High-resolution 32/33/34/36SO2 absorption cross-section measurements for revealing Archean atmospheric composition

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Many geological and geochemical records suggest a reducing Archean atmosphere. Revealing Archean atmospheric composition is important proxy for the understanding of the origin and evolution of life. The discovery and explanation of sulfur mass-independent fractionation (S-MIF) signatures in Archean sedimentary rocks possess as a key to unravel Archean atmospheric composition. Our SO_2 photochemical experiments generated large S-MIF ($\Delta^{33}S > +5‰$) and reproduced basic character of the Archean S-MIF signature ($\Delta^{36}S/\Delta^{33}S = -1$) under a specific condition for the first time (Endo et al. 2016). Self-shielding of SO_2 photodissociation and intersystem crossing (ISC) form singlet SO_2 to triplet SO_2 are shown as key mechanisms. Next, we simulated large S-MIF signature ($\Delta^{33}S > +5‰$) in our box numerical model, and we showed that Archean S-MIF trend ($\Delta^{36}S/\Delta^{33}S = -1$) can be explained when there are several ppm level of SO_2 (like the plume of volcanic gas) and 2% (2 kPa) CO or 3% (3 kPa) CH_4 in the atmosphere. But box model’s calculation is not completely correct because photochemical reaction rate and fractionation factor (such as self-shielding) strongly depends on the altitude. Then we need to develop 1-D atmospheric model.
Our group's new 1-D model which focuses on UV spectra because reactions and fractionation factor (such as self-shielding) change delicately as a function of irradiative photon flux. Fractionation factor of photodissociation can be calculated by isotopologue cross-section and irradiative photon flux. Then in order to develop 1-D atmospheric model including sulfur isotopes, SO_2 isotopologue cross-sections ($^{32/33/34/36}SO_2$) are necessary. Although SO_2 isotopologue cross-section have been measured, they are too low-resolution to estimate self-shielding (Danielache et al. 2008, Endo et al. 2015). Here, we report preliminary results of high resolution (~1cm^{-1}) $^{32/33/34/36}SO_2$ absorption cross-sections and estimation of fractionation factor including self-shielding effect.

Referces: Endo et al. (2016), EPSL, Danielache et al. (2008), JGR Atmospheres, Endo et al. (2015), JGR Atmospheres

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