Impact of Mn authigenesis on Mo isotopes, Landsort Deep, Baltic Sea

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The formation of Mn oxides in the ocean is thought to require the presence of high-potential oxidants such as free O_2. However, anoxygenic photosynthesis prior to the evolution of oxygenic photosynthesis could also led to Mn^{2+} oxidation. The redox sensitive element Mo is scavenged by Mn oxides. Thereby, isotopically light Mo is preferentially adsorbed. Observed co-variation between authigenic Mn enrichments and Mo isotopic composition ($\delta^{98/95}$Mo) in Archean and Paleoproterozoic marine sediments have therefore been interpreted as evidence for free O_2 in the water column. However, Mn oxides are commonly not preserved due to their reductive dissolution within the sediment, which also affects the cycling of Mo and possibly the sedimentary Mo isotope composition. Therefore, the preservation of primary Mo isotope signatures during early diagenesis needs to be investigated in modern marine analogs.

The Landsort Deep, Baltic Sea, represents an appropriate locality to study the impact of Mn oxides on trace metal cycling and their isotope signatures. Bottom-water redox conditions change on annual to decadal scales due to inflows of O_2-containing waters from the North Sea. While euxinic stagnation periods allow accumulation of dissolved Mn^{2+} in bottom waters, inflows are able to oxidize the entire water body fostering enhanced deposition of Mn-oxides. Anoxic conditions within the sediment provoke the reduction of Mn-oxides and the formation of secondary Mn-carbonate phases.

Here we present Mo isotope data from a dated short core that covers the last ~60 years. The formation of Mn-rich carbonates in these sediments clearly indicates hypoxic but non-euxinic bottom water conditions during deposition. Despite the early diagenetic reduction of Mn and redistribution of Mo, the negative co-variation beween Mn content and $\delta^{98/95}$Mo values indicates the retention of isotopically light Mo during Mn-carbonate formation. This is supported by Mo isotope data from sediment traps and suspended particulate matter. Our results confirm that Mo isotopes in Mn-rich marine sediments are indeed useful to reconstruct temporal changes in depositional redox conditions.