

## Mass independent fractionation by UV photolysis of optically thin SO<sub>2</sub>

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Sulfur mass independent fractionation (S-MIF) of Archean sediment is regarded as a proxy of the atmosphere at that time. S-MIF is produced by photolysis of SO<sub>2</sub> in oxygen-free environment. However, the elementary reaction and the mechanisms of fractionation in the atmosphere are not fully understood. We present here a newly developed experimental setup to reveal the atmospheric photochemistry observed in the geological record. The photochemical system consists of a D<sub>2</sub> light-source, two gas chambers attached to a monochromator and a UV detector designed to operate with no interference of atmospheric air. Here we present the first round of experiments of SO<sub>2</sub> photolysis conducted under SO<sub>2</sub> at low partial pressure (<5 Pa) and high amount of CO. The purpose of this experiment is to test a different experimental conditions from previously reported results where the environment of high pressure SO<sub>2</sub> is oxidative and optically thick. The optically thick condition of the past experiments causes self-shielding of SO<sub>2</sub>, possibly resulting in unique S-MIF. But self-shielding may have not operated or not be important in the Archean atmosphere, because atmospheric SO<sub>2</sub> concentration unlikely exceeded over ppm level. Then, our experiment of SO<sub>2</sub> photolysis was conducted under the optically thin setting. Additionally, reducing atmosphere with a large amount of CO produces a stable amount of OCS (Ueno et al.,2009). Results demonstrated that OCS is produced by SO<sub>2</sub> photolysis under CO atmosphere. The product OCS shows clear MIF signature. We calculated fractionation factors of SO<sub>2</sub> photolysis (185-220 nm) and also the chemistry associated with SO<sub>2</sub> photoexcitation (250-320 nm) as an additional source of MIF. We discuss a source of MIF involving not only SO<sub>2</sub> photodissociation but also the chemistry associated to the photoexcited SO<sub>2</sub>\* species in relation to the MIF signal measured on the geological record.

Keywords: Archean, ancient atmosphere, mass independent fractionation