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Decoding the Evolution of Early Atmosphere: Experimental Reconstruction of the D36S/D33S Chemostratigraphy

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Sulfur Mass-Independent Fractionation (S-MIF) has potential to monitor chemistry of the Earth's early atmosphere (Farquhar et al., 2000). Nonetheless, detailed mechanism of the S-MIF occurred in the Archean atmosphere is still poorly understood. Previous laboratory experiments indicate the anomalous isotopic fractionation depends largely on (1) wavelength or spectrum of the incident light source and (2) partial pressure of SO₂, though none of these experiments have not yet succeeded to fully reproduce the S-MIF recorded in the Archean sedimentary rocks (e.g., Danielache et al., 2008; Masterson et al., 2011; Whitehill & Ono, 2012). We have developed a new photochemical chamber for determining isotopic effect of the SO₂ photolysis under optically thin condition. Also, a new direct fluorination technique of carbonyl sulfide allowed us precise isotopic analysis down to 50 nmolS of photolysis product. The results indicate that the basic character of the S-MIF observed in the Archean record can be reproduced when SO₂ column density is reasonably low (i.e. 10 to 50 times higher than preindustrial atmosphere). The results with a numerical modeling of the atmospheric reaction network suggest that the observed change in D36S/D33S ratio can be adequately explained by the two factors: (1) SO₂ partial pressure and (2) amount of reducing gas (H₂, CH₄ and CO). In light of the new perspective, we have re-evaluated the geological record of the D36S/D33S ratio with additional analyses of Archean sedimentary sulfides from South Africa and India. Based on the magnitude of the S-MIF and the D36S/D33S ratio, the Archean period can be subdivided into four stages (i.e. > 3.0 Ga, 3.0-2.7 Ga, 2.7-2.5 Ga and 2.5-2.4 Ga). These changes probably reflect both intensity of volcanic SO₂ emission and concentration of reducing gasses under the O₂-free atmosphere. Particularly, the maximum scatter of D33S values observed in the stage 3 (2.7-2.5 Ga) requires high volcanic emission as well as very reducing atmospheric condition in the atmosphere at that time.

Keywords: Archean, atmospheric chemistry, mass independent fractionation