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Sulfur mass-independent fractionation in SO_2 photolysis: comparison between absorption spectra measurements and photolysis experiments of SO_2 - *GSJ Medal Lecture*

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Mass-independent fractionation of sulfur isotopes (MIF-S; non-zero $\Delta^{33}S$ values) in Archean sedimentary rocks will provide a hint of atmospheric composition at that time. However, the origin of MIF-S is still debated. SO_2 photolysis experiments produced large MIF-S signatures, and the results were highly sensitive to the experimental conditions [1]. Understanding the MIF-S mechanism in SO_2 photolysis is essential to explain the Archean MIF-S signatures quantitatively.

Isotope fractionation in SO_2 photolysis is predicted by absorption spectra of SO_2 isotopologues. Here, we measured the photoabsorption cross-sections of $^{32}SO_2$, $^{33}SO_2$, $^{34}SO_2$, and $^{36}SO_2$ from 206 to 220 nm at 296 K [2]. The spectral resolution of the present study (~1 cm^{-1}) is 25 times higher than that of previous studies [3,4]. SO_2 exhibit complex ro-vibrational structures in their UV absorption spectrum; SO_2's absorption causes MIF-S so-called "self-shielding" by slowing photolysis rate of only $^{32}SO_2$, which is the most abundant isotopologue. Using our new spectra, we calculated the sulfur isotope fractionation for self-shielding during SO_2 photolysis. The calculated fractionation factors are compared with isotope fractionation factors observed in previous SO_2 photolysis experiments. We discuss the link of MIF-S between photolysis experiments and spectroscopic measurements. Additionally, we introduce some advances in understanding MIF-S mechanisms and modeling Archean atmospheric chemistry after the paper [2] was published. We performed MIF-S in SO_2 photolysis experiments in low-temperature/pressure atmospheres [5] and are developing a vertical atmospheric model with sulfur isotopes based on MIF-S observed in photolysis experiments. Finally, we summarize experimental and modeling studies of Archean MIF-S.

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