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Stable tungsten isotopic composition of seawater over the past 80 million years

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The operation of the Earth's surface systems is intimately linked to the cycling of redox-sensitive elements such as oxygen, carbon, sulfur and iron. Thus, isotopic records of redox-sensitive elements in seawater can shed light on important changes over Earth's history. The stable isotopes of tungsten (W) show great potential for this purpose because tungstate (WO_4^{2-}), the main tungsten species in oxidized environments, shows high particle reactivity with light tungsten isotopes preferentially adsorbed onto Fe-Mn oxyhydroxides *(1)*. In contrast, thiotungstate ($WO_{4-x}S_x^{2-}$) which forms in highly sulfidic environmments is more soluble *(2)*.

Here we present the seawater stable isotopic composition of tungsten ($\delta^{186/184}W$) as recorded in ferromanganese crusts spanning the past 80 Ma. The $\delta^{186/184}W$ of seawater displays a pronounced decrease of ~0.2‰ between 80 Ma and 40 Ma followed by stable values thereafter. Based on our recent work on W isotope systematics on the earth's surface *(3)*, a simple box model and comparison to other proxies suggest that the Late Cretaceous to Early Cenozoic decrease in seawater $\delta^{186/184}W$ was most likely caused by decreasing W isotopic fractionation between seawater and W sinks. This can be linked to shifting sedimentation regimes. Specifically, increasing sediment supply and associated burial of organic carbon in response to the closure of the Neotethys Ocean and the subsequent India-Eurasia collision may have increased the availability of reactive iron, which in turn promoted rapid scavenging of pore-water W to generate the smaller isotopic fractionation associated with the W sinks.

Our work shows that seawater $\delta^{186/184}W$ is a promising new proxy for early sediment diagenesis that intimately links the cycling of W and redox-sensitive sulfur and iron. Importantly, our new record of seawater tungsten isotope compositions extending back to the Late Cretaceous helps to explain a major shift in the sulfur cycle that occurred in the early Cenozoic.

[1] Kashiwabara et al. (2017) *GCA* **204**, 52-67 [2] Mohajerin et al. (2014) *GCA* **144**, 157-172 [3] Yang et al. (2022) *GCA* **in press** (doi: 10.1016/j.gca.2022.01.006)