SO2 photolysis and non mass dependent isotope fractionation

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Photolysis of Sulfur dioxide is believed to be responsible for Non Mass Dependent (NMD) sulfur isotopic anomalies observed in stratospheric aerosol and in minerals deposited before 2.3 billion years ago. In order to simulate the photochemical NMD fractionation, we have obtained high-resolution UV absorption spectra of isotopomers of SO2 (32SO2, 33SO2 and 34SO2) and calculated wavelength dependence of 34S/32S and 33S/32S fractionation factors. The results demonstrate that fractionation factors both for d34S and D33S are very sensitive to wavelength. This implies that single line photolysis by artificial laser UV courses NMD fractionation, but should not be directly applied to atmospheric environment, in which solar irradiation has broad UV spectrum. We have then calculated NMD effect resulted from solar UV as a function of overhead column densities of O2, O3, CO2, H2O and SO2 itself. We demonstrate that SO2 dissociation by solar irradiation causes significant NMD fractionation. Assuming 190-220 nm photolysis of SO2 is responsible for the NMD fractionation, our calculation also suggests that aerosol sulfate may have positive D33S anomaly under O2-free condition even if including self-shielding effect. This is inconsistent with the inferred negative D33S of Archean sulfate aerosol. Hence, the Archean NMD reaction pathways should have been more complex.