Cr reduction and associated isotope fractionation restricted to anoxic shelf waters in the Peruvian Oxygen Minimum Zone

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Chromium (Cr) is a transition metal present only at trace concentrations in seawater. Under well oxygenated conditions the predominantly soluble and weakly adsorbing Cr(VI) generally accounts for >70% of dissolved Cr. However, owing to the high redox potential of the Cr(VI)/Cr(III) couple, the reduction of Cr(VI) is easily achieved and the redox transition imposes substantial isotope fractionation. Light ^{52}Cr preferentially partitioning into the reduced Cr(III) species that forms insoluble, particle-reactive hydroxide complexes and is efficiently scavenged onto Fe(III) oxyhydroxides and hence removed from solution. Chromium reduction may occur either photo- and biochemically mediated, through reducing agents, such as organic matter and Fe(II), or reducing conditions in the water column. The latter has stimulated interest in utlizising stable Cr isotopes as a paleo-redox proxy, however, there is yet a modern analague to find, that verifies chromium removal and isotopic fractionation in low oxygen waters.

Here we present stable Cr isotope data for water column depth profiles from the Peruvian upwelling, which hosts one of the most pronounced Oxygen Minimum Zones (OMZ) of the modern ocean. Oxygen concentrations at oceanographic stations span a large range from 260 µmol/kg to detection limit (~2 µmol/kg) and cover biogeochemically different areas of the continental margin. Corresponding Cr concentrations [Cr] vary from 1.5 to 4.23 nmol/kg, whereby lowest [Cr] are detected in anoxic bottom waters on the shelf -constistent with reductive removal of Cr(III)- while highest [Cr] were found in oxic deep waters further offshore. Consistently, Cr stable isotopes show the heaviest values (δ^{53}Cr = 1.59 ± 0.03 ‰) at lowest [Cr] and the lightest (δ^{53}Cr = 0.86 ± 0.03 ‰) where highest [Cr] prevail. However, samples from within the OMZ yet offshore from the shelf show no clear signs of reductive Cr removal and Cr isotopic compositions do not correlate with oxygen concentrations either. In addition, it appears that the location within the upwelling area is crucial (shelf vs. lower slope), which may imply a relationship to Fe(II) availability and transport from the shelf.