Tungsten stable isotopes as a redox-proxy for the evolution of the anoxic Archean Ocean

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Stable molybdenum (Mo) isotope variations in black shales have been widely employed to monitor the oxygen evolution of Earth's atmosphere and oceans. Thereby, the authigenically enriched Mo in black shales mirrors the isotopic composition of the ambient seawater, but only if H_2S concentrations in the depositional regime are >11 µmol L^{-1}. The Archean deep ocean, however, was most likely anoxic and ferruginous with little or no free H_2S, posing difficulties to use Mo isotopes in anoxic black shales as a direct proxy for the ocean's O_2 content. Tungsten (W), similarly to Mo, fractionates during adsorption onto Mn-Fe oxides (i.e. shallow Archean ocean) [1]. In contrast to Mo, W is very soluble in H_2S-rich porewaters [2] but might be authigenically buried in anoxic, ferruginous black shales (deep Archean ocean). Hence, W isotopic variations of black shales may represent a complementary proxy to trace the Archean ocean's redox state.

We tested this hypothesis by measuring stable W isotope compositions ($\delta^{186/184}W$) [3] of black shales selected from scientific drilling programs to cover the Archean (ABDP, Pilbara Craton, AUS, 3.46-2.5 Ga) and the Great Oxidation Event (GOE; Agouron drilling project, Kapvaal Craton, ZA, 2.45-2.32 Ga). Paleoarchean $\delta^{186/184}W$ values are within the range of igneous rocks (+0.085 ± 0.019 ‰) [4]. 2.94 to 2.5 Ga old samples, however, show a significant shift towards heavier values of up to +0.241 ‰ in $\delta^{186/184}W$. Interestingly, stable W isotopic compositions of black shales that cover the onset of the GOE, are again indistinguishable from igneous $\delta^{186/184}W$ values. Our preliminary study shows that Archean black shales indeed show variable W isotopic signatures, potentially revealing redox changes in ocean chemistry before the GOE. The return to igneous $\delta^{186/184}W$ values for samples enclosing the GOE may result from a potential reservoir effect or from ascending sulfidic conditions.

[1] Kashiwabara et al. (2017), GCA 204, 52ff.
[2] Mohajerin et al. (2016), GCA 177, 105ff.
[3] Kurzweil et al. (2018), Chem.Geol 476, 407ff.
[4] Kurzweil et al. (2019). GCA 251, 176ff.