Unprecedented high δ^{98}Mo of the Ottawa River: implications for marine palaeoredox reconstruction

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Accurate use of Mo mass balance modelling in marine palaeoredox reconstruction relies on the accurate representation of the δ^{98}Mo composition of Mo sources and sinks. Here we present unprecedented heavy δ^{98}Mo compositions of the Ottawa River, indicating the existence of a previously unidentified source of isotopically heavy Mo.

In recent years, studies have shown that the global riverine Mo flux, previously assumed to closely reflect that of the weathered source rock, is isotopically highly variable and consistently heavy up to ~ 1.6 ‰. The Ottawa River, Canada, has previously been identified as having an anomalously heavy δ^{98}Mo close to seawater (2.3 ‰), which questions previous attempts to explain heavy signatures in rivers.

Previous work has identified potential sources of heavy Mo to river waters via weathering of evaporites, black shales and sulfides, and mechanisms of fractionation by adsorption onto Fe-Mn oxyhydroxides in suspended particles and soils. We collected 32 water samples from the Ottawa River and surrounding lakes. Filtered samples were analysed for major and trace elements as well as δ^{98}Mo.

Our results confirm previously measured heavy δ^{98}Mo and reveal a progressive upstream trend towards values even heavier than seawater, up to 3.5 ‰. Low Mo concentrations correlate positively with δ^{98}Mo and both decrease downstream, arguing against contamination from sulfide mining activities, adsorption of light isotopes and increased input from intense weathering. Thus, our observations are best explained as the dilution of a yet unidentified point source of heavy Mo upstream, or a - unknown if not unlikely - significant permanent sink for light isotopes existing only in the upper reaches of the Ottawa River Valley. In both cases, anthropogenic contribution from industry along the river must be considered.

In the case of an anthropogenic source or sink for Mo, the use of modern large river systems as an analogue for pre-anthropogenic input is challenged. If the heavy signature proves to be of a natural origin, assumptions of paleo-ocean input are nevertheless complicated. Regardless, marine palaeoredox reconstructions may have to be refined.