

Mass Independent Sulfur Isotope Fractionation during Elemental Sulfur Photochemistry

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Signatures of mass-independent sulfur isotope fractionation (S-MIF) are observed in sedimentary rocks older than 2.3 billion years old, representing a chemostratigraphic marker of the Great Oxidation Event (GOE). S-MIF is thought to be produced through photochemistry in an atmosphere devoid of molecular oxygen, but the exact mechanism responsible for its genesis remains unidentified [1]. Laboratory experiments produce S-MIF during SO₂ and CS₂ photochemistry; however, none of them were able to reproduce the pattern of $\Delta^{33}\text{S}/\delta^{34}\text{S}$ and $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios observed in the rock record [2].

We carried out a series of photochemical experiments to test whether the photochemistry of elemental sulfur (S_n, n=1-8) produces S-MIF. Spectroscopic perturbations between the B' and B states of S₂ may result in a symmetry-dependent isotope effect [3]. In our experiments, elemental sulfur was produced from photolysis of OCS in a flow-through reactor. In contrast to previous work that produced little or no S-MIF within their photochemical products [4], experiments carried out at low total gas pressure (as low as 13 mbar) produced elemental sulfur carrying a S-MIF signal dependent on the location in the reactor where the elemental sulfur was sampled. Our results are consistent with S-MIF production during photolysis and polymerization of elemental sulfur.

[1] Farquhar et al., 2000 Science., 289, 5480, 756-758 [2]

Ono, 2017 Annu. Rev. Earth Planet. Sci. 2017. 45:301-29;

[3] Hull et al., 2018, Goldschmidt conference 2018. [4] Lin et al., 2011 Atmos. Chem. Phys., 11, 10283-10292.