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The chromium isotope composition of reducing and oxic marine sediments

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Abstract

The chromium (Cr) isotope composition of marine sediments has the potential to provide new insights into the evolution of Earth-surface redox conditions. There are significant but poorly constrained isotope fractionations associated with oxidative subaerial weathering and riverine transport, the major source of seawater Cr, and with partial Cr reduction during burial in marine sediments, the major sink for seawater Cr. A more comprehensive understanding of these processes is needed to establish global Cr isotope mass balance and to gauge the utility of Cr isotopes as a paleoredox proxy. For these purposes, we investigated the Cr isotope composition of reducing sediments from the upwelling zone of the Peru Margin and the deep Cariaco Basin. Chromium is present in marine sediments in both detrital and authigenic phases, and to estimate the isotopic composition of the authigenic fraction, we measured δ^{53}Cr on a weakly acid-leached fraction in addition to the bulk sediment. In an effort to examine potential variability in the Cr isotope composition of the detrital fraction, we also measured δ^{53}Cr on a variety of oxic marine sediments that contain minimal authigenic Cr. The average δ^{53}Cr value of the oxic sediments examined here is -0.05 ± 0.10‰ (2σ, $n = 25$), which is within the range of δ^{53}Cr values characteristic of the bulk silicate Earth. This implies that uncertainty in estimates of authigenic δ^{53}Cr values based on bulk sediment analyses is mainly linked to estimation of the ratio of Cr in detrital versus authigenic phases, rather than to the Cr-isotopic composition of the detrital pool. Leaches of Cariaco Basin sediments have an average δ^{53}Cr value of $+0.38 \pm 0.10$‰ (2σ, $n = 7$), which shows no dependency on sample location within the basin and is close to that of Atlantic deepwater Cr ($\sim$+0.5‰). This suggests that authigenic Cr in anoxic sediments may reliably reflect the first-order Cr isotope composition of deepwaters. For Peru Margin samples, the average δ^{53}Cr values of bulk sediments ($+0.59 \pm 0.06$‰; 2σ) and leach fractions ($+0.61 \pm 0.06$‰; 2σ) are also comparable with those of Cariaco Basin samples and modern deepwater values. Finally, we found that the δ^{53}Cr of Peru Margin samples correlates with δ^{15}N on glacial–interglacial timescales, which we attribute to secular variation in basinal or global-ocean redox conditions. Thus, the δ^{53}Cr stratigraphic record of Peru Margin sediments indicates that Cr isotopes may be suited to tracking geologically short-term changes in ocean oxygenation.

Keywords: Chromium isotope; Nitrogen isotope; Redox proxy; Glacial–interglacial; Ocean oxygenation

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1. INTRODUCTION

Developments in mass spectrometry over the past two decades have given rise to the burgeoning field of 'non-traditional' stable isotope systematics. In particular, isotopic variability associated with the different redox states of transition metals such as Fe, Mo, U and Cr has catalyzed great interest, and these isotopic systems have been used as biogeochemical tracers in efforts to reconstruct Earth's redox evolution. Despite pioneering work on these isotope systems (see Anbar, 2004; Beard and Johnson, 2004; Schauble, 2004; Anbar and Rouxel, 2007; and references therein), we still lack a comprehensive understanding of the factors controlling the isotopic budget of these elements in Earth's surface environments and in the marine realm. In particular, the chromium (Cr) isotope system has recently emerged as a potentially powerful redox proxy (Frei et al., 2009, 2011, 2013, 2014; Crowe et al., 2013; Reinhard et al., 2013, 2014; Planavsky et al., 2014), but there are few Cr isotope studies of modern marine sediments (Bonnand et al., 2013; Reinhard et al., 2014; Pereira et al., 2015).

The marine Cr cycle is primarily controlled by dissolved/particulate inputs derived from oxidative weathering on the continents and removal of Cr via authigenic burial in reducing continental margin sediments and anoxic marine basins (Van der Weijden and Reith, 1982; Reinhard et al., 2013). In the continental crust, Cr occurs largely in reduced form as Cr(III) in Cr-rich accessory minerals such as chromite (Fandeur et al., 2009). The initial mobilization of Cr in soils and further transport of Cr in aqueous solution requires the presence of oxidizing conditions on continental surfaces that make possible the production of soluble Cr(VI) species during oxidation of insoluble Cr(III) species. More specifically, the oxidation of Cr(III) to Cr(VI) in modern soils is catalyzed by interaction between Cr(III) and Mn-oxide phases (MnO_2) (Bartlett and James, 1979; Eary and Rai, 1987; Fendorf, 1995; Oze et al., 2007). Oxidation of Cr(III) to Cr(VI) results in the formation of very soluble chromate oxyanion species ($HCrO_4^-$, CrO_4^{2-}) that are subsequently transported by rivers to the oceans. Upon delivery to the oceans, Cr is removed from the oceanic pool through burial in reducing environments where reduction of soluble $Cr(VI)O_4^{2-}$ to Cr(III) by a range of reductants results in the partitioning of Cr into the authigenic fraction of marine sediments. There are reports of significant dissolved Cr(III) in some riverine systems (e.g., Yusof et al., 2007), but the broad applicability of these observations and long range fate of this Cr (e.g., in estuaries) are not well constrained. High-temperature and low-temperature (off-axis) hydrothermal systems represent sinks for seawater Cr (Elderfield and Schultz, 1996; Reinhard et al., 2013), but these fluxes are small compared to the riverine flux (i.e., ~0.60% and ~0.02% of the riverine flux respectively, Reinhard et al., 2013) suggesting that the influence of hydrothermal systems on the modern isotope mass balance of Cr is limited.

Much of the recent interest in the Cr cycle is linked to the view that the isotopic composition of natural Cr species is governed principally by shifts in redox state – with significant isotopic fractionations expected for both equilibrium exchange between Cr(III) and Cr(VI) species and incomplete reduction of Cr(VI) to Cr(III) (Schauble et al., 2004; Zink et al., 2010; Wang et al., 2015). However, due to the long time-scales of isotopic exchange between Cr(III) and Cr(VI) under Earth-surface conditions (e.g., Wang et al., 2015), the isotope systematics of low-temperature Cr cycling are likely to be dominated by kinetic fractionations associated with partial Cr(VI) reduction. In any case, both equilibrium and kinetic processes ultimately produce Cr(VI) that is isotopically heavy (i.e., ^{53}Cr-enriched, isotopic values are expressed in permil using a delta notation, $\delta^{53}Cr = [(^{53}Cr/^{52}Cr)_{sample}/(^{53}Cr/^{52}Cr)_{NIST\text{-}979} - 1] \times 1000‰$) by up to 6‰ (Schauble et al., 2004). In marked contrast to other redox tracers such as Fe or Mo, Cr isotope fractionations associated with non-redox-dependent processes such as precipitation of mineral phases (e.g., oxides) or adsorption onto mineral surfaces are currently thought to be negligible (Ellis et al., 2004; Johnson and Bullen, 2004; Schauble et al., 2004). Heavy-isotope (^{53}Cr) enrichment of the riverine Cr flux to the oceans relative to upper continental crust (UCC) is indicated both by experimental results and by empirical δ^{53}Cr data from South American rivers (from +0.23 to +0.45‰; Frei et al., 2014), Indian river waters (from +0.67‰ to +1.33‰; Paulukat et al., 2015), and global seawater (~+0.5‰; Bonnand et al., 2013; Paulukat et al., 2015; Scheiderich et al., 2015).

Significant efforts have been undertaken to better characterize the Cr isotope composition of modern seawater. Scheiderich et al. (2015) measured the δ^{53}Cr of seawater bodies from the Arctic (Beaufort Sea), Pacific, and North Atlantic oceans, as well as seawater samples from the Paraná estuary, and obtained δ^{53}Cr values ranging from +0.61‰ to +1.55‰. The authors attributed this relatively large range of Cr isotope variation to fractionation during Cr(VI) reduction to Cr(III) in surface waters and oxygen minimum zones based on an observed correlation between Cr concentrations and δ^{53}Cr values. They determined an isotope fractionation factor of −0.80‰ during Cr(VI) reduction to Cr(III) as inferred from a Rayleigh fractionation model applied to their data. However, studies on the effect of Cr reduction on Cr speciation in seawater remain scarce (Elderfield, 1970; Cranston and Murray, 1978; Cranston, 1983; Murray et al., 1983; Rue et al., 1997; Li et al., 2009), and the influence of particles (e.g., scavenging processes) and organic ligands for stabilizing Cr species in seawater are also poorly documented. In addition, although the reduction of Cr(VI) in open-ocean OMZ (oxygen-minimum zone) regions has been observed (Cranston and Murray, 1978; Cranston, 1983; Murray et al., 1983; Rue et al., 1997), the actual effect of this process on the Cr isotope composition in the water column has not been demonstrated in natural samples. Lastly, the Cr isotope variation in deep open-ocean seawater is also not well established. Therefore, as emphasized by Scheiderich et al. (2015), more in-depth investigations of Cr reduction reactions in the water column are needed in order to explore the proposed 'Rayleigh model' for global variations of Cr isotopes in modern oceans.

Non-quantitative Cr removal due to partial Cr reduction, such as in low-oxygen sedimentary depositional environments