase. Titan tholins' results of mass spectrometry of gas species also display that HCN and cyanides, such as CH_3CN and possibly C_2H_5CN, are produced in the experiments in addition to hydrocarbons. As discussed in the previous study [4], these our results support the idea that the formation of Titan tholin is initiated by the production of CN radicals and subsequent cyanide formations.

Our results show that the production rates of early Earth tholins (produced from the gas mixtures of N_2-CH_4-CO and N_2-CH_4-CO_2) are several times less than that of Titan tholins (produced from the gas mixture of N_2-CH_4). We find that the production of CN radicals and subsequent cyanide productions also take place in the experiments of early Earth tholin formation. Contrary to the formation of Titan tholin, excited CO is observed in the plasma irradiation to the gas mixtures of both N_2-CH_4-CO and N_2-CH_4-CO_2. Our results also suggests the abundant existence of C=O bonds in early Earth tholins. In the gas phase, nevertheless, we cannot find the significant productions of O-bearing organic compounds, such as aldehydes. These results suggest that production and incorporation of CO into the tholins also occur in the formation of early Earth tholins.

Titan tholin is known to dissolve in polar solvents, such as methanol [5]. We find that early Earth tholins display dissolution to methanol as well as to low-polar solvents, such as CH_2Cl_2. These results suggest that both non-polar and polar structures are coexisting in early Earth tholins. Furthermore, our results of UV-VIS spectroscopy of CH_2Cl_2 solution of early Earth tholins displayed an absorption band in the wavelength of 350–420 nm. The absorption in this wavelength is typical to fused ring aromatic compounds or heterocyclic compounds. These results may imply the possibility that organic aerosols produced in the atmosphere of early Earth could have provided N-bearing compounds as well as amphiphilic organic compounds to pre-biotic oceans.

References: [1] Strobel D.F. et al. (2009) Titan from Cassini-Huygens (book), Chp. 10. [2] Hörst S.M. et al. (2014) *Astrobiology 12*, 809–817. [3] Imanaka H. et al. (2004) *Icarus 168,* 344-366. [4] Imanaka H. & Smith M.A. (2010) *PNAS 107 (28),* 12423–12428. [5] He C. and Smith M.A. (2014) *Icarus 232,* 54-59.