

## Total pressure dependence of sulfur mass-independent fractionation by SO<sub>2</sub> photolysis

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Sulfur mass-independent fractionation (S-MIF) in Archean sedimentary rocks is a useful proxy for atmospheric chemistry. Archean S-MIF signatures typically show that  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  values are close to  $-1$ . We have succeeded to reproduce the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope experimentally (Endo et al., 2016). Based on the experimental results, we suggested that Archean S-MIF can be explained by a combination of two effects: (1) self-shielding of SO<sub>2</sub> photolysis ( $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim -2.4$ ) and (2) intersystem-crossing in excited SO<sub>2</sub> ( $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim +0.7$ ). However, several results of previous photochemical experiments cannot be explained only by the two effects (Ono et al. 2013, Masterson et al. 2011). Total pressure may cause an additional effect on the S-MIF, though the mechanism is poorly understood. Here, we conducted SO<sub>2</sub> photolysis experiments under various total pressures from 0.1 bar to 1.7 bar and measured sulfur isotope fractionations. Measured  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  values changed depending on total pressure. We discuss the mechanism of total pressure dependence of S-MIF by SO<sub>2</sub> photolysis in terms of pressure broadening effect (Lyons et al., 2018) and present an implication for the total pressure of the Archean atmosphere.

Keywords: Archean atmosphere, Sulfur isotopes, Mass-independent fractionation, Self-shielding