Strong evidence that chromium in shales and ironstones tracks environmental cycling

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Chromium (Cr) enrichments have been used widely as a redox proxy in both modern and ancient settings, and more recently the Cr isotope system has emerged as a powerful redox proxy for detecting major shifts in atmospheric oxygen levels in the Precambrian. There are both detrital (particulate) and authigenic (redox-driven, seawater sourced) components that comprise the total Cr found in marine sediments. For both enrichment and isotopic studies, constraining this background detrital component in the sedimentary archive of interest is vital for any interpretation of depositional redox environment, and the influence of this detrital component on isotopic signatures has become a topic of debate. To move forward this debate we have taken two approaches: 1) We have used a petrographic approach to better understand where Cr resides in sedimentary rocks, based foremost on electron microprobe mapping. In previously examined ironstones, we find that Cr is primarily located in iron oxide phases rather than in clays or as Cr-rich detrital grains, suggesting that Cr isotopic signatures are dominantly authigenic. 2) To understand variability in detrital contribution on a broader scale, we have examined a USGS soil database covering the continental US, and we observe large and laterally extensive variability in Cr relative to detrital tracers (Ti or Al) in topsoils which will directly become the detrital marine flux. Further, recent marine sediments also show wide variation, and frequent depletion, relative to the traditionally used single crustal average. Using a catchment-scale resampling procedure we suggest a new confidence interval for the detrital input of Cr to marine siliciclastic sediments, and highlight the utility of large isotopic datasets when considering small authigenic enrichments. Based on detailed petrographic work and the use of a large modern database to understand crustal variability, there is strong evidence that Proterozoic ironstones and shales are tracking environmental Cr cycling and current Cr isotope datasets provide evidence for low environmental oxygen levels.