# Application of isotopologues for studies on the atmospheric sulfur cycle

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One way in which the atmospheric sulfur cycle is important is by forming atmospheric sulfate ($SO_4^{2-}$) aerosols which have a notable but uncertain impact on the global radiation budget and cloud lifetimes. Atmospheric $SO_4^{2-}$ also comprises a major component of fine particulate matter mass in urban regions, affecting visibility and public health. However, the scientific understanding of the climatic and environmental impacts of $SO_4^{2-}$ aerosols is low, because there are multiple sources of sulfur in the atmosphere, including anthropogenic and natural sources, and there are many unknowns about the atmospheric chemical reaction processes involved in aerosols formation.

Stable isotope composition is an effective indicator to track the origin of sulfur and atmospheric chemical reactions. Particularly, the mass-independent fractionation (MIF) for oxygen isotopes (defined as $\Delta^{17}O$) of $SO_4^{2-}$ provides insight into atmospheric $SO_4^{2-}$ formation mechanisms. I have used isotopic information of sulfur species for elucidation of the source and formation mechanisms for the stratospheric and tropospheric sulfate (Figure 1), by combining these observations of ice cores and atmospheric aerosols and the global chemical transport models implemented with isotope tracers.

In the presentation, I will introduce the followings three important scientific problems for the atmospheric sulfur cycle solved by our unique isotopic measurements: (1) Missing source of atmospheric carbonyl sulfide (OCS) (Hattori et al., 2015 *Anal. Chem.*; Hattori et al. 2020 *PNAS*), (2) Identification of climate-impacting volcanism (Hattori et al. 2013 *PNAS*; Gautier et al. 2019 *Nature Comm.*), (3) Identification of the chemical feedback mechanisms weakening the reduction of $SO_4^{2-}$ to $SO_2$ emission control (Hattori et al. 2021 *Science Advances*; Wang et al. 2021 *Atmos. Chem. Phys.*).

Besides, I have started my new research career in International Center for Isotope Effect Research (ICIER, https://www.icier-nju.org/) in Nanjing University (NJU), China. My motivation is open to new developments of analytical methods of new isotopologues including MIF, position-specific isotopic analysis (PSIA), and doubly-substituted (Clumped) isotopologues in the next direction. The recent development of the electrospray hyphenated with Quadrupole Orbitrap mass spectrometry (ESMS) potentially enables us to overcome some limitations of the conventional method using an isotope-ratio mass spectrometer (IRMS). This new technique yield a satisfying accuracy for conventional small delta ($\delta$) of $\delta^{34}S$ and $\delta^{18}O$ in sulfate and $\delta^{15}N$ and $\delta^{18}O$ in nitrate with nano-mole level samples, which is about 1/100 smaller than the conventional methods requiring micro-mole level samples (Neubauer et al. 2020 *Anal. Chem.*). It is worth noting that, this ESMS method could measure the less abundant variants such as $\delta^{17}O$, $\delta^{33}S$, $\delta^{36}S$, and the $^{34}S$–$^{18}O$ "clumped" isotopologues, for example in $SO_4^{2-}$. I will also report on the latest progress in the development of this new analytical method at ICIER/NJU.

Keywords: Sulfate aerosols, Sulfur cycle, Triple oxygen isotopic composition, Mass-independent fractionation, Clumped isotope, Isotopologue