

**EXPLORING MOLYBDENUM AND URANIUM ISOTOPE FRACTIONATION ACROSS THE CHEMOCLINE OF FAYETTEVILLE GREEN LAKE, NEW YORK.** X. Chen<sup>1</sup>, A. Sherry<sup>2</sup>, S. J. Romaniello<sup>1</sup>, J. Havig<sup>3</sup>, M. McCormick<sup>4</sup>, and A. D. Anbar<sup>1,2</sup>. <sup>1</sup>School of Earth & Space Exploration, Arizona State University, Tempe, AZ, USA, xchen147@asu.edu, <sup>2</sup>School of Molecular Sciences, Arizona State University, Tempe, AZ, USA, <sup>3</sup>Department of Geology, University of Cincinnati, Cincinnati, OH, USA, <sup>4</sup>Hamilton College, 198 College Hill Rd., Clinton, NY, USA.

Our understanding of the Earth's redox history is crucially dependent on a wide variety of geochemical paleoredox proxies, which must be examined and calibrated in modern analog environments. The fidelity of these proxies relies on extrapolation from modern analogs to ancient environments. The danger in this approach is that we overlook or fail to discover crucial biogeochemical pathways or processes that were important in Earth's past, but are rare or seem unimportant at present. For example, because the modern oceans are almost entirely oxygenated, geochemists are forced to rely on observations in a relative small number of isolated anoxic basins to reconstruct ancient marine processes when anoxia were more widespread. There is good reason to expect that these rare modern analogs undersample and distort the range of processes occurring in ancient oceans.

One way to broaden our understanding and empirically test our conceptual models is to seek out and develop new analog field sites to provide novel, independent observations. While modern anoxic marine localities are limited and often difficult and/or expensive to access, freshwater lakes offer a wider range of chemistry and physical circulation patterns and are often much easier to access. This approach thus offers the potential to explore a wider range of analog environments, but comes with the additional challenge of truly understanding these unique lacustrine systems, including circulation, groundwater inputs, and a proximate sources of allochthonous sediments and detritus.

Fayetteville Green Lake (FGL), a 0.25 km<sup>2</sup> meromictic lake located in upstate New York, has been extensively studied with respect to its hydrology, chemistry, and geomicrobiology [1-2]. The lake is salinity-stratified and features a strong pycnocline and redoxcline at ~18 m, which is characterized by a dense layer of purple sulfur bacteria [2]. Redox-sensitive trace elements such as molybdenum and uranium are significantly depleted below the chemocline [3]. In this project, we extend this prior work by collecting detailed profiles of Mo and U isotopic variations in the water column and sediments and constructing detailed isotopic budgets for elemental cycling in FGL.

U concentration (from 10 to 3 nM) and isotopic compositions (from -0.5 to -0.96 ‰) significantly decreased across the chemocline as observed in other euxinic basins and lakes [4, 5]. Such depletions are

caused by U(VI) reduction to insoluble U(IV), which preferentially enriches in heavier U isotopes and sinks down to the bottom of the lake [6].

Surprisingly, Mo isotopes fractionated in the opposite direction across the chemocline in FGL compared to other similar euxinic basins and lakes, where <sup>98</sup>Mo/<sup>95</sup>Mo became heavier in the sulfidic water [4, 5]. Variations in Mo concentration (from 16 to 1 nM) and isotopic ratios (from 2.40 to 0.96 ‰) in the water column of FGL shared the same trend as U.

Two possible mechanisms are proposed to interpret the lighter <sup>98</sup>Mo/<sup>95</sup>Mo in the euxinic water column. First, the non-quantitative removal Mo from the water is possibly the result oversaturation of the Fe-Mo-S mineral – Fe<sub>5</sub>Mo<sub>3</sub>S<sub>14</sub> [7], which we assume to preferentially remove heavier Mo isotopes. Second, the soluble Mo in the euxinic water column might be the result of Mo associated with non-sinking particulate organic matter (e. g., colloidal, and < 0.2 μm particulate organic matter) [8]. Laboratory experiments and field samples demonstrated that lighter Mo isotopes were preferentially associated with organic matter, with an isotope fractionation of 1.5 - 1.9 ‰ [9, 10].

Further work is needed to test these hypotheses, including experimental synthesis of the theorized Fe-Mo-S mineral and determination of the Mo isotopic compositions of dissolved and suspended colloidal organic matter in natural waters.

**References:** [1] Brunskill G. J. and Ludlam K. H. (1968) *Limnol. Oceanogr.* 14, 817-829. [2] Thompson J. B. et al. (1990) *Palaios*, 52-75. [3] Havig J. R. et al. (2015) *Geochim. Cosmochim. Acta*, 165, 389-406. [4] Nägler T. F. et al. (2011) *Chem. Geol.*, 289, 1-11. [5] Dahl T. W. et al. (2010) *Geochim. Cosmochim. Acta*, 74, 144-163. [6] Andersen M. B. et al. (2014) *Earth Planet. Sci. Lett.*, 400, 184-194. [7] Helz G. R. et al. (2011) *Chem. Geol.*, 284, 323-332. [8] Dahl T. W. et al. (2016) *Geobiology*, 1-13. [9] King E. K. et al. (2016) *AGU*, Abstract#V54a-07. [10] Neely R. et al. (2016) *AGU*, Abstract#V51A-3039.