Minor sulfur isotope constraints on the composition of Earth's Archean atmosphere

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The presence of minor sulfur isotope anomalies in the sedimentary record constrains atmospheric oxygen to trace levels prior to 2.3 billion years ago, and indirectly indicates the presence of a reducing gas (likely H2 or CH4) at this time. The database of mass-independently fractionated sulfur isotopes (MIF-S) has grown substantially in the previous decade and reveals complex time- and facies-dependent changes in MIF-S magnitudes. The complicated structure within the sedimentary MIF-S record suggests that constraints beyond an "on-off" switch for atmospheric O2 are possible is we can better understand the mechanisms that generate and preserve the signal in the rock record.

Recently, I proposed a quantitative framework necessary for accurate predictions of MIF-S generated in the atmosphere [1]. One conclusion of this study was that additional constraints on Archean atmospheric chemistry beyond the lack of O2 were not possible without new fundamental laboratory measurements of MIF-S generation mechanisms. Two recent studies have removed some of these roadblocks. Identification of MIF-S arising from the photoexcitation band of SO2 [2] and new measurements of the SO2 photoabsorbtion cross-section [3] provide critical new ground-truth on all 4 isotopes of sulfur, enabling much stronger constraints on the composition of the reducing atmosphere.

This presentation will present 1-D photochemical modeling results using these new fundamental laboratory data in conjunction with sedimentary multiple sulfur isotope data, in order to constrain the steady-state composition of the Archean atmosphere and time-dependent perturbations to it.

[1] Claire et al., *Geochimica et Cosmochimica Acta* (2014) [2] Whitehill et al., *Proceedings of the National Academy of Sciences* (2013) [3] Endo et al., *Journal of Geophysical Research* (2015)