Experimental study on SO_2 photochemistry under reducing atmosphere and S-MIF

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Sulfur mass-independent fractionation (MIF) in the Archean sedimentary rock is a key to trace the chemistry of atmosphere at the time. However, the mechanisms of isotopic fractionation originated from SO_2 photochemistry is not fully understood. We conducted photochemical experiments of low $p$$SO_2$ (1-10 Pa) condition under 0.1 atm CO atmosphere. The SO_2 column density was down to 10^{16} molecules/cm^2, which should be a realistic SO_2 optical thickness for atmospheric thin conditions as well as providing a reducing condition. Monitoring the gas composition in the chamber together with numerical modeling of the photochemistry revealed complicated reaction pathways in the chamber. Measured isotopic fractionations depend largely on SO_2 column density. Photoproducts (OCS) showed positive $\Delta^{33}S$, whereas residual SO_2 showed negative $\Delta^{33}S$. The $\Delta^{36}S/\Delta^{33}S$ ratio showed about -1 when ultraviolet spectrum is similar to the solar spectrum (i.e. low pSO_2 condition), that is consistent with the geological record. The $\Delta^{36}S/\Delta^{33}S$ ratio reflects conbination of the two MIF effects. One came from the self-shielding of SO_2 direct photolysis resulting in the SO_2 column density dependence with $\Delta^{36}S/\Delta^{33}S$ slope of ~-2.4. Another MIF is derived from photoexcitation of SO_2 showing $\Delta^{36}S/\Delta^{33}S$ ratio of ~+0.7 due to inter system crossing (ISC) from singlet SO_2 to triplet SO_2. To transfer the ISC signal into photoproducts, excited state of SO_2 needs to react with reducing gases (e.g., H_2, CH_4 and CO) and to be reduced into SO. Thus, the Archean S-MIF ($\Delta^{36}S/\Delta^{33}S$ = ~1) requires reducing gases in the atmosphere. For example, the late Archean atmosphere ($\Delta^{36}S/\Delta^{33}S$ = ~-1; $\Delta^{33}S$ > +5 ‰) may contain high concentration of SO_2 gas (more than 5 ppbv) and of reducing gases (CH_4 or CO) where the ISC-derived MIF contribute 2.3%. Therefore large S-MIF is useful for monitoring partial pressure of SO_2 and reducing gasses.