Wavelength dependent isotope effect as a tracer for paleoatmosphere and solar evolution?

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Discovery of sulfur isotope anomaly in Archean sedimentary rocks demonstrated that Earth’s early atmosphere was virtually oxygen-free (Farquhar et al., 2000). The anomalous fractionation is produced by photolysis of SO2. The fractionation factors are sensitive to the wavelength of irradiated UV (Danielache et al., 2008), thus is a potential tracer to understand chemistry of atmosphere and possibly change in solar spectrum. We newly determined higher resolution UV absorption cross sections of not only 32SO2, 33SO2 and 34SO2 but also 36SO2 within the two absorption bands: (1) 190 - 220 nm and (2) 250 - 320 nm. These data together with atmospheric reaction model allow us to predict isotopic compositions of photochemical product. The calculated photochemical fractionation pattern assuming broadband solar UV flux reproduce our previous work (Danielache et al., 2008), though the effect of UV shielding by each atmospheric species including SO2 itself differ from previously estimated trend. Nonetheless, almost all of the simulations result in D36S/D33S ratio of -0.9 ~ -1.1, generally reproducing those observed in Archean sedimentary rocks. Thus, we conclude that photodissociation of SO2 was a primary MIF-yielding reaction in the Archean atmosphere. Our simulation predict, however, the remaining SO2 after UV photolysis acquires positive D33S as opposed to widely-accepted previous model where H2SO4 (-D33S) and S8 (+D33S) aerosols carried opposite MIF signals into ocean and sediment (Pavlov and Kasting, 2002; Ono et al., 2003). We speculate the possibility that almost Archean sulfide deposits were produced by sulfate reduction. The new model requires relatively inert reducing form of sulfur reservoir. If the atmosphere was strongly reducing and contained high level of CO or CH4, photolytically produced SO was finally transferred into OCS (Ueno et al., 2009) or organo-sulfur compounds (Dewitt et al., 2010), respectively, which remained in the atmosphere and were not readily converted into sulfide. Occasional oxidation of the reducing sulfur pool enhanced sulfate concentration and deposited rare sulfate minerals with negative D33S. The new dynamical sulfur cycle model may explain observed heterogeneity of S-MIF records in the basin to microscopic scale. This scenario is tested by our ongoing photochemical chamber experiment. If correct, this implies more reducing Archean atmosphere than previously thought.

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