The origin and process tracing for molecules of biogeochemical interests through isotopologue analysis featuring position specific isotope abundance of bioelements

Naohiro Yoshida[1,2]

[1]*Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology*
[2]*Earth-Life Science Institute, Tokyo Institute of Technology*

Since the 1950's, the stable isotope compositions of naturally occurring molecules have been proved to be a strong tool for the study of geological, biological, and anthropogenic processes, and their evolution and effect on biogeochemical cycles of environmental molecules. However, due to technical and conceptual limitations, the complete set of information potentially contained in molecules remains largely unexplored especially in the different modes of isotopic substitution as 1) to 3) stated below. We have developed series of new methodologies that allow analysis of isotopically substituted molecules, through each mode. We are also integrating those in the study of geological, biological and anthropogenic processes which affect the Earth's environment.

1) Position specific isotope abundance analysis (PSIA): We have pioneered PSIA of nitrogen in N_2O[1,2)] and of carbon and hydrogen in organic molecules using classic isotope mass spectrometry[3)] and nuclear magnetic resonance[4,5)]. We have shown that PSIA of hydrocarbons and organic acids allows us to differentiate processes as distinguishing between biological and non-biological processes[4,6)]. 2) Mass-independent fractionation (MIF): The discovery of MIF of sulfur and oxygen in terrestrial molecules has revolutionized environmental geochemistry and our understanding of the evolutionary history of the Earth's environment and life[7-9)]. 3) Clumped isotopes (i.e. isotopologues with 2 or more minor isotopes) provide unique information about the temperature history of molecules such as carbonates[10)] or organic compounds[11-13)].

We are currently developing new and improved tracers of environmental and biogeochemical processes and apply them to the environmental diagnosis. We have established and standardized new methods for the analyses of above 3 higher dimensional modes of isotopic substitution, and unifying them to develop ultimate environmental diagnosis. The development and application of these new isotopic tools to the environment evolution on the Earth, in modern and ancient eras, represents an important conceptual advance in Earth and life sciences. This will open new areas of research about, for example, the geological production of some atmospheric gases, metabolic processes and the biological fixation of atmospheric greenhouse gases, the production and cycling of pollutant gas by industrial processes. As a whole, these new tracers will be integrated together for diagnosis of the Earth's environment.

The research achievements so far obtained will be reviewed and a perspective will be stated in this talk as I am currently leading a research project "Environmental diagnosis with

isotopologue tracers", a Kiban-S grant-in-aid for 5 yrs until 2022, and co-editing "Handbook of Isotopologue Biogeochemistry" [14].

References; 1)Yoshida & Toyoda, 2000 *Nature*; 2)Yamazaki, Toyoda, Yoshida, et al., 2014 *Biogeosciences*; 3)Yamada, Yoshida, et al., 2002 *RCM*; 4)Gilbert, Yamada, Yoshida, 2013 *Anal. Chem.*, and 5) Gilbert, Yamada, Yoshida, 2014 *Anal. Chim. Acta*; 6)Gilbert, Yamada, Ueno, Yoshida 2016 *Geochim. Cosmochim. Acta*; 7)Danielache, Ueno, Yoshida et al., 2008 *J. Geophys. Res.*; 8)Hattori, Danielache, Ueno, Yoshida et al., 2013 *PNAS*, 9)Ueno, 2015 *Science*; 10) Yoshida, Abe, Yamada et al., RCM, 2013; 11)Tsuji, Yamada, Yoshida et al., 2012 *Sensor;*: 12)Ono et al., 2014 *Anal. Chem.*; 13)Stolper et al., 2014 *Science*; 14)Yoshida, Gilbert, Foriel eds, Handbook of Isotopologue Biogeochemistry, 2019 to be published by Springer-Nature.