Dissolved Mo in the Archean oceans - a case study from the 2.63 Ga Jeerinah Formation, Australia

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It is generally accepted that atmospheric oxygen levels remained consistently below 10^{-3} % PAL throughout the Archean Eon. However, a growing number of geochemical studies suggest that transient periods of atmospheric/surface oxygenation occurred as early as ca. 3 Ga. Here, we present Mo isotope compositions of black shales from the 2.63 Ga Jeerinah Formation, in order to test whether the Mo isotopic system may have recorded Archean oxygenation. Using the Fe speciation criteria for euxinic conditions ($Fe_{HR}/Fe_T > 0.38$ and $Fe_{Py}/Fe_{HR} > 0.8$), several euxinic samples were identified with weak Mo enrichments (5.5 ± 2.1 ppm) and higher TOC levels. Following a correction for the detrital Mo contribution (based on Mo/Al ratios), our samples yielded an estimate for contemporaneous seawater of $\delta^{98}Mo_{SW}$ = 1.1 ± 0.1‰ (relative to the Rochester Mo standard).

Calculation of the Mo residence time in the late Archean ocean, based on estimates for the Mo riverine input (3.6×10^9 g/yr) and seawater Mo concentrations (<5nM), gives a range of 17 to 140 ky. This is considerably longer than the ocean mixing time, assuming it was similar to the modern ocean (t=1.6 ky). Thus, we suggest that the oceans were homogenous with respect to Mo at this time and, hence, Mo isotope compositions derived from euxinic black shales may be used as a paleo-redox proxy for the global oceans.

Considering that the Mo source (igneous and Archean sedimentary rocks) show $\delta^{98}Mo$ = 0 ± 0.5‰, our seawater estimate of $\delta^{98}Mo_{SW}$ = 1.1 ± 0.1‰ indicates that surface sulfide oxygenation, delivery of molybdate (MoO_4^{2-}) to the ocean and Mo fractionation during Mo removal must have occurred at this time. Moreover, this occurrence of Mo enrichment and the positive isotope signature suggests that enhanced surface sulfide weathering could have generated sufficient sulfate flux to overwhelm the oceanic hydrothermal Fe flux and promote the development of euxnic conditions while maintaining the mass-independent fractionation of sulfur.