Total pressure effect on mass-independent fractionation of sulfur isotopes: laboratory experiment of SO_2 photochemistry

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Sulfur mass-independent fractionation (S-MIF) is a useful proxy to understand atmospheric chemistry. Photochemistry of SO_2 accompanies large S-MIF. The isotopic fractionation of SO_2 photochemistry is known to change depending on total pressure [1,2,3], though the detailed mechanism is still uncertain. We examined total pressure dependence of S-MIF by photochemical experiments of SO_2 under various total pressures from 0.01 bar to 1.7 bar. In contrast to previous study [1], our experiment designed for simulating reducing atmosphere including CO and reasonably low pSO_2 condition, two of which are both critical to reproduce S-MIF observed in Archean sediment [4]. The results show that the $\Delta^{33}S$ and $\Delta^{36}S$ of photochemical products clearly depend on total pressure. At higher total pressure, the $\Delta^{33}S$ value is approaching to 0, which is qualitatively consistent with pressure broadening with self-shielding [3]. Also, under the experimental setting, SO produced from the photoexcitation channel is sufficiently smaller than photolysis channel. Thus, the observed total pressure effect probably derived from pressure broadening of SO_2 absorption spectra. Consequently, S-MIF originated from photodissociation channel can be addequately modeled considering two factors: pressure broadening (i.e. total pressure) and self-shielding effect (i.e. pSO_2). Moreover, at high total pressure over 1 bar, the $\Delta^{36}S/\Delta^{33}S$ and $\Delta^{33}S/\delta^{34}S$ ratios are clearly different from those observed in Archean sediments. The low total pressure of Archean atmosphere is consistent with the previous estimate [5]. Accordingly, S-MIF may provide a useful constraints on total pressure of Archean atmosphere.

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