**OBSERVATION OF WAVELENGTH-SENSITIVE MASS-INDEPENDENT SULFUR ISOTOPE EFFECTS DURING SO2 PHOTOLYSIS: IMPLICATIONS FOR SULFUR ISOTOPE COMPOSITIONS OF SNC METEORITES AND ANCIENT TERRESTRIAL SAMPLES.** J. Farquhar[^1-2], J. Savarino[^1], S. Airieau[^3-4] and M. H. Thiemens[^1], 1Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla Ca 92093, 2Earth System Science Interdisciplinary Center and Department of Geology, University of Maryland, College Park MD 21702, 3Astronomy Department, San Diego State University, San Diego Ca, 92182.

**Introduction:** Here we present the results of sulfur dioxide photolysis experiments with four light sources (ArF excimer laser (193 nm), mercury resonance lamp (184.9 nm and 253.7 nm), xenon arc lamp (>220 nm continuum) and KrF excimer laser (248 nm)). We also investigate the implications of these experiments for recent observation of mass-independent composition sulfur in SNC meteorites (Nakhla and ALH84001) [1,2], and in some of the oldest terrestrial sulfide and sulfate minerals [3,4]. Sulfur isotope mass-independent isotopic signatures for $\delta^{34}S$, $\delta^{33}S$, and $\delta^{36}S$ produced in our photolysis experiments of sulfur dioxide exhibit a strong wavelength dependence and large sulfur isotope fractionation effects. These observed properties of the reactions make it feasible to identify their characteristic signatures in planetary atmospheres, present and past.

**Experimental Design:** Photolysis experiments were conducted in sealed glass photocells with MgF$_2$ windows. Experiments were conducted at 10-20 torr of SO$_2$. Liquid water and carbon dioxide (~700 Torr) were also present in the reaction cell in certain cases. Reaction products were extracted from the photocells either in gas phase (residual sulfur dioxide) or by solvent extraction (sulfate and elemental sulfur). Isotopic analyses were undertaken using standard techniques [5,6].

**Experimental results:** Photolysis experiments conducted with a KrF excimer laser (248 nm) and Xe arc lamp (>220 nm continuum) (data from [1]) produce sulfate and residual sulfur dioxide that define an isotopic compositional array with product sulfate that is $^{34}S$-enriched and follow $\delta^{33}S \sim 0.63 \delta^{34}S$. Products of KrF excimer laser photolysis follow $\delta^{36}S \sim 1.4 \delta^{34}S$ and products of Xe arc lamp photolysis follow $\delta^{36}S \sim 1.75 \delta^{34}S$.

Experiments undertaken with ArF excimer laser (193 nm) and the low pressure mercury resonance lamp (184.9 and 253.7 nm) exhibit a different fractionation behavior from those undertaken with longer wavelength ultraviolet radiation. Residual sulfur dioxide and the products (sulfate and elemental sulfur) do not form a single fractionation line indicating that more than one mass-independent fractionation effect was produced in the experiments. In both experiments, product elemental sulfur is $\delta^{35}S$ enriched and $\delta^{34}S$ depleted; residual sulfur dioxide is $\delta^{33}S$ depleted and $\delta^{34}S$ enriched; and product sulfate is $\delta^{33}S$ depleted relative to the mass fractionation line and $\delta^{34}S$ enriched. The behavior of $\delta^{36}S$ was different in these two experiments. $\delta^{36}S \sim 0.6 \delta^{34}S$ for experiments undertaken with the mercury lamp, and $\delta^{36}S \sim 2.4 \delta^{34}S$ for experiments undertaken with the ArF excimer laser were observed.

At present, we do not have a light source that produces continuum radiation below 220 nm, so we make the assumption that our observations at 193 nm can be extrapolated to a wider spectral region. The similarity in the fractionation for $\delta^{33}S$ vs $\delta^{35}S$ between the 193 nm photolysis and 184.9 nm photolysis products supports this, indicating that photolysis in this waveband shares a similar electronic and photolytic chemistry, but the different behavior for $\delta^{36}S$ indicates that additional complexities occur. Both photolysis reactions result in production of elemental sulfur and both photolysis reactions are thought to include predissociation effects for SO$_2$ (below 216 nm) and also for SO (below ~200 nm). The physical chemical sources of the effects remain to be identified.

**Implications for Mars and early Earth:** Products of sulfur dioxide photolysis undertaken with 193 nm radiation exhibit characteristics that are similar to sulfur multiple-isotope data for the SNC meteorites Nakhla and ALH84001 [1,2] (Fig 1), and for sulfide and sulfate documented for terrestrial sedimentary rock samples older than 2450 million years (Ma) of [3] (Fig 2, 3). Products of photolysis experiments undertaken with radiation at other wavelengths (longer than 220 nm, and at 184.9 nm) exhibit different characteristics and do not reproduce the meteoritic and rock observational data. We suggest that photolysis at (or near) the 193 nm region contributed to the isotopic effects observed in SNC meteorites and the ancient terrestrial samples. Although the similarities do not rule out the possibility of other atmospheric reactions as sources, they provide the first viable atmospheric source that we have identified. Further experimental investigation is needed.

The waveband that includes 193 nm radiation lies just above the absorption edges of oxygen and carbon dioxide and just below the Harline bands of ozone. The assertion that photolysis in this waveband contributed to the observed isotope effects requires atmospheric transparency and a source of sulfur dioxide. The present Martian atmosphere is transparent for this waveband, and it can be shown that reduction of oxy-
gen concentrations by two orders of magnitude from PAL will allow this chemistry to occur throughout the Earth’s atmosphere. Volcanic sources of sulfur dioxide are thought to be a sufficient source to satisfy the second requirement for this chemistry.

The occurrence of this chemistry also carries implications for planetary sulfur cycles and our interpretations of isotopic data in their context. These particular atmospheric reactions represent a global source of elemental sulfur and sulfate that will be deposited to the planetary surface. An understanding of the isotopic characteristics of photochemical products deposited to the planetary surface is important because such signatures may be translated through surface chemistry (including chemistry generated by biota that might use these species as energy sources) and imprinted on minerals and other species in the regolith. An appreciation of atmospheric fractionation effects will allow us to extract relevant geological or biogeochemical information. Because atmospheric isotopic fractionations can be very large, care should be taken when interpreting isotopic data in environments that are different from the present-day terrestrial atmospheric environmental analogue. (In our experiments we observed effects up to several hundreds of permil.)