

## Heterogeneity of Cr in *Mytilus edulis*: Implications for the Cr isotope system as a paleo-redox proxy

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Changes in  $^{53}\text{Cr}/^{52}\text{Cr}$  ( $\delta^{53}\text{Cr}$ ) values recorded by biogenic carbonates are emerging as a proxy for variations in the redox state of the Earth's oceans and atmosphere (e.g. [1], [2]). We investigate the ability of modern carbonate shells (*Mytilus edulis*) to record the  $\delta^{53}\text{Cr}$  composition of ambient seawater in order to assess their utility as a paleo-redox proxy. Samples of cultivated *M. edulis* from the Kiel Fjord, Germany, were analyzed for their  $\delta^{53}\text{Cr}$  composition and Cr concentrations [Cr] using TIMS. To disentangle the pathway of Cr into the carbonate shell, a series of step-digestions of their organic outer sheaths (periostraca) and their intra-layer composition were performed.

Bulk analyses of specimens with intact periostraca returned 16 to 34 ppb Cr with  $\delta^{53}\text{Cr}$  values ranging from 0.28 to  $0.65 \pm 0.1$  (2SE) and thus fall within the range of surface seawater from the Baltic Sea (0.3 - 0.6 ‰ [3]). Partial removal of periostraca resulted in lower [Cr] (5 to 17 ppb) and  $\delta^{53}\text{Cr}$  values ( $-0.05 \pm 0.15$  ‰). These results show a positive correlation between the amount of organic matter present in a sample and both [Cr] and  $\delta^{53}\text{Cr}$  ( $n = 9$ ). With nearly complete removal of periostraca, the remaining [Cr] is significantly lower (less than 5 ppb) and can only be accessed by incineration of the carbonate shell.

The correlation between [Cr],  $\delta^{53}\text{Cr}$  and the amount of periostracum present in bulk samples indicates that a significant proportion of preserved Cr may be associated with the organic outer sheath. The Cr endmember accessed after incineration is less likely associated with the carbonate crystal lattice. Instead, the  $\delta^{53}\text{Cr}$  values obtained after incineration are similar to those reported from terrestrial rocks, suggesting the influence of detrital particles. Alternatively, Cr may be reduced and subsequently re-oxidized during the mineralization of biogenic carbonates [4]. Seasonal changes in primary productivity in seawater may further influence the shell's Cr isotopic composition [3]. A detailed understanding of the processes causing the observed heterogeneity of [Cr] and  $\delta^{53}\text{Cr}$  in modern carbonate shells is crucial for the use of the Cr isotope system as a potential paleo-redox proxy.

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