Reduction of Cr in ODZ waters in the ETNP leaves residual heavy Cr isotope signature

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Even though the chromium isotope system has been used extensively as a geological paleo redox proxy in recent years (e.g. [1, 2]), data on Cr isotopes in modern seawater is sparse [3, 4] and totally absent for oxygen deficient zones (ODZs).

In our work, total dissolved Cr in the seawater samples is first converted to Cr(III) and preconcentrated by $Mg(OH)_2$ co-precipitation. Further elimination of the seawater and reagent matrix is achieved by three-column ion exchange chromatography with isotope analysis on an IsoProbe MC-ICP-MS. Double spike addition of ^{50}Cr and ^{54}Cr allows for accurate correction of $^{53}Cr/^{52}Cr$ mass fractionation during sample handling and mass spectrometry.

We present data from three stations in the Eastern Tropical North Pacific off of Mexico that show for the first time that the reduction of Cr(VI) to Cr(III) in an ODZ is accompanied by significant isotope fractionation. The lighter isotope is preferentially transformed into Cr(III) which is scavenged by particles and removed from the water column, leaving behind heavier residual Cr. We observe the heaviest Cr isotope signatures within the upper ODZ with $\delta^{53}Cr$ increasing to maxima of +1.26 and +1.52 per mil (wrt SRM979). The location of the maximum implies that microbial reduction limited by sinking organic matter is the main pathway for Cr reduction. A water column profile from the Santa Barbara Basin shows the heaviest Cr isotope signatures within the anoxic bottom layer ($\delta^{53}Cr$ = +1.47 per mil), where Cr concentrations decrease markedly because of reduction.

In contrast, a typical open ocean profile exhibits the heaviest $\delta^{53}Cr$ at the surface due to preferential uptake of light Cr isotopes during phytoplankton growth followed by export by sinking particles. As organic matter is respired the lighter Cr is being released back into the seawater at depth. We will show a profile from an Arctic Ocean station that is consistent with this model and previously published data [4].

[1] Frei *et al*. (2009) *Nature* **461**, 250-253. [2] Planavsky *et al*. (2014) *Science* **346**, 635-638. [3] Bonnand *et al*. (2013) *Earth Planet. Sci. Lett*. **382**, 10-20. [4] Scheiderich *et al*. (2015) *Earth Planet. Sci. Lett*. **423**, 87–97.