

Redox control on the seawater tungsten isotope composition

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Manganese oxides are a major sink for dissolved marine WO_4^{2-} and MoO_4^{2-} . During adsorption of WO_4^{2-} and MoO_4^{2-} onto Mn oxides the coordination of W and Mo changes from tetrahedral to octahedral [1]. Light isotopes are preferentially adsorbed due to the weaker bonding structure in octahedral coordination. Sulfidic settings are another major sink for Mo, but not for W [2, 3]. In contrast to Mo, the $\delta^{186/184}\text{W}$ of seawater and authigenic sediments is therefore expected to be independent of the global extension of sulfidic conditions but more intimately linked to the extension of oxic marine conditions.

We present seawater $\delta^{186/184}\text{W}$ and W concentration data from the South Atlantic Ocean and the South China Sea showing an average $\delta^{186/184}\text{W}$ of $+0.543 \pm 0.046$ ‰ (2SD; n = 10) at an average W concentration of 0.050 ± 0.007 nM (2SD; n = 10). These estimates are perfectly consistent but more precise than a previous estimate on Northern Pacific seawater [4] and clearly indicate a conservative distribution of W in modern open ocean seawater. In contrast, seawater from a redox-stratified basin in the more restricted Baltic Sea (Landsort Deep) shows more variable W isotope compositions ($\delta^{186/184}\text{W}$ between +0.347 and +0.810 ‰) and W concentrations (between 0.054 and 0.223 nM). Consistent with experimental studies [1], the preferential scavenging of isotopically light W by Mn oxides that form along the redoxcline in this basin increases the $\delta^{186/184}\text{W}$ of surrounding seawater, whereas the re-dissolution of Mn oxides causes decreasing seawater $\delta^{186/184}\text{W}$. Our findings suggest that redox-related processes cause variations in the abundance and stable isotope composition of marine W thus providing the initial framework for the future application of stable W isotopes as a new paleo-redox proxy.

[1] Kashiwabara *et al.* (2017) *GCA* 106, 364-378.

[2] Mohajerin *et al.* (2016) *GCA* 177, 105-119.

[3] Dellwig *et al.* (2019) *ESR* 193, 1-23.

[4] Fujiwara *et al.* (2020) *Chemical Geology* 555, 119835.