The cycling of Molybdenum and Iron across a Paleoproterozoic redoxcline

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Stable isotopic variability of redox sensitive elements in marine sediments have been used as evidence for the existence of local to regional marine oxygen oases long before atmospheric oxygenation around 2.4 billion years (Ga) ago [1]. For molybdenum in particular the proposed mechanism to explain the stable isotopic variability is isotopic fractionation induced by partial adsorption on particle surfaces. In the context of the occurrence of oxygen oasis particle shuttling at the oxic/anoxic water interface might thus have caused large isotopic heterogeneities within the contemporaneous water column, which might then have been stored within the sedimentary record.

Stable molybdenum (Mo) and iron (Fe) isotopic data of carbonate and silicate iron formations of the 2.48 Ga old Koegas Subgroup, South Africa, which were deposited at the anoxic-oxic interface of a local oxygen oasis, show a negative correlation with manganese (Mn) oxide content. This might highlight the substantial role of MnO particle shuttling for the stable Fe and Mo isotopic distribution within these redox stratified water bodies. The reason for the negative correlation with δ^{98}Mo values is linked to the preferential adsorption of isotopically light Mo onto Mn-oxides. The latters distribution and flux to the sediment is dependent on the vertical position of the depositional environment along the redoxcline. The negative correlation between MnO and δ^{56}Fe values is given by increasing rates of Fe^{2+} oxidation and Fe-oxide precipitation towards higher rates of Mn-oxide particle formation, resulting in a progressively lighter dissolved Fe^{2+} pool.

Although these processes can be observed in modern analogues with redox stratified water bodies [2], the preservation of such covariing isotopic patterns within Archean and Proterozoic sedimentary records will likely require more extended redoxclines compared to modern settings.

[1] Planavsky et al. (2014), Nature Geoscience 7, 283-286

[2] Busigny et al. (2014), GCA 133, 443-462