**QUANTITATIVE CONSTRAINT ON MOLYBDENUM-NITROGEN CO-LIMITATION IN THE PROTEROZOIC OCEAN.** M. Mansor[1], J.L. Macalady[2] and M.S. Fantle[2]. [1]Pennsylvania State University (muammar10@gmail.com). [2]Geosciences Department, Pennsylvania State University.

During the middle Proterozoic, the lag between a shift from a microbially-dominated world to the emergence of eukaryotes has been hypothesized to be a result of molybdenum (Mo) deficiency, driven by intense burial of Mo under euxinic conditions pervasive during that time period [1]. Mo is a trace nutrient that is vital for nitrogen fixation, with levels below ~5 nM causing Mo-N co-limitation to ecosystems and potentially impeding the development of eukaryotes in the middle Proterozoic [2,3]. No quantitative proxy currently exists to constrain Mo concentrations in the ancient open ocean. The Mo contents of pyrite deposited in black shales and shallow carbonate deposits have been suggested to directly reflect dissolved Mo concentrations, but this approach is still non-quantitative [4,5]. We determined the relationship between dissolved Mo concentrations and Mo contents of experimentally-precipitated pyrite at 80°C. The Mo contents of pyrite were found to correlate strongly with Mo concentrations irrespective of pH and pyrite precipitation rates. Applying the observed correlation directly to Mo contents of geological pyrite, seawater Mo in the middle Proterozoic typically vary between 10-50 nM, above the 5 nM threshold for nitrogen fixation. This suggests that biological stasis during the Proterozoic may not be attributable to Mo-N co-limitation. However, modern pyrite deposited under euxinic water columns displays 20 to 3,000 fold enrichments in Mo content compared to prediction from the experimentally-derived relationship. Therefore, ancient pyrite minerals likely overestimate seawater Mo concentrations especially in euxinic conditions thought to have been prevalent in the Proterozoic.

**References:** [1] Anbar and Knoll (2002) *Science*, *297*, 1137-1142. [2] Reinhard et. al. (2013) *PNAS*, *110*, 5357-5362. [3] Glass et. al. (2009) *Geobiol*, *7*, 100-123. [4] Large et. al. (2014) *EPSL*, *389*, 209-220. [5] Gallagher et. al. (2015) *Geobiol*, *13*, 316-339.