

Transfer of S-MIF signals from reducing late Archean atmosphere

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Sulfur Mass Independent Fractionation (S-MIF) is a useful tracer for atmospheric chemistry. Our recent experiment of SO₂ photochemistry first succeeded to reproduce the basic character of the Archean S-MIF (i.e. $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio from -1.5 to -0.85). Our experimental results indicate that a key factor to change the isotopic fractionation is partial pressure of SO₂. Depending of the optical thickness of SO₂, magnitude of MIF signal is changed due to isotopic self-shielding. Also, high pSO₂ atmosphere provides excess O atoms, resulting in an oxidizing condition which is probably dissimilar to the Archean atmosphere. In other words, the S-MIF signature reflects mainly pSO₂ as well as redox state of the atmosphere even without any molecular oxygen. Based on the experiment, we have developed photochemical model of S-O-C system including 200 reactions. The model successfully reproduces not only our experimental results but also most previous laboratory experiments, when assuming MIF only in the two reactions: (1) $\text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}$ and (2) $^1\text{SO}_2 + \text{M} \rightarrow ^3\text{SO}_2 + \text{M}$. Moreover, the model indicates that the large S-MIF ($\Delta^{33}\text{S} > +4\%$) observed in late Archean sediments requires sufficiently high SO₂ levels ($\sim 10^{16}$ molecules cm⁻²) suggesting high volcanic activity at that time. The observed $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of -1.5 ~ -0.85 can be produced by solar UV irradiation under the presence of reducing gasses (e.g., several % of CH₄ and/or CO). The late Archean from 2.8 to 2.5 Ga, the atmosphere may have been more reducing than before and after this interval.