Bioavailability of Mo in the Palaeoproterozoic ocean

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Tracing how and when the Earth's oceans became oxic is essential for our understanding of the interaction between ocean chemistry, biological evolution, and nutrient controls on primary productivity. Recent work has highlighted the potential of the molybdenum isotope system as a global palaeoredox indicator, based on the distinct isotopic signatures of Mo incorporated into oxic and euxinic marine sediments [e.g. 1]. Less is known, however, about isotopic fractionations in shales deposited in an anoxic Fe-rich water column. Such conditions were prevalent throughout much of the Archaean and early Palaeoproterozoic, and thus represent an important depositional setting for Mo over an extended period of Earth's history.

We report Mo isotope compositions recorded in shales from the 1.88 Ga Pine Creek Basin, Australia. Fe-S-C systematics record a clear transition from an anoxic Fe-rich water column to a sulfidic water column, providing further evidence for a widespread transition to sulfidic conditions at this time [2]. Sediments deposited under anoxic Fe-rich conditions have an average $\delta^{97/95}$Mo of 0.23 ± 0.13‰, and sediments deposited under sulfidic conditions have a similar $\delta^{97/95}$Mo of 0.03 ± 0.23‰.

The Mo isotope data imply widespread ocean euxinia, and demonstrate that anoxic Fe-rich environments preserve isotope compositions very close to the input ratio. This, and high Mo concentrations, implies that Mo removal from the oceans was near-quantitative both in the presence of sulfide and under Fe-rich conditions. Existing models have suggested that Mo bioavailability may have been severely restricted under euxinic conditions [3]. Our data confirm this, and additionally suggest that a high degree of Mo removal under Fe-rich ocean conditions may have severely restricted primary productivity prior to the widespread occurrence of sulfidic conditions. This, in turn, may help to explain the apparent protracted oxidation of the biosphere after the evolution of oxygenic photosynthesis.

References

[1] G.L. Arnold et al. (2004) *Science* **304**, 87-90.

[2] S.W. Poulton et al. (2004) *Nature* **431**, 173-177.

[3] A.D. Anbar and A.H. Knoll (2002) *Science* **297**, 1137-1142.