Sulfur isotope anomalies in sulfate aerosols and solar system materials: Understanding the present is a key to the past

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The isotopic signature of sulfur compounds in solar system materials bears witness to present and past natural phenomena. Sulfur Mass Independent Fractionation (S-MIF) in Archean rocks is used to quantify atmopsheric oxygen levels. The anomaly is created by sulfur (SO_2, SO_3) photochemistry at short UV wavelengths (< 240nm). However, only a small fraction of possible wavelengths have been studied and wavelength dependent isotopic photodissociative effects may not be calculated *a priori*.

High temporal resolution sulfur isotope data of sulfate in a south pole snow pit revealed the presence of large S isotope anomalies in a volcanically quiescent time [1]. The presence of sulfur isotope anomalies in both stratospheric and nearly all tropospheric sulfate aerosols suggests that there are sulfur processses occuring that presently are inadequately identified. The observed pervasive occurance in the troposphere is unexplained at present. The presence of some of the largest sulfate anomalies in ice cores during times of no volcanic activity requires additional processes, including massive equatorial SO_2 injections during biomass burning in climatically anomalous times, injection of copious OCS, which is converted to SO_2 in the middle stratosphsere (26 km), or both. Altitude (wavelength) may be a contributing factor if photochemistry occurs higher.The observed data isotopically resides within the Archean cluster in four isotope space which may be significant.

The role of photolytic wavelength is a key paramter in all environments, be they Earth's present day, Archean, Martian, or nebular. Meteoritic sulfur isotopic anomlies are consistent with photochemical proecss(es). The photochemical isotope effects as a function of wavelength are indequaetly known, and recent work has shown that at very short wavelengths a variety of isotopic fractionation effects are observed in H_2S, additonally illustrating the importance of chemical speciation [2]. The recent ice core work [1] has shown that the role of differing sulfur compounds and wavlength are both critically important, but indequately experimentally resolved.

[1] R. Shaheen *et al.*, *PNAS (2014)* **111**, 11979-83. [2] S. Chakraborty *et al.*, PNAS (2013) **110**, 17650-55.