Advances in quantifying the composition of the ancient atmosphere

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The twenty-first century has witnessed the generation of a remarkable dataset of quadruple sulfur isotopes in ancient sedimentary rocks. The earliest and broadest interpretation of the presence of mass-independent-fractionation of sulfur isotopes (MIF-S) remains robust, relevant, and radical – they are the "smoking-gun" evidence for a reducing atmosphere prior to 2.3 billion years ago, but there is still more to learn from the temporal MIF-S record.

Like countless other stable isotope systems, our ability to generate MIF-S data far exceeds our ability to quantitatively interpret it. Bulk rock and in situ studies have revealed multiple intriguing correlations between the four sulfur isotopes (and increasingly, other biogeochemical proxies) all of which hint at the opportunity to constrain far more than a simple on/off switch for atmospheric oxygen. In parallel, theoretical and experimental chemistry has revealed a multitude of processes which can generate MIF-S. However, forward modeling of atmospheric chemistry utilizing these measured and theoretical sulfur isotope fractionation factors has been unable to reproduce many of the details seen in the geological database. There are four broad classes of hindrances which could contribute to this dilemma: (1) Our ability to model ancient atmospheric chemistry has too many uncertainties to predict the resulting sulfur isotope values with any confidence. (2) Some incorrect assumptions about the composition of the ancient atmospheric widely persist. (3) Post-atmospheric but pre-depositional processes exert a significant control on the signal perserved in the rock record. And/or, (4) Important additional sulfur isotope fractionation mechanisms remain to be uncovered.

Aspects of all four are likley involved, but I will focus on providing solutions to (1) and (2), with implications for (4). Using all currently described fractionation mechanisms, results from Monte Carlo uncertainty propagation and sensitivity analyses studies will be presented which demonstrate for the first time in an early Earth atmosphere: (a) which reactions contribute the most uncertainty in predictions of atmospheric sulfur species and isotopic behavior (and are thus high priority for experimentalists), and (b) the range of "atmospheric parameter space" that can produce results consistent with the rock record.