Chromium isotope speciation in seawater

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Chromium (Cr) isotopes have emerged as a powerful paleoredox proxy. Oxidative weathering results in fractionation of Cr isotopes—a signal ultimately transferred to seawater through runoff and buried in marine sediments following Cr removal from seawater. The relationships between Cr in runoff, the isotopic composition of seawater, and its translation to a sediment signal, however, remain uncertain. This uncertainty comes, in part, from lack of information of the controls on Cr speciation in seawater and the pathway(s) that ultimately transfer this Cr to sediments. Given that Cr is soluble as Cr(VI), removal to sediments implies reduction to Cr(III), which may be accompanied by a fractionation. To determine the changes in isotope composition through various possible pathways of Cr removal, we have developed a magnesium hydroxide coprecipitation method, which provides information on the speciation and isotopic composition of both Cr(III) and Cr(VI) by resolving the Cr(III) and Cr(tot) (Cr(III) and Cr(VI)) pools separately. The method recovery is >95% for Cr(III) and Cr(tot) and the Cr(III) pool captures organic Cr(III) species.

We used this method to create a time series data set of Cr speciation in seawater from Saanich Inlet, British Columbia. Saanich Inlet is a seasonally stratified fjord in which we can interrogate Cr geochemistry across a spectrum of redox conditions. Our data reveal seasonal dynamics in Cr speciation possibly linked to reactions with organic matter during photosynthetic blooms. We also used the method to determine the δ^{53}Cr of coexisting Cr(III) and Cr(VI) at depths of 40 and 75m. These proof-of-concept measurements yielded δ^{53}Cr for Cr(III) and Cr(VI) of 0.00 and -0.05 ± 0.03‰, and 1.47 and 3.68 ± 0.1‰, at 40 and 75m depth, respectively. These data suggest that coexisting Cr(III) and Cr(VI) species are isotopically distinct and can be discriminated using our magnesium hydroxide coprecipitation technique. On-going work is extending these measurements throughout the time series to learn more about Cr isotope fractionations imparted by redox reactions in marine environments.