Geochemical origin/cycle analysis with isotopologues and isotopomers

*Naohiro Yoshida¹

1. Department of Chemical Science and Engineering, Earth-Life Science Institute, Tokyo Institute of Technology

Since the 1950's, the stable isotope composition of natural samples has proved to be a unique tool for the study of geological and biological processes, their evolution and effect on Earth's surface environment. However, due to technical and conceptual limitations, the complete set of information potentially contained in the different modes of isotopic substitution remains largely unexplored. In this study, using new methodological developments that allow analysis of more isotopically substituted molecules, we are developing new tracers in 3 modes of isotopic substitution, fully integrated in the study of geological, biological and anthropogenic processes which affect the origin and evolution of the Earth's surface environment.

3 modes of substitution of stable isotopes in a single molecular species are;

1) Position specific isotope abundance (PSIA): Our group has pioneered PSIA of $N_2O^{1,2)}$ and organic molecules using classic isotope mass spectrometry³⁾ and nuclear magnetic resonance^{4,5)}. We have shown that PSIA of hydrocarbons and organic acids allows to distinguish between biological and non-biological processes^{4,6)}.

2) Mass-independent fractionation (MIF): The discovery of MIF of sulfur and oxygen in terrestrial samples has revolutionized environmental geochemistry and our understanding of the evolutionary history of the Earth's environment and life⁷⁻⁹⁾.

3) Clumped isotopes (i.e. isotopologues and isotopomers with 2 minor isotopes) provide unique information about the temperature history of molecules such as carbonates¹⁰⁾ or organic compounds¹¹⁻¹³⁾.

We are currently developing new and improved tracers of environmental and biogeochemical processes and applying them to the environmental diagnosis. We are establishing and standardizing new methods for the analyses of every 3 complex 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, in modern and more 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 CO_2 , 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.

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) 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*.

Keywords: isotopomer, isotopologue, geochemical cycle, light element stable isotopes