

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

Sylvie Bruggmann, Robert Kläebe, and Robert Frei

Department of Geosciences and Natural Resource Management, University of Copenhagen, Copenhagen, Denmark

article wasysym

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 ± 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 ± 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.

[1] Bonnard, P., James, R. H., Parkinson, I. J., Connelly, D. P., and Fairchild, I. J. (2013). The chromium isotopic composition of seawater and marine carbonates. *Earth and Planetary Science Letters*, 382:10-20.

[2] Holmden, C., Jacobsen, A. D., Sageman, B. B., Hurgten, M. T. (2016). Response of the Cr isotope proxy to Cretaceous Ocean Anoxic Event 2 in a pelagic carbonate succession from the Western Interior Seaway. *Geochimica et Cosmochimica Acta*, 186:227-295.

[3] Paulukat, C., Gilleaudeau, G. J., Chernyavskiy, P., Frei, R. (2016). The Cr-isotope signature of surface seawater - A global perspective. *Chemical Geology*, 444:101-109.

[4] Pereira, N. S., Voegelin, A. R., Paulukat, C., Sial, A. N., Ferreira, V. P., and Frei, R. (2015). Chromium-isotope signatures in scleractinian corals from the Rocas Atoll, Tropical South Atlantic. *Geobiology* 1-14.