Chromium isotope fractionation between seawater and carbonate sediment in the Caribbean Sea

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In recent years, chromium isotopes have emerged as a promising new proxy for reconstructing past redox conditions in the oceans, and marine carbonate sediment is being investigated as a substrate that might record these redox-driven changes in seawater Cr isotope values. Laboratory studies show that chromate, the main species of Cr in oxidized seawater, co-precipiates with calcite without any change in oxidation state, and only on a small positive isotopic fractionation effect ($\Delta^{53}Cr_{(p\text{-}is)}$) +0.06‰ to +0.18‰.[1] However, when we analysed shallow water carbonate sediment from the modern Caribbean Sea[2], we found an a apparent fractionation of -0.45‰ ($\Delta^{53}Cr_{(CaCO3\text{-}SW)}$) between seawater ($\delta^{53}Cr$=1.14‰) and bulk carbonate sediment ($\delta^{53}Cr$=0.69 ‰), implying fractionation of Cr(VI) to Cr(III) during removal of seawater chromate into carbonate.The studied carbonate sediment is composed of green algae ($\delta^{53}Cr$=0.55‰), forams ($\delta^{53}Cr$=0.74‰), molluscs ($\delta^{53}Cr$=0.44‰), red forams ($\delta^{53}Cr$=0.58‰), and red algae ($\delta^{53}Cr$=0.85‰).

In addition, we measured $\delta^{53}Cr$ in living Halimeda opuntia (green algae) ($\delta^{53}Cr$=0.33‰), *Amphiroa tribulus* (red algae) ($\delta^{53}Cr$= -0.06‰) and several species of coral ($\delta^{53}Cr$= -0.21‰ to -0.48‰), which are very different from their counterparts in the sediment (values mentioned earlier). The difference in the values points to the role of the organism (precipitating the carbonate) in the preferential intake of lighter Cr isotopes. Because most marine carbonate production is biologically mediated, it is important to understand the biological sources of Cr isotope fractionation during sediment production. We are currently using mass balance and mixing approaches to inform development of conceptual models for explaining the observed fractionation of seawater Cr isotopes during removal into marine carbonate.

[1] Rodler *et al*. (2015) *Geochimica et Cosmochimica Acta* **164**, 221-235

[2] Holmden *et al*. (In review) *Geochimica et Cosmochimica Acta*