

## Present Day Atmospheric S-cycle Provide Clues to the Mystery of Precambrian S-MIF Signal.

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The Atmospheric sulfur (S) cycle and quadrupole S-isotope observations has played a key role in developing understanding of the paleo atmosphere of Earth and Mars. Laboratory experiments helped resolve molecular level details of the processes of sulfur MIF effects. The S-isotope anomaly in precambrian rock reflects atmospheric oxygen levels based on SO<sub>2</sub> photolysis under varying conditions. There are many aspects of photochemistry controlling the magnitude of S-isotope anomaly and  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope based upon photolytic mechanisms and wavelength dependencies with a range of uncertainty [1,2]. Our high resolution quarter century S-MIF of sulfate aerosols at South Pole depicted large S isotope anomalies in an oxygen rich atmosphere in non volcanic sulfates. Combined oxygen triple and S-quadruple isotope data and the satellite ozone record suggest carbonyl sulfide (COS) as another source of S-isotope anomaly because of its long lifetime and secondary conversion to SO<sub>2</sub> at high altitude (short UV < 240nm) [3,4]. Recent aerosol measurements of four stable and a radiogenic (<sup>35</sup>S) isotope reveal new information that are relevant to interpreting the Archean S-MIF signal. The new data [5] suggest recombination reactions in burning are important now and in the Precambrian and ice cores. Reactions in burning involving symmetry dependent reactions observed in our experiments occur during polymerization of sulfur during biomass burning and volcanism not accounted for in atmospheric S-cycle models of past and present atmosphere of Earth. They are likely of importance and are also sources of COS and SO<sub>2</sub>. Anomalous <sup>33</sup>S and <sup>36</sup>S effects are decoupled during aerosol production and transport processes. New sources of S-isotope anomaly need to be included in decrypting the Archean, polar, and present day atmospheric S-isotope record to better understand how these new reaction pathways occur in nature and allow better interpretations of present and past records.

[1] Farquhar et al., (2000) *Science* **289**, 756. [2] Pavlov and Kasting (2002) *Astrobiology* 2, 27. [3] Shaheet et al., (2013) *PNAS*, 110(44):17662-7. [4] Shaheen et al., (2014) *PNAS* 111(33)11979-8. [5] Mang Lin, Ph.D. thesis UCSD e-library.