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Tungsten (isotope) cycling in modern marine basins and implications for paleoredox reconstructions

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The stable tungsten (W) isotope composition of modern seawater ($\delta^{186/184}$W = +0.543 ± 0.046 ‰; [1]) is markedly heavier than the main input source of marine W, the upper continental crust ($\delta^{186/184}$W of +0.080 ± 0.053 ‰; [2]). In analogy to Mo, the driving mechanism for this isotopic difference is the preferential adsorption of isotopically light W onto manganese (Mn) oxides in (hyp)oxic marine settings. Therefore, temporal changes in the seawater stable W isotope composition might be linked to the areal extent of (hyp)oxic conditions. The rise of marine oxygen concentrations in Earth's history would shift the seawater $\delta^{186/184}$W towards higher values. However, the application of stable W isotopic compositions as a new palaeoredox proxy initially requires a better understanding of stable W isotope fractionation during sediment deposition and diagenesis and the identification of sediments that preserve temporal trends in the $\delta^{186/184}$W of seawater.

Here we present stable W isotope data for sediments from the Landsort Deep in the Baltic Sea [2]. In this basin redox stratified conditions with hypoxic or euxinic bottom waters repeatedly alternated with fully oxic conditions during the last ~1,700 years. During long-lasting fully oxic periods the detrital component controls Mn and W abundances in the sediments leading to crust-like $\delta^{186/184}$W values between -0.008 and +0.112 ‰. During periods of bottom water hypoxia sediments are authigenically enriched in Mn and W showing higher $\delta^{186/184}$W values up to +0.226 ‰. Smooth depth trends in $\delta^{186/184}$W during hypoxic phases ultimately mirror temporal changes in the inflow intensity of O_2 bearing Baltic seawater. High inflow rates enhance the shuttling of Mn oxides that preferentially scavenge isotopically light W. As a consequence, the $\delta^{186/184}$W of residual bottom waters and subsequently formed sediments increases. Therefore, temporal variation in sedimentary $\delta^{186/184}$W values is linked to the extent of Mn oxide formation that in turn depends on changing marine redox conditions. This relationship highlights that stable W isotopes are a promising new proxy for the reconstruction of marine redox conditions in early Earth history.

[1] Kurzweil et al. (2021) *PNAS* 118 (18) e2023544118; [2] Kurzweil et al. (2022) *EPSL* 578, 117303.