

**THE “WHIFF” OF OXYGEN 2.5 BILLION YEARS AGO: GLOBAL OR LOCAL?** C. M. Ostrander<sup>1</sup>, B. Kendall<sup>2</sup>, G. W. Gordon<sup>1</sup>, S. J. Romaniello<sup>1</sup>, and A. D. Anbar<sup>1,2</sup>, <sup>1</sup>School of Earth and Space Exploration, Arizona State University, <sup>2</sup>Earth and Environmental Sciences, University of Waterloo, <sup>3</sup>School of Molecular Sciences, Arizona State University.

There is now abundant evidence for minor surface oxidation in the geologic record prior to the Great Oxidation Event (GOE). Perhaps the most well-studied stratum is the 2.5 billion year old (Ga) Mt. McRae Shale, where there is clear evidence for oxidative weathering of the continental crust<sup>[1][2][3]</sup>, shallow ocean and/or riverine oxygenation<sup>[4][5]</sup>, and a transition from an anaerobic to aerobic nitrogen cycle<sup>[6]</sup>. Despite extensive work, however, the spatial extent of these “whiffs” of O<sub>2</sub> remains unconstrained. Were these local events that impacted individual basins, or were they global in extent?

To better constrain the spatial and temporal distribution of Archean “whiffs” of O<sub>2</sub>, we conducted a high-resolution molybdenum (Mo) concentration and isotope analysis of the Mt. McRae Shale (~4 samples per meter). Our high-resolution analyses show a gradual increase in Mo concentration first demonstrated in Anbar et al. (2007) with a peak enrichment at ~50 ppm Mo (145.22m core depth). However, the new high-resolution record displays a sharp decline to ~20 ppm which was not apparent in the previous, lower-resolution analyses (~2 samples per meter). This sharp decrease is coeval with the onset of peak FeHR/FeT and FePy/FeHR (143.45m), signifying the most reduced and sulfidic local depositional environment in the section. New high-resolution Mo isotope analyses also display a shift to slightly lighter values across this redox boundary, which was likewise not apparent in the previous record<sup>[5]</sup>.

If the “whiff” was a localized event, Mo concentrations should increase with stronger euxinia and isotope compositions should become heavier. This is precisely what is observed in the modern environment: Mo burial rates increase with stronger euxinic conditions<sup>[7]</sup> and measured sedimentary isotope compositions become heavier, closer to matching the overlying water value<sup>[8]</sup>. However, our high-resolution analysis reveals a dramatic decline in Mo concentrations and a shift to isotopically lighter values as burial conditions become more strongly euxinic.

Instead, we interpret the muted enrichment and lighter isotope compositions during peak euxinia as evidence for expansion in the global euxinic sink. As previously mentioned, euxinic sediments have high burial rates. Thus, expansion of global euxinic deposition would aid depletion of the global oceanic reservoir, muting enrichments in sediments worldwide. All

marine sediments preferentially incorporate isotopically light Mo from seawater. Generally speaking, the more oxic and H<sub>2</sub>S-poor a sediment is (i.e. further from euxinic), the greater the fractionation from seawater. Since euxinic sediments minimally fractionate Mo isotopes, an increase in the area of this sink would decrease the area of seafloor preferentially incorporating isotopically light Mo. In-turn, this would drive the Mo isotope composition of seawater toward lighter values. Because oxidative weathering promotes delivery of Mo and sulfate (required for euxinia) to the ocean, our interpretation supports a global “whiff” of O<sub>2</sub>.

Though molecular oxygen is not necessary for life, it certainly facilitated the rise of eukaryotes, metazoan, etc.. Thus, a better understanding of its distribution on early-Earth provides a backdrop to guide hypotheses of the origin and subsequent evolution of life.

#### References:

- [1] Anbar A. D. et al. (2007) *Science*, 317, 1903-1906. [2] Reinhard C. T. et al. (2009) *Science*, 326, 713-716. [3] Stueken E. E. et al. (2015) *Geology*, 43, 259-262. [4] Kaufman A. J. et al. (2007) *Science*, 317, 1900-1903. [5] Duan Y. et al. (2010) *Geochim. Cosmochim. Acta*, 74, 6655-6668. [6] Garvin J. et al. (2009) *Science*, 323, 1045-1048. [7] Scott C. and Lyons T. W. (2012) *Chemical Geology*, 324, 19-27. [8] Barling J. et al. (2001) *Earth Planet. Sci. Lett.*, 193, 447-457.