

Elucidating biogenic components of the $\delta^{53}\text{Cr}$ cycle in the modern ocean

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The redox-driven control on dissolved chromium (Cr) concentrations and stable isotope composition ($\delta^{53}\text{Cr}$) have motivated strong interest in $\delta^{53}\text{Cr}$ as a paleoredox proxy. While a growing body of modern data are helping to elucidate biogeochemical controls on Cr^{VI} , which can in turn inform $\delta^{53}\text{Cr}$ -based paleoreconstructions, key uncertainties remain in the modern biogeochemical Cr cycle. To improve the mechanistic understanding of Cr cycling and its paleoproxy potential, we present new data targeting biogenic components of the Cr cycle. Regeneration incubation experiments with near-surface biogenic particles show release of isotopically light Cr, which appears to be decoupled from O_2 respiration and the regeneration of macronutrients. The isotope enrichment factor ($\Delta^{53}\text{Cr}_{\text{particle-dissolved}} \approx -0.66 \text{ ‰}$ for Cr released from particles is similar to that implied by the global $\delta^{53}\text{Cr}$ - $\ln(\text{Cr})$ array ($\sim -0.7 \text{ ‰}$), supporting recent data demonstrating biological control on $\delta^{53}\text{Cr}$ in surface waters^[2]. Porewaters from oxic biogenic sediments are strongly enriched in dissolved Cr relative to overlying waters, and bottom waters are isotopically light and Cr-rich compared to the same water mass away from sediments, demonstrating oxic sediments can serve as a diffusive source of Cr to overlying waters. Scarce global data limit quantitative extrapolations of this source; however, based on the local magnitude, it may be of comparable or greater global importance as other known sources. Future research should help to better constrain this source on a global scale. Mass balance calculations indicate that the benthic Cr flux likely reflects Cr scavenged from the water column rather than lithogenic material. The calculated porewater $\delta^{53}\text{Cr}$ is isotopically lighter than surface and intermediate waters by approximately 0.7 ‰, again matching the fractionation implied by the global $\delta^{53}\text{Cr}$ - $\ln(\text{Cr})$ array. These data demonstrate biological export and release from particles in the water column and/or sediments help to shape global $\delta^{53}\text{Cr}$ distributions, and therefore that sedimentary $\delta^{53}\text{Cr}$ records may reflect processes other than O_2 availability.

[1]Scheiderich et al. (2015). *Earth Planet. Sci. Lett.* **423**, 87-97. doi: 10.1016/j.epsl.2015.04.030.

[2]Janssen et al. (2020). *Glob. Biogeochem. Cy.* **34**(1), e2019GB006397. doi: 10.1029/2019GB006397.