



## **The origin of sulfur MIF effects in ancient rocks based on isotopic SO<sub>2</sub> cross sections**

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The discovery of unusual sulfur isotope fractionation in Archean and Paleoproterozoic ( $> 2.4$  Ga) rocks has promised to yield insights into the rise of O<sub>2</sub> and the nature of the sulfur cycle on ancient Earth, but interpretation has been hampered by the lack of a clear mechanism for the sulfur isotope signature. Proposed mechanisms for the unusual sulfur isotope signatures (termed mass-independent fractionation or MIF) include SO<sub>2</sub> photolysis, atmospheric S<sub>3</sub> (thiozone) formation, and thermal sulfate reduction in sediments. We report high-resolution ultraviolet cross section measurements of the sulfur isotopologues of SO<sub>2</sub> that demonstrate that SO<sub>2</sub> photolysis yields a sulfur MIF signature due to small offsets in the cross sections for low abundances of SO<sub>2</sub> ( $\sim 0.1$  ppb), with additional MIF by self-shielding by <sup>32</sup>SO<sub>2</sub> at higher abundances (up to  $\sim 3$  ppb). The required atmospheric abundances of SO<sub>2</sub> are consistent with variable SO<sub>2</sub> injection rates from volcanic plumes, with rates comparable to modern day to about 10 times modern. A recent suggestion that OCS was an abundant greenhouse gas in the Archean, based on low-resolution SO<sub>2</sub> cross section data, is not supported by our results.