Molybdenum speciation in modern and ancient euxinic settings

ANTHONY CHAPPAZ[1]*, JEREMY D. OWENS[2] AND TIMOTHY W. LYONS[3]

[1]Institute for Great Lakes Research – Dep. of Earth and Atmospheric Sciences – Dep. of Chemistry, Central Michigan University, Mount Pleasant, MI 48859, USA
[2]Geology and Geophysics Dep., Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[3]Dept. of Earth Sciences, University of California – Riverside, CA 92521, USA

Molybdenum (Mo) has emerged as a powerful paleo-indicator of sulfidic conditions in studies of the evolution of Earth's early oxygenation, either by examining patterns of Mo enrichment and/or the δ^{98}Mo isotopic signature in sedimentary records. In oxygenated water, inorganic Mo speciation occurs dominantly as unreactive molybdate ($Mo^{VI}O_4^{2-}$). When sulfide is present, sulfur substitutes progressively for oxygen in MoO_4^{2-}, leading to reactive tetrathiomolybdate ($Mo^{VI}S_4^{2-}$) by way of transient intermediates ($Mo^{VI}O_xS_{4-x}^{2-}$). However, the processes leading to Mo incorporation in sulfidic sediments are still unknown, limiting its use as a proxy.

A successful first step was recently taken by determining Mo speciation using XAFS in lacustrine sediments deposited under permanently euxinic conditions, representing ten thousand years of deposition [1]. Here we used the same approach to study changes in Mo oxidation state and molecular coordination environment in samples from the Cariaco Basin (a modern euxinic marine setting) and the Cenomanian-Turonian oceanic anoxic event (Demerara Rise—a euxinic locality during widespread reducing conditions).

The coordination number for all samples—determined via EXAFS analysis—is always four, but the oxygen-to-sulfur ratio fluctuates, possibly suggesting some periods of less reducing conditions for both sites. Interpretation of XANES data indicate some reduction of Mo(VI), which is consistent with our previous study.

These results are especially important at times of intense drawdown of Mo either due to global expansion of euxinic conditions or basinal restriction that can affect Mo concentrations and isotopic signatures [2]. Further, we propose that a detailed exploration of other redox sensitive proxies (e.g. Fe, Mo, Cr) will complement the current systematic approaches and will offer new insights into redox fluctuations in modern and ancient oceans.

[1] Dahl *et al* (2013) *GCA* **103** *213-231,* [2] Reinhard *et al* (2013) *PNAS* **110** *5357-5362*