

Origin and implications of Archean sulfur mass-independent fractionation

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Signatures of sulfur isotope mass-independent fractionations (S-MIF) in Archean sulfate and sulfide minerals have been considered as the most convincing evidence for early anoxic atmosphere, and constrain the atmospheric oxygen level to less than a few ppm until before 2.3 Ga [1] [2]. Despite the critical importance in understanding early evolutionary history of atmospheric oxygen and biosphere, the source reaction(s) and physical mechanism of S-MIF are poorly constrained. We will review the research on the origin of S-MIF for 15 years since its discovery, and discuss future directions and promises in our understanding in the chemistry of an early atmosphere.

Since the pioneering study by Farquhar et al., [3] SO₂ photolysis with <220 nm UV radiation has been the main candidate for the source of S-MIF. Later laboratory photochemistry experiments, however, yield much smaller magnitude S-MIF [4] [5]. Theoretical *ab initio* calculations suggest only weak perturbations in the C state SO₂ [6]. Furthermore, the latest spectroscopy measurements showed small isotopologue dependent cross section amplitude difference [7]. What is the S-MIF source reaction if it is not SO₂ photolysis? SO₂ photoexcitation at 240 to 340 nm produces large MIF [8]. The long life time of the low lying ³B excited state allows expression of isotopologue specific perturbation in the photochemical products (organic-S or sulfate). In addition, we are investigating the photochemistry of SO and S₂ as the source of S-MIF. Photochemical model suggests the preservation of S-MIF signal from SO (and S₂) would be more favored than that from SO₂ photolysis [9]. We will discuss implications for Archean sulfur cycle and pO₂ constraints if SO₂ photolysis is not the S-MIF source reaction.

[1] Farquhar et al. (2000) *Science* **289**, 756-758 [2] Pavlov & Kasting, (2002) *Astrobiology* **2**, 27-41 [3] Farquhar et al., (2001) *J Geophys Res* **106**, 32829-32839 [4] Masterson et al., (2011) *Earth Planet Sci Lett* **306**, 253-260 [5] Ono et al., (2013) *J Geophys Res* **118**, 2444-2454 [6] Tokue & Nanbu, (2010) *J Chem Phys* **132**, 024301 [7] Endo et al., (2015) *J Geophys Res* [8] Whitehill et al., (2013) *PNAS* **110**, 17697-17702 [9] Ono et al., (2003) *Earth Planet Sci Lett* **213**, 15-30