## Tracking the local accumulation of free oxygen within Archean marine systems using a coupled Fe-Mo-Tl stable isotope approach

Rybacki, K.S<sup>1</sup>, Owens, J.D.<sup>2</sup>, Planavsky, N.J.<sup>3</sup>, Reinhard, C.T.<sup>1</sup>

<sup>1</sup> School of Earth & Atmoshperic Sciences, Georgia Institute of Technology, Atlanta, GA, USA; <u>kyle.rybacki@eas.gatech.edu</u>

<sup>2</sup> Department of Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, FL, USA

<sup>3</sup> Department of Geology & Geophysics, Yale University, New Haven CT, USA

The emergence of oxygenic photosynthesis is one of the most important milestones in the history of life on Earth. The primary waste product of this process, molecular oxygen, has rendered the Earth's biosphere detectable from space for vast intervals of geologic time, and ultimately set the stage for the emergence and expansion of complex life. However, we have a very poor understanding of when this evolutionary innovation first emerged, with current estimates spanning nearly one billion years of Earth's earliest history. This is partly due to a lack of proxies that undoubtedly represents increased oxygen. As such, inorganic geochemical systems (e.g., trace elements and stable isotopic systems) have emerged as the most promising tools for reconstructing environmental conditions in the ancient geological record since one cannot directly measure the chemical composition of Earth's atmosphere and oceans in the ancient past.

Here, we use a novel coupled Fe-Mo-Tl stable isotope approach to trace local accumulation of  $O_2$  in Archean marine systems via its link to the burial of manganese (Mn) oxides. We will demonstrate that this coupled isotope approach is uniquely designed to overcome the many 'false positives' that plague current approaches for inorganic biosignatures, as well as to peer through the secondary processes that often reshape the geochemistry of sedimentary rocks during deep burial and later exhumation. We will present simple modeling results demonstrating that regardless of the Mn-oxide formation mechanism molecular  $O_2$  is required to stabilize and preserve the Mn-oxide phase, as well as preliminary data that Mnoxide precipitation was occurring in locally oxygenated marine environments more than 500 Ma before the 'Great Oxidation Event'.