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Combined stable W and Mo isotopic evidence for increasing redox-potentials from the Paleo- to Neoarchean Oceans

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The stable tungsten (W) isotope system has lately been the target of a number of studies investigating its potential as a new marine redox proxy. Dissolved W (as WO_4^{2-}) adsorbs onto Fe- and Mn-oxides with associated equilibrium stable isotopic fractionations $e^{186/184}W$ of 0.51 and 0.59 ‰, respectively [1], resulting in modern seawater that is isotopically heavy ($\delta^{186/184}W$ = +0.55 ‰ [2]) when compared to the detrital input source from the continents (-0.01 to +0.10 ‰). Unlike Mo enhanced solubility of thiolated W species prevents substantial burial in euxinic sediments [3], but W can be strongly authigenically enriched in shales deposited under hypoxic/anoxic conditions [4]. Additionally, WO_4^{2-} is stable at lower redox potentials than MoO_4^{2-}. Thus, variation in the stable W isotopic composition of Archean shales may be a new and complementary tool to investigate changes in the redox state of the ferruginous Archean ocean.

We tested this hypothesis by measuring the stable W isotopic composition of well-characterized 3.47 to 2.50 Ga old marine black shale suites that were deposited under ferruginous conditions (Archean Biosphere Drilling Project, Pilbara Craton, Australia). Determination of the $\delta^{186/184}W$ values of Archean-Paleoproterozoic igneous rocks to establish the detrital isotopic signal of contemporary shaly sediments revealed the same $\delta^{186/184}W$ range as for modern igneous rocks [5]. All shale suites show mixing trends in $\delta^{186/184}W$ values from this detrital background towards an isotopically heavier endmember of up to +0.246 ‰. Our observation indicates that oxidized WO_4^{2-} must have existed in the Archean ocean as early as 3.47 Ga. In contrast, all these samples with the exception of the youngest 2.5 Ga shales suite have crustal-like $\delta^{98/95}Mo$ values. Combining these findings, we devise a multi-step redox evolution model for the Archean ocean, showing continuously increasing redox potentials from shallow to deep ocean water masses.

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