July 16-21, 2017 at UC San Diego, CA, USA

Revisiting Redox State of the Early Earth's Atmosphere and Prebiotic Synthesis

Y. Ueno[1,2,3*], Y. Endo[1], X. Znag[1] and W. Kawade[1]
[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro Tokyo, 152-8551, Japan; [2]Earth-Life Science Institute (WPI-ELSI), Tokyo Institute of Technology, Meguro Tokyo, 152-8550, Japan; [3]Laboratory of Ocean-Earth Life Evolution Research (OELE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Natsushima-cho, Yokosuka 237-0061, Japan
*ueno.y.ac@m.titech.ac.jp

Redox state of the atmosphere is important for prebiotic synthesis. A CO_2-dominated atmosphere is oxidizing and thus not preferable to synthesize prebiotically-important molecules either by Miller-Urey-type processes or by UV-driven photochemistry [1]. It is largely uncertain how reducing the early Earth's atmosphere in the Hadean period. Recently, our recent photochemistry experiment suggested that the Archean atmosphere would have been more reducing than previously thought, possibly including % levels of CO or CH_4 to explain the Sulfur Mass-Independent-Fractionation (S-MIF) preserved in sedimentary rocks older than 2.4 Ga [2]. Also, in order to preserve the S-MIF record, atmospheric CO_2 level should be much less than 1 bar. Considering the higher heat flux of the earlier Earth, Hadean Earth would also have such a very reducing atmosphere that may have been maintained by supply of reducing agent like ferrous iron from hydrothermal activity into ocean, potentially buffering redox state of ocean-atmosphere system. In such a reducing ocean with CO-bearing low pCO_2 atmosphere, UV induced photochemistry is important for prebiotic chemistry especially at the interface between atmosphere and hydrosphere.

We have performed UV synthesis experiment of H-C-N-O systems under various redox conditions with a presence of liquid water for simulating chemistry at the surface of hydrosphere. The results of our experiment showed that formaldehyde, acetaldehyde, formate, acetate, propionate, and normal alkanes are synthesized under CO- and CH_4-bearing atmosphere, whereas all these compounds are not detectable under pure CO_2-atmopshere. Nonetheless, when liquid-phase contains Fe(II), formaldehyde, formate and acetate are formed even when the gas phase is pure CO_2. Also, our experiment showed that NH_3, methylamine, glycine and other amino acids can be synthesized when gas phase containing CO and N_2O.

These results suggest that the production rate and speciation of organic matter depends on the availability of H_2O as well as total redox state of the whole atmosphere and ocean system. UV-photochemistry could continuously supply prebiotic compounds everywhere on the surface of the Earth, thus has a potential to sustain network reactions (geometabolism) in the hydrosphere.

References:

[1] Chyba & Sagan (1992) *Nature* **355**, 125-132.

[2] Endo et al. (2016) *Earth and Planetary Sciences Letters* **453**, 9-22.