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 $\delta^{53}\text{Cr}$ 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 $\delta^{53}\text{Cr}$ on a variety of oxic marine sediments that contain minimal authigenic Cr. The average $\delta^{53}\text{Cr}$ value of the oxic sediments examined here is $-0.05 \pm 0.10\text{‰}$ (2σ , $n = 25$), which is within the range of $\delta^{53}\text{Cr}$ values characteristic of the bulk silicate Earth. This implies that uncertainty in estimates of authigenic $\delta^{53}\text{Cr}$ 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 $\delta^{53}\text{Cr}$ value of $+0.38 \pm 0.10\text{‰}$ (2σ , $n = 7$), which shows no dependency on sample location within the basin and is close to that of Atlantic deepwater Cr ($\sim +0.5\text{‰}$). 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 $\delta^{53}\text{Cr}$ values of bulk sediments ($+0.59 \pm 0.06\text{‰}$; 2σ) and leach fractions ($+0.61 \pm 0.06\text{‰}$; 2σ) are also comparable with those of Cariaco Basin samples and modern deepwater values. Finally, we found that the

$\delta^{53}\text{Cr}$ of Peru Margin samples correlates with $\delta^{15}\text{N}$ on glacial-interglacial timescales, which we attribute to secular variation in basinal or global-ocean redox conditions. Thus, the $\delta^{53}\text{Cr}$ stratigraphic record of Peru Margin sediments indicates that Cr isotopes may be suited to tracking geologically short-term changes in ocean oxygenation.

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; Frei et al., 2011; Crowe et al., 2013; Frei et al., 2013; Reinhard et al., 2013; Frei et al., 2014; Planavsky et al., 2014; Reinhard 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 (MnO₂) (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 (HCrO₄⁻, CrO₄²⁻) 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)O₄²⁻ 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 timescales 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., ⁵³Cr-enriched,

isotopic values are expressed in permil using a delta notation, $\delta^{53}\text{Cr} = [({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{sample}}/({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{NIST-979}} - 1] \times 1000 \text{ ‰}$ 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 (${}^{53}\text{Cr}$) enrichment of the riverine Cr flux to the oceans relative to upper continental crust (UCC) is indicated both by experimental results and by empirical $\delta^{53}\text{Cr}$ data from South American rivers (from +0.23 and +0.45 ‰; Frei et al., 2014), Indian river waters (from +0.67 ‰ and +1.33 ‰; Paulukat et al., 2015), and global seawater ($\sim +0.5 \text{ ‰}$; 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 $\delta^{53}\text{Cr}$ of seawater bodies from the Arctic (Beaufort Sea), Pacific, and North Atlantic oceans, as well as seawater samples from the Paraná estuary, and obtained $\delta^{53}\text{Cr}$ 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 $\delta^{53}\text{Cr}$ 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 (with $\text{O}_2 < 5 \mu\text{mol.kg}^{-1}$ and no H_2S present) (Rue et al., 1997), may be accompanied by a relatively large Cr isotope fractionation between bottom waters and authigenic Cr precipitated into the sediment (Reinhard et al., 2014). However, authigenic Cr in anoxic marine sediments may in some cases approximately capture the Cr isotope composition of ambient seawater without measurable fractionation provided that uptake is quantitative or nearly so (Reinhard et al., 2014). This is expected to be the case in anoxic water bodies because of rapid reduction of Cr(VI)O_4^{2-} by a wide range of natural reductants (Graham and Bouwer, 2012). Authigenic Cr in marine sediments thus potentially provides a means for tracking seawater Cr isotope variability through time (assuming limited isotope variability in the globally integrated riverine Cr flux to the oceans). Although estimates are scarce, Cr appears to have a shorter residence time (~ 9 kyr; Reinhard et al., 2013) than other redox-sensitive trace elements with tractable isotopic systems such as U and Mo (~ 800 kyr and ~ 400 kyr; Morford and Emerson, 1999; Dunk et al., 2002). Chromium isotopes are thus potentially sensitive to short-term perturbations (e.g., on the timescales of glacial-interglacial cycles and other relatively rapid geologic events).

Isotopic variation in the Earth-surface Cr cycle is mainly due to (1) the net effect of processes leading to isotopic fractionation during subaerial weathering and transport of Cr, and (2) partial reduction in reducing marine facies and the integrated mass flux into such

sediments, the latter of which scales with their spatial distribution in the marine realm. Both temporal fluctuations of redox conditions in modern and ancient environments and the impact of imbalances between the riverine Cr source flux (i.e., continental oxidative weathering) and the size of the marine reducing sink flux on the oceanic Cr budget remain poorly constrained at present. However, carbonates and oxic siliciclastic sediments are thought to account for a relatively small fraction of the Cr sink flux in the oceanic Cr budget, and the Cr isotope compositions of these facies are not expected to be strongly fractionated relative to the oceanic pool (Schoenberg et al., 2008; Frei et al., 2011; Bonnand et al., 2013). Further study should lead to an improved understanding of Cr isotope behavior in marine sediments during sedimentation, burial and post-depositional remobilization, which will be essential for evaluating the factors governing the marine Cr isotope system.

In the modern oceans, two types of sediment deposited under reducing conditions potentially influence the marine Cr mass balance: (1) sediments deposited in stratified basins with anoxic bottom waters such as the Cariaco Basin and the Black Sea; and (2) sediments deposited in reducing continental margin settings, and in particular along eastern ocean boundaries, where bottom waters may contain some dissolved oxygen but organic carbon fluxes are relatively high and much of the sediment column is reducing. Anoxic sediments of the Cariaco Basin (northern Venezuela, Caribbean Sea) show roughly constant Cr isotope compositions for most of the last ~14.5 kyr (Reinhard et al., 2014), and $\delta^{53}\text{Cr}$ values corrected for detrital Cr inputs fall within the range of published Atlantic deepwater values. This observation is consistent with the hypothesis that, in some cases, quantitative CrO_4^{2-} reduction can provide a reliable record of the Cr isotope composition of ambient seawater.

In contrast to sediments deposited in anoxic basins where contact between dissolved Cr(VI) and potential reductants is controlled largely by advection and turbulent mixing, reducing continental margin sediments are deposited in bottom waters commonly containing

small but non-zero amounts of dissolved oxygen. In this case, CrO_4^{2-} reduction may not be quantitative and instead can occur within the sediment below a diffusive boundary layer. This process was described by Reinhard et al. (2014), building on models developed by Bender (1990), Brandes and Devol (1997), and Clark and Johnson (2008). If the depth of oxygen penetration into the sediment is small relative to the reaction-diffusion length scale (i.e., the ratio between the diffusion coefficient of CrO_4^{2-} and the apparent rate constant of a single-step reduction reaction), partially reduced Cr can escape from the sediment column, leading to significant Cr isotope fractionation within the sediment. If diffusional processes dominate the system (i.e., at small oxygen penetration depths), isotopic fractionation should drive the authigenic Cr towards lighter $\delta^{53}\text{Cr}$ values than the seawater pool. On the other hand, if the diffusive boundary layer is large relative to the reaction-diffusion length scale, reduced Cr is mostly retained within the sediment, and Cr isotope fractionation relative to seawater will be minimal. If sediment oxygen penetration dramatically exceeds the reaction-diffusion length scale, reduced Cr will be mostly retained but authigenic burial fluxes will be very low (e.g., Clark and Johnson, 2008). Thus, both authigenic burial fluxes and Cr isotope fractionation during authigenic enrichment depend strongly on the thickness of the oxygenated sediment layer, a relationship that may be of primary importance in regulating oceanic Cr isotope mass balance (e.g., Reinhard et al., 2014).

Building on this framework, we conducted a study focusing on: (1) sediments deposited since ~160 kyr B.P. within the oxygen minimum zone of the Peru Margin, representing an eastern boundary upwelling zone, with the aim of investigating Cr isotope systematics in reducing continental margin sediments and their potential as an archive for ambient seawater Cr isotope composition; (2) modern core-top sediment samples covering the entire anoxic Cariaco Basin, with the objective of confirming that minimal isotopic fractionation occurs during scavenging of Cr into authigenic phases in anoxic marine basins;

and (3) oxic siliciclastic deep-sea sediments from around the globe, with the dual aims of (i) confirming that removal of Cr into such settings is accompanied by minimal isotopic fractionation and has limited impact on the oceanic Cr cycle, and (ii) providing constraints on the Cr isotope composition of a sediment type that dominates modern seafloor deposits.

2. Geological setting and sample description

2.1. Peru Margin

Samples from the Peru Margin were collected at Site 680 Hole A during Ocean Drilling Program (ODP) Leg 112 (Suess and von Huene, 1988; Dean et al., 1990). The drilling site is located in the Salaverry Basin on the shallow continental shelf of the Peru Margin, and is situated within the OMZ at ~250 m water depth (Fig. 1a) where oxygen concentrations in bottom waters are $<8.9 \mu\text{mol.L}^{-1}$. Strong offshore Ekman transport along the western edge of South America leads to coastal upwelling of cold and nutrient-rich waters from the upper thermocline, promoting high levels of surface productivity ($>1 \text{ gC.m}^{-2}.\text{day}^{-1}$) along the Peru Margin. Accordingly, seawater column chemistry in this region is characterized by an intense OMZ that impinges on the continental shelf/slope between ~50 and 500 m water depth (Suess and von Huene, 1988). Continental shelf sediments in this area receive a high organic matter flux that results in rapid depletion of oxygen in the sediment column with depth.

Three depositional units have been identified in the three drillcores (A, B, C) from Site 680 (Aplin et al., 1992), but only Units 1 and 3 were recovered in hole A. The samples investigated in this study are entirely from Unit 1 and range from core depths of 0.23 m to 13.00 m. Sediments of Unit 1 (0-56 m core depth, hole A) are composed of mm- to cm-scale laminated, dark brown-olive diatomaceous muds with elevated organic matter content.

Age control for the Site 680 drillcore is based on oxygen isotope stratigraphy and

biostratigraphy (Wefer et al., 1990). Oxygen isotope compositions were measured in the benthic foraminifera *Bolivina seminuda humilis*. Comparison of the O isotope profile for the study section (Wefer et al., 1990) with the standard marine O-isotope curve from Imbrie et al. (1984) shows consistent results and allows the study section to be accurately dated on this basis. The estimated uncertainties for O-isotope-based dates are ± 2.5 kyr (Martinson et al., 1987). Note that recent radiometrically calibrated SPECMAP O-isotope stacks have not appreciably changed the timescale used in this study (Lisiecki and Raymo, 2005; Thompson and Goldstein, 2006).

2.2. Cariaco Basin

The Cariaco Basin is located on the northern (Venezuelan) continental shelf of South America and covers a surface area of ~ 7000 km² (Fig. 1b), which makes it one of the largest anoxic basins on the modern Earth (Peterson et al., 1991; Scranton et al., 2001; Alvera-Azcárate et al., 2009). It consists of two relatively deep sub-basins of ~ 1400 m depth separated by a ~ 900 -m-deep saddle. Seawater exchange with the Caribbean Sea is limited by the presence of shallow sills on the western (146 m depth) and northern basin margins (120 m depth). Below the mixed surface layer, a strong pycnocline associated with a temperature gradient limits vertical mixing of seawater within the basin itself, restricting ventilation of the deep watermass. Below ~ 300 m water depth, the basin is anoxic due to a combination of limited deep water renewal and high surface productivity supplying organic matter that promotes microbial respiration, oxygen depletion, and the accumulation of hydrogen sulfide (e.g., Scranton et al., 2001).

Two depositional units have accumulated in the Cariaco Basin since the Last Glacial Maximum (~ 19 kyr B.P.). The upper unit consists of finely laminated dark gray to dark green silty clays, whereas the lower unit is composed of yellowish to brownish silty clays lacking

lamination and showing fine bioturbation. The contact between the two units records an up-section shift from oxic to anoxic conditions in the sediment that occurred at 14.5 kyrs B.P. (Peterson et al., 1991; Dean et al., 1999; Piper and Dean, 2002; Lyons et al., 2003).

The sediment samples investigated in this study were collected during the PLUME-07 cruise that took place in June 1990 on the R/V Thomas Washington (Fig. 1b). A total of 104 cores from different areas of the basin were collected, including piston cores, box cores, and gravity cores. In this study, samples were taken from the uppermost one centimeter of sediment in seven box cores having a wide distribution across the basin. These surface samples can be compared with the long stratigraphic record obtained from the Ocean Drilling Program (ODP) Site 1002 drillcore (Reinhard et al., 2014), which was sampled at depths from 10 cm to 785 cm below seafloor. Because the surface fluff layer may have been lost during sampling, the age of the surface sediments is probably a few hundred years.

2.3. Oxic marine sediments

We investigated a suite of oxic marine sediments from various regions around the globe (Fig. 1c), with site choices motivated by the aim of constructing a representative Cr isotope dataset for oxic pelagic surface sediments. Dried sediments were collected from cores housed in the sediment repository of Woods Hole Oceanographic Institution (WHOI). Sediment samples were collected at core depths between 0 and 9 cm, and were drawn from cores taken below 1000 m water depth, with most samples coming from depths below 3000 m. Sediment lithologies consist predominantly of oxidized fine-grained pelagic clay ranging from light to dark brown or greenish-gray in color, with smaller amounts of calcium carbonate phases and calcareous ooze.

3. Sample preparation and analytical methods

3.1. Elemental concentrations

Elemental analyses for Peru Margin sediments were performed in the Department of Geology at the University of Cincinnati. Samples were dried in an oven at 80°C for 24 hours, ground in an agate ball mill, and stored in plastic vials for later chemical analysis. A wavelength-dispersive Rigaku 3040 X-ray fluorescence (XRF) spectrometer was used for determination of major- and trace-element concentrations on pressed-powder samples. Raw intensities were calibrated with both USGS (SDO-1, SCo-1, SGR-1) and internal black shale standards (analyzed by the commercial company XRAL, X-Ray Assay Laboratories Ltd., Canada). Analytical precision was better than $\pm 2\%$ for major elements and $\pm 5\%$ for trace elements, and detection limits were $\sim 1\text{--}2$ ppm for most trace elements. Total organic carbon (TOC) was determined using an Eltra 2000 C-S analyzer with results calibrated to USGS and internal laboratory standards. An aliquot of each sample was digested in 1N HCl at 50°C for 12 hours and then washed and filtered to remove carbonate carbon prior to analysis. Analytical precision was better than $\pm 2.5\%$ of reported TOC values.

Major and trace element composition of total digests from Cariaco Basin surface sediments and oxic marine sediments were analyzed by ICP-MS (Element XR, Thermo-Finnigan) in the Department of Geology and Geophysics at Yale University using a quartz spray chamber introduction system. An aliquot of the 6N HCl stock solution obtained after total digests (see below) was diluted in 5% HNO₃, and major (Fe, Ti, Mn) and trace elements (Cr, Ba, Co, Ni, Cu, Zn, Mo, V, U, Nb, Cd, La, Ce, Tl, Pb, Th) were measured in medium resolution. Measurement precision on raw intensities for major and trace elements was generally better than $\pm 4\%$ and USGS geostandards BHVO-2 and NOD-A-1 that were processed with samples during each run are within a $\pm 10\%$ range of reported values.

3.2. Chromium isotope analyses

For total digests dried sediments were ashed at 500°C for 8 hours to break down organic matter. Ashed samples were then digested using a concentrated HF-HNO₃ mixture followed by aqua regia digestion of dried residues. Final residues were dissolved in 5 ml 6N HCl for stock solutions.

Chromium isotope compositions were determined for both bulk sediment and leach fractions of samples from the Peru Margin, the Cariaco Basin, and the suite of globally distributed oxic marine sediments. Because the Cr isotope composition of authigenic phases is likely different from the detrital fraction of Cr, and the latter typically represents a substantial fraction of total Cr in most siliciclastic marine sediments, it is essential to be able to isolate the authigenic component of the bulk sediment. Our approach was based on a leaching method developed by Reinhard et al. (2014) and previously employed in constructing a downcore Cr isotope record from ODP Site 1002 (Cariaco Basin). Briefly, the authigenic Cr fraction was separated by leaching non-ashed dried sediment with cold 3N HNO₃ for ~24 hours.

Chromium isotopes were measured by MC-ICP-MS using a double-spike correction for instrumental mass bias. A mixture of ⁵⁰Cr and ⁵⁴Cr isotopes was added to the samples with a constant spike/sample ratio of ~0.5 prior to Cr separation on chromatographic columns. The following protocol included three separation steps (Schoenberg et al., 2008; Reinhard et al., 2014) that ensured complete removal of Fe, Ti and V during chemical separation in order to avoid major isobaric interferences of ⁵⁴Fe, ⁵⁰Ti and ⁵⁰V on Cr isotopes.

In the first step, a split of the 6N HCl stock solution was spiked and evaporated to dryness and residues were taken up in 1N HCl. Prior to loading on 2 ml AG1-X8 anionic resin (100-200 mesh) and because only Cr(VI) is retained on the column, complete oxidation of Cr(III) to Cr(VI) was ensured through addition of ammonium persulfate and heating of the samples for 2 hours at 110°C. AG1-X8 resin was cleaned with mQ water, 3N HNO₃ and 6N

HCl. The matrix was then eluted with 24 ml of 0.2N HCl and 4 ml 2N HCl, with Cr subsequently collected with 5 ml 2N HNO₃ and 0.5% H₂O₂.

The second step removed traces of Fe that may remain after the first elution. Microcolumns filled with 0.2 ml AG1-X8 resin were cleaned mQ water and 3N HNO₃, and samples are loaded and collected with 1.2 ml 6N HCl.

In the third step, traces of Ti were removed using a cationic resin AG50W-X8 (200-400 mesh). The resin was cleaned with mQ water, 3N HNO₃ and 6N HCl followed by sample loading in 3 ml 0.5N HNO₃ and by matrix elution with 1 ml 0.5N HNO₃, 2 ml 0.5N HF and 6 ml 1N HCl. Cr was finally collected with 5 ml 1.8N HCl. Residues were redissolved in 5% HNO₃ for MC-ICP-MS analysis. Chemical yields are generally between 75% and 85%.

Chromium isotopes were measured on a Neptune Plus (Thermo-Finnigan) MC-ICP-MS at Yale University according to the analytical protocol of (Schoenberg et al., 2008; Reinhard et al., 2014). Samples were run in high-resolution mode to resolve polyatomic interferences such as ⁴⁰Ar¹²C⁺, ⁴⁰Ar¹⁴N⁺ and ⁴⁰Ar¹⁶O⁺. Although our chemical procedure should ensure complete removal of Fe, Ti and V, the presence of these three elements was monitored by measuring ⁵⁶Fe, ⁴⁹Ti and ⁵¹V, which were used to correct our samples for potential interferences of ⁵⁴Fe on ⁵⁴Cr, and ⁵⁰Ti and ⁵⁰V on ⁵⁰Cr. Standard-sample-bracketing was employed during the analytical session by measuring a spiked Cr isotope standard NIST SRM 979 before and after each natural sample. Chromium isotope ratios are reported relative to bracketing standards using conventional delta notation ($\delta^{53}\text{Cr} = [({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{sample}}/({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{NIST-979}} - 1] \times 1000 \text{ ‰}$). Addition of the double-spike to the samples allowed correction of potential Cr isotope fractionation during chromatographic separation as well as correction of the instrumental mass bias occurring during introduction of the sample in the mass spectrometer. The double-spike data reduction model is based on the iterative method described by (Siebert et al., 2001).

External precision is reported as two sigma (2σ) uncertainty, calculated based on duplicate analysis of geological reference materials (GRMs) processed through ion-exchange chromatography columns along with samples (BHVO-2 and Nod-A-1 were systematically processed with 18 samples). The $\delta^{53}\text{Cr}$ value for BHVO-2 is $-0.12 \pm 0.09 \text{ ‰}$ ($n=25$), which is similar to published values in the literature for BHVO-1 (a geostandard collected at the same location as BHVO-2; Schoenberg et al., 2008), and Nod-A-1 yielded a $\delta^{53}\text{Cr}$ value of $0.07 \pm 0.09 \text{ ‰}$ ($n=16$). Sample duplicates including column procedure duplicates, digested duplicates, and replicate measurements on the MC-ICP-MS revealed a 2σ uncertainty similar to that determined for GRMs, i.e. $\leq 0.09 \text{ ‰}$ on the reported delta values. Measurement precision is calculated via replicate measurements of the isotopic standard NIST SRM 979 during each analytical session (two standards bracket every sample) and 2σ values are better than 0.06 ‰ on the reported delta values. In addition, a two-standard deviation of the mean ($2se$) is systematically calculated using the 50 cycles of measurement obtained for each sample during MC-ICP-MS analysis and is generally about 0.04 ‰ on the reported delta values.

Chromium in marine sediments is distributed between the detrital component and the authigenic component of the sediment. The Cr isotope composition of the authigenic fraction can be estimated based on Cr/Ti ratios of the bulk sediment and an assumed Cr/Ti ratio and $\delta^{53}\text{Cr}$ value for the detrital component. The detrital Cr/Ti can be set equal to the average upper continental crust (UCC) ratio of $0.024 \mu\text{g} \cdot \mu\text{g}^{-1}$ (Rudnick and Gao, 2014) or, if possible, estimated from a local detrital baseline, whereas the $\delta^{53}\text{Cr}$ value of the detrital component can be assumed similar to that of the Bulk Silicate Earth (BSE) ($\delta^{53}\text{Cr} = -0.124 \pm 0.101 \text{ ‰}$; Schoenberg et al., 2008). Using a detrital Cr/Ti ratio (i.e., UCC or local detrital baseline) and $\delta^{53}\text{Cr}$ value of the bulk sediment, the concentration and isotope composition of authigenic Cr is then calculated by mass balance:

$$\delta^{53}\text{Cr}_{\text{bulk sediment}} = f_{\text{detrital}} \times \delta^{53}\text{Cr}_{\text{detrital}} + (1-f_{\text{detrital}}) \times \delta^{53}\text{Cr}_{\text{authigenic}} \quad (1)$$

where f_{detrital} is equal to $(\text{Cr/Ti})_{\text{detrital}}/(\text{Cr/Ti})_{\text{sample}}$. We can then compare $\delta^{53}\text{Cr}$ values measured in leach fractions directly with $\delta^{53}\text{Cr}$ values calculated for the authigenic fractions by mass balance.

3.3. Nitrogen isotopes

Nitrogen stable isotopic compositions were determined at the University of Kentucky Environmental Research Training Laboratory. Samples containing ~100 μg of nitrogen were weighed into tin capsules and combusted using a Costech 4010 elemental analyzer coupled via a ConFlo-III device to a ThermoFinnigan DeltaPlusXP isotope-ratio-mass spectrometer. Nitrogen isotope values are reported as per mille (‰) variation relative to $\delta^{15}\text{N}_{\text{air}}$, where $\delta^{15}\text{N}_{\text{sample}} = ({}^{15}\text{N}/{}^{14}\text{N}_{\text{sample}}/{}^{15}\text{N}/{}^{14}\text{N}_{\text{air}} - 1) \times 1000$ ‰. The $\delta^{15}\text{N}$ of samples was calibrated using three in-house glycine standards that were previously calibrated against international standards. Analytical precision is better than ± 0.05 ‰ for reported $\delta^{15}\text{N}$ values.

4. Results

4.1. Peru Margin

Geochemical and isotopic results for Peru Margin samples are given in Figure 2 and Table 1a. Total organic content (TOC) displays a large range of values from ~18 wt% to ~0.7 wt%, though most TOC values are >5 wt%. The highest TOC values are found in the upper sequence during the last ~14 kyr. Cr/Ti ratios vary from 0.02 to 0.11 but most values are ~0.05 which is higher than the Cr/Ti of ~0.02 for average UCC (Rudnick and Gao, 2014).

$\delta^{53}\text{Cr}$ values range from +0.40‰ to +0.91‰ in the bulk sediment and from +0.44‰ to

+0.95‰ in the leach fractions (Fig. 2d), Cr isotope values in the bulk sediment are essentially indistinguishable from the associated leach fraction as exemplified by similar isotopic patterns. This suggests that the majority of the Cr in the samples is authigenic, despite a range of Cr/Ti ratios and Cr/Ti ratios that are sometimes within the range of crustal concentrations, suggesting that Cr and Ti can sometimes be decoupled in detrital materials. More specifically this may suggest that the Cr/Ti ratio of detrital materials can be lower (Smith et al., 2013) than typically imagined (e.g., Reinhard et al., 2014). Alternatively, this might suggest that there are detrital Cr fractions that are liberated in weak acid leaches, which would decrease the $\delta^{53}\text{Cr}$ in the leach. The proportion of clay minerals in the sediment can be as high as ~40%. However, the Cr present in the detrital fraction is much less soluble in our leaching method than the Cr in the authigenic phases precipitated within the sediment. The clay-bound Cr that could also be released during the leaching process is negligible compared to the high amount of authigenic Cr. The release of trace amounts of detrital Cr and clay-bound Cr would likely have a negligible impact on the Cr composition of the leach, which is mostly controlled by release of authigenic Cr. The same is true for the Cr isotope composition of the bulk sediment, there is likely limited detrital Cr. The Cr/Ti ratios in some sediment leachates are reported in Table 1b.

Comparison of the average $\delta^{53}\text{Cr}$ value for Peru Margin sediments with average deep seawater values (Bonnand et al., 2013; Scheiderich et al., 2015) is not straightforward given the potential for variable seawater values. However, if we take Peru Margin samples deposited within the last ~15 kyr, the resulting average values are $\delta^{53}\text{Cr}_{\text{bulk}} = +0.59 \pm 0.03\text{‰}$ (2σ) and $\delta^{53}\text{Cr}_{\text{leach}} = +0.61 \pm 0.03\text{‰}$ (2σ), both of which are very well constrained and essentially identical to previously published values from Cariaco Basin Site 1002 (Reinhard et al., 2014). Interestingly, despite being similar to deep Atlantic and Pacific seawater and strikingly invariant, these values are significantly lighter than those of surface seawater from

the Atlantic Ocean, Pacific Ocean, and Beaufort Sea (Scheiderich et al., 2015).

The Peru Margin $\delta^{53}\text{Cr}$ values are not correlated with variations in enrichment of other redox-sensitive trace elements such as U and Mo (Fig. 3a-b), or with sediment TOC (Fig. 3c). Variations in $\delta^{53}\text{Cr}$ are also not systematically correlated with variations in authigenic Cr enrichment (as manifested in variable Cr/Ti ratios; Fig. 3d). However, the chromium and nitrogen isotope profiles display significant secular co-variation, with generally higher $\delta^{53}\text{Cr}$ and $\delta^{15}\text{N}$ corresponding to interglacial intervals and lower $\delta^{53}\text{Cr}$ and $\delta^{15}\text{N}$ values to glacial intervals (Fig. 2c-d). This covariation is also evident in a roughly linear relationship between $\delta^{53}\text{Cr}$ and $\delta^{15}\text{N}$ values ($R^2=0.66$; and $R^2=0.80$ without the two outliers, Fig. 4).

4.2. Cariaco Basin

$\delta^{53}\text{Cr}$ values of the bulk sediment and associated authigenic fractions of the seven core-top samples from the Cariaco Basin investigated in this study are given in Figure 5 and Table 2. For all samples, the isotopic composition of the leach aliquot is substantially ^{53}Cr -enriched relative to the corresponding bulk sediment value. The average Cr isotope composition of the authigenic fraction of the leach aliquot is $+0.38 \pm 0.10\text{‰}$ (2σ ; $n = 7$), which is in the lower range of previously published values for the Cariaco Basin of $+0.58 \pm 0.10\text{‰}$ and the range of published Atlantic seawater values (Fig. 5), hence most of our Cariaco sites appear to be systematically slightly ^{53}Cr -depleted relative to a potential seawater source. Note that surface sediments were not measured for ODP Site 1002 (i.e., measurements start at ~ 20 cmbsf). In contrast to Peru Margin sediments, the Cr isotope composition of Cariaco Basin bulk sediment is lighter with an average of $+0.25 \pm 0.12\text{‰}$ (2σ ; $n = 7$). Lower Cr/Ti ratios of ~ 0.03 are consistent with the presence of a higher detrital component in the bulk sediment of the Cariaco Basin compared to the Peru Margin (mean Cr/Ti ~ 0.05) and also with potentially higher detrital Cr/Ti ratios in the Cariaco Basin sediments (see discussion).

Two samples (numbers 4 and 7 in Fig. 5), both located near the northwestern margin of the Cariaco Basin, display slightly lighter $\delta^{53}\text{Cr}$ values for the bulk sediment. There are no other obvious relationships between $\delta^{53}\text{Cr}$ values and sample location, nor is there any significant difference in overall authigenic enrichment of the bulk sediment.

4.3. Oxic marine sediments

The average bulk $\delta^{53}\text{Cr}$ value of the globally distributed oxic sediments is $-0.05 \pm 0.10\text{‰}$ (2σ ; $n = 25$) (Fig. 6). Crustal Cr isotope values are observed over a relatively large range of Cr/Ti ratios in these samples (0.002 to 0.039; Table 3). However, over 90% of these samples have Cr/Ti between 0.01 and 0.02. The $\delta^{53}\text{Cr}$ values measured on the leach fractions of these samples range from -0.21 to $+0.03\text{‰}$ (Table 3) and are indistinguishable from the bulk sediment $\delta^{53}\text{Cr}$ values.

5. Discussion

5.1. The Cr isotope composition of oxic deep-ocean sediments and assessment of detrital Cr isotope variability

For purposes of calculating the isotope composition of the authigenic Cr component in this study, the detrital component was assumed to have an invariant Cr/Ti ratio and $\delta^{53}\text{Cr}$ value equal to those of BSE (Schoenberg et al., 2008). However, the possibility that some isotopic variability exists in the detrital fraction of marine sediments cannot be ruled out. The suite of marine oxic sediments covering most of the oceanic regions of the globe investigated here enables us to directly address this possibility. It has been assumed that there is limited Cr isotope fractionation between seawater and the oxic and anoxic sinks of chromium (Bonnand et al., 2013; Reinhard et al., 2014). If correct, then the oxic sink should have a negligible influence on temporal fluctuations in seawater Cr isotope composition. This assumption is

reasonable based on experimental data showing that Cr sorption onto Fe- and Al-oxides (i.e., the primary mineral phases that host Cr in oxic sediments) is not accompanied by isotope fractionation (Ellis et al., 2004). However, confirmation of this hypothesis via analysis of a range of natural samples is crucial for a full understanding of the Cr isotope redox proxy framework.

The average Cr isotope composition of oxic marine sediments ($\delta^{53}\text{Cr} = -0.05 \pm 0.10\text{‰}$, 2σ ; $n = 25$; Fig. 6) is slightly heavier than that of the BSE ($-0.124 \pm 0.101 \text{‰}$; Schoenberg et al., 2008) and that of high-temperature rocks ($-0.12 \pm 0.13\text{‰}$; Wang et al., 2016) over a large range of Cr/Ti ratios (i.e., 0.002 to 0.039 with an average of 0.017), but it is still well within the uncertainty range of the latter and similar to the estimated value for the bulk mantle Cr ($-0.079 \pm 0.129\text{‰}$; Farkaš et al., 2013). Student t-tests indicate that the difference between the mean of oxic sediments and the means of high-temperature rocks and the bulk mantle Cr is not significant. Reinhard et al. (2014) argued that sediments deposited under oxic conditions in the Cariaco Basin have an average Cr/Ti ratio (~ 0.021) indistinguishable from that of the UCC, which is also similar to the average Cr/Ti ratio calculated for the oxic deep-ocean sediments from this study (0.017). Similar $\delta^{53}\text{Cr}$ values in the leach fractions and in the bulk sediment likely indicate a negligible authigenic fraction and dominant detrital fraction of Cr in the sediment. Our results clearly show a restricted range of Cr isotope variation in oxic marine sediments, suggesting that (1) removal of marine Cr to oxic sediments has a negligible influence on the Cr isotope composition of seawater; and (2) assuming that these sediments contain negligible amounts of authigenic Cr, the $\delta^{53}\text{Cr}$ value of the detrital Cr component of marine sediments can be assumed to be fairly constant.

5.2. Evaluation of spatial variability in authigenic $\delta^{53}\text{Cr}$ in anoxic marine basins: A case study from the Cariaco Basin

The Cariaco Basin core-top samples exhibit a range of bulk sediment $\delta^{53}\text{Cr}$ values, with some as heavy as Atlantic seawater values (Bonnand et al., 2013) and others comparatively lighter (e.g., samples 4 and 7 in Fig.5). This variability is somewhat difficult to explain given that all sites are located below the chemocline and exhibit similar sediment chemistry (including Cr/Ti ratios). In contrast, the estimated $\delta^{53}\text{Cr}$ values of the authigenic component are remarkably consistent from site to site, with a mean of $+0.38 \pm 0.10\text{‰}$. This suggests that either Cr isotope fractionation during authigenic uptake in sediments is roughly constant across the basin, or that uptake during reduction is effectively quantitative and fractionations due to partial reduction are minimized (e.g., Reinhard et al., 2014). A more systematic assessment of this pattern and full delineation between these two possibilities awaits detailed measurements of dissolved $\delta^{53}\text{Cr}$ in Cariaco Basin waters.

It is also possible that variations in sedimentation rate and sediment provenance across the Cariaco Basin can account for observed variation in isotopic compositions. Sites 4 and 7, which are both located along the northwestern margin of the basin, can be distinguished on the basis of their bulk sediment $\delta^{53}\text{Cr}$ values, and Site 4 has the lightest authigenic $\delta^{53}\text{Cr}$ value. A potential explanation is that sediments in the northwestern portion of the basin have a somewhat different detrital source, e.g., inputs from Tortuga Island that have a different bulk sediment composition (Yarincik et al., 2000; Martinez et al., 2007; Martinez et al., 2010). It is also possible that the behavior of Cr and Ti are decoupled and that some Cr has been lost from the detrital fraction during transport from its source to the marine environment. This process could produce variable Cr/Ti ratios in detrital particles deposited in the Cariaco Basin, which would presumably have proceeded without isotopic fractionation in order to be consistent with the constant Cr isotope composition of detrital Cr, as reflected in the limited range of values measured in marine oxic sediments. Decoupling of detrital Cr and Ti in Cariaco Basin bulk sediments could account for lighter $\delta^{53}\text{Cr}$ values (i.e., $+0.17\text{‰}$) for Sites 4

and 7 in comparison to heavier $\delta^{53}\text{Cr}$ values (i.e., $\sim +0.30\%$) for Sites 1, 2, 3, 5 and 6 despite similar Cr/Ti ratios (~ 0.03). In this case, Sites 4 and 7 would have a detrital fraction with higher Cr/Ti ratios and lower authigenic Cr enrichment, whereas the opposite would characterize Sites 1, 2, 3, 5 and 6. This mechanism remains speculative and additional investigation is needed to clarify whether it applies to our samples. However, despite isotopic variability in the bulk sediment, as discussed above, the estimated authigenic $\delta^{53}\text{Cr}$ values at these sites are nonetheless consistent with those observed elsewhere within the Cariaco Basin.

5.3. Authigenic Cr in reducing continental margin sediments: the Peru Margin

The sedimentary succession from the Peru Margin comprises sediments deposited at water depths of ~ 250 m, which is within the center of the OMZ on the South American continental slope. As a result, this depositional system provides both an interesting contrast to the anoxic Cariaco Basin and a potential record of secular variation in the Cr isotope composition of Pacific Ocean seawater going back to at least 160 kyr B.P. For this reason, the Cr isotope data from the Peru Margin will be examined both in relation to our Cariaco Basin data and also from the perspective of the chemical evolution of Pacific Ocean seawater through late Quaternary glacial-interglacial cycles.

There are two notable contrasts between the sediment records from the Peru Margin and Cariaco Basin. First, the Peru Margin sediments are significantly more ^{53}Cr -enriched than the Cariaco Basin sediments and generally isotopically heavier than published Atlantic and Pacific ocean deepwater values. Second, the Cr isotope composition of the leach fraction of Peru Margin samples is remarkably similar to that of the bulk sediment in most samples, which is likely mainly a result of the large authigenic Cr enrichments. In highly productive continental margin settings, the variations of Cr, Mo and U content of the sediment due to variable redox conditions is generally similar (e.g., Muñoz et al., 2012), so the general lack of

co-variation between $\delta^{53}\text{Cr}$ values and elemental redox proxies such as Mo and U in our Peru Margin samples (Fig. 3) indicates that marked shifts in local benthic redox conditions were not a major factor controlling $\delta^{53}\text{Cr}$ values. Therefore, the observed depth trends in $\delta^{53}\text{Cr}$ values are likely to have been caused by variation in the Cr isotopic composition of either the regional eastern Pacific watermass or the global deep-ocean watermass (see below).

5.3.1. Preservation of seawater Cr isotope composition during Cr removal in reducing continental margin sediments

Although the range of $\delta^{53}\text{Cr}$ values from +0.40 to +0.95‰ in the Peru Margin is within the range of new Cr isotope measurements for surface and deep seawater (+0.44‰ to +1.55‰), including North Pacific seawater (Scheiderich et al., 2015), the $\delta^{53}\text{Cr}$ value of the local seawater source of authigenic Cr for Peru Margin sediments is, to our knowledge, not known yet. In this light, it is not possible to determine accurately the potential effect of partial Cr reduction during Cr removal from seawater to the sediment. One must also use caution when interpreting Cr isotope variations in seawater because photo-reduction of Cr(VI) catalyzed by Fe and organic matter (e.g., phytoplankton) in surface waters (Kieber and Helz, 1992; Connelly et al., 2006; Li et al., 2009) may induce significant Cr isotope variation in the photic zone, but this process would not be applicable to Cr isotope variations in deep seawater. Additional work is clearly needed to improve our knowledge of the Cr isotope composition of modern seawater, particularly for the open-ocean deep watermass.

5.3.2. Relationships between $\delta^{15}\text{N}$ and $\delta^{53}\text{Cr}$ values in reducing continental margin sediments and the link with interglacial/glacial stages

Perhaps the most notable feature of the Peru Margin data is the striking positive correlation between the $\delta^{53}\text{Cr}$ and $\delta^{15}\text{N}$ profiles (Fig. 4), which appear to track

interglacial/glacial cycles over the last 160 kyr B.P. (Fig. 2). Nitrogen isotope systematics can potentially provide insight into the controls on $\delta^{53}\text{Cr}$ variations in Peru Margin sediments. The $\delta^{15}\text{N}$ record from the Peru Margin is broadly consistent with previously inferred changes in the intensity and/or extent of areas of water-column denitrification between glacial and interglacial periods, i.e., lower $\delta^{15}\text{N}$ during glacial stages and higher $\delta^{15}\text{N}$ during interglacial stages (Fig. 2c; see Galbraith and Kienast, 2013; Moore et al., 2013). Because sediments deposited in highly productive ocean-margin environments typically record the $\delta^{15}\text{N}$ of thermocline NO_3^- (e.g., Thunell et al., 2004), the conventional interpretation of this pattern is that thermocline suboxia was more widespread during interglacial periods. Increases in water-column denitrification under extremely low oxygen concentrations will fractionate N isotopes in nitrate towards heavier $\delta^{15}\text{N}$ values by up to 20 ‰ (e.g., Galbraith et al., 2008). The isotopically heavy nitrate produced by this process is then transferred to surface waters by upwelling and assimilated by phytoplankton. Ultimately, sinking organic matter will transfer this heavy N isotope signature to the sediment. Although we consider it premature to definitively link this pattern to a single mechanism, in principle temporal changes in the areal extent or intensity of thermocline suboxia could regulate seawater $\delta^{53}\text{Cr}$ values in one of three ways (none of which are mutually exclusive): (1) expansion/contraction of the seafloor area over which partial Cr reduction operates; (2) changes in the reactively neutral diffusive length scale of continent-margin sediments (see above), e.g., as a result of changes in organic matter flux to the sediment-water interface or bottom water O_2 concentrations; or (3) changes in the extent of partial Cr reduction within the water column (analogous to the effect of water-column denitrification on $\delta^{15}\text{N}$ signals). Additional studies on the behavior of Cr isotopes in the water column (e.g., magnitude of the Cr isotope fractionation factor), in particular across large OMZs, will help to untangle this issue.

Considerably more data will be needed to establish the presence/absence of significant

Cr isotope heterogeneities in the modern oceans and to test potential controls on sediment Cr isotope compositions in highly productive continent-margin settings. In addition, quantification of the actual Cr isotope fractionation that could potentially occur during Cr burial will need to be verified in the future by measuring the Cr isotope composition of the overlying water column including surface and bottom waters along the Peru Margin. Regardless of these uncertainties, our Peru Margin results suggest that the Cr isotope system may allow for an independent means to assess changes in ocean oxygenation state on relatively short timescales. This inference is based on the pronounced temporal coherency of the $\delta^{53}\text{Cr}$ profile and its striking relationship with the $\delta^{15}\text{N}$ record, as well as the short marine residence time of Cr (~ 9 kyr) relative to the tempo of glacial-interglacial transitions. Our results thus provide a strong impetus to explore other continent-margin sedimentary Cr isotope records to improve our understanding of the modern and ancient marine Cr cycle. The intriguing results of this study will hopefully foster comprehensive investigations of the Cr isotope cycle in a range of oceanic environments.

6. Conclusions

Investigation of the Cr isotope composition of reducing sediments from the upwelling zone of the Peru Margin and the deep Cariaco Basin and of oxic marine sediments from multiple sites globally provides insights into the marine Cr cycle. Oxic deep-sea surface sediments yielded a restricted range of $\delta^{53}\text{Cr}$ values (-0.05 ± 0.10 ‰) that are within error of the Cr isotope composition of average UCC and BSE. This indicates that, when determining the isotope composition of the authigenic Cr fraction from bulk marine sediment analyses, the largest current uncertainty is linked to estimates of the proportions of detrital versus authigenic Cr rather than to the $\delta^{53}\text{Cr}$ value of detrital Cr component. Cariaco Basin core-top samples yielded an average $\delta^{53}\text{Cr}$ value ($+0.38 \pm 0.10$ ‰) that is in the lower part of the range

of previously published Cr isotope values for Atlantic seawater and the authigenic Cr fraction of Cariaco Basin Site 1002 sediments. Finally, Peru Margin sediments dating to <160 kyr B.P. yielded an estimated $\delta^{53}\text{Cr}$ value for the authigenic Cr component of $+0.61 \pm 0.06 \text{ ‰}$, showing a strong positive correlation between $\delta^{53}\text{Cr}$ values and $\delta^{15}\text{N}$ values. Our data suggest that intensification or expansion of the oxygen-minimum zone in the oceanic thermocline during interglacial periods may have influenced Cr isotope fluctuations in seawater, providing a strong impetus for further high-resolution work on the $\delta^{53}\text{Cr}$ composition of reducing continental margin sediments. Coherent downcore Cr isotope trends at a glacial-interglacial timescale provide strong support for the idea that Cr isotopes can be used to track short-term seawater redox variations.

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Figure captions:

Figure 1. Geographical location maps of samples investigated in this study. (a) Location of the Ocean Drilling Program (ODP) Site 680 (red dot) on the Peru continental margin along with positions of other cores collected during the ODP Leg 112; (b) Map of the Cariaco Basin including bathymetric contour lines (meter depth, adapted from Reinhard et al., 2014) showing positions of the core tops represented by colored and numbered symbols (see Table 2 for core info); (c) Map showing locations of oxic marine sediments in global oceans (red circles).

Figure 2. Chemostratigraphic profiles of Peru Margin (Hole 680A) bulk sediment samples showing (a) total organic content (TOC), (b) Cr/Ti ratios, (c) N isotope composition, and (d) Cr isotope composition. Transitions between glacial and interglacial periods are specified by horizontal dashed lines. Also shown in (d) is a light grey curve representing variation in Antarctic air temperature reconstructed from the deuterium content of Antarctic ice (Jouzel et al., 2007). The 2σ error for Cr isotope measurements was calculated on replicated measurements of the isotopic standard NIST SRM 979 (see text for more details).

Figure 3. Peru Margin crossplots of the Cr isotope composition of the bulk sediment (grey circles) and leach fractions (red stars) versus (a) U/Ti ratios, (b) Mo/Ti ratios, (c) TOC, and (d) Cr/Ti ratios of the bulk sediment. The lack of correlation between Cr isotope composition and geochemical proxies for sediment redox conditions indicates a minimal role for variations in local sediment redox conditions in driving Cr isotope variations. Other details as in Figure 2.

Figure 4. Peru Margin Cr isotope composition versus N isotope composition. Note the positive linear correlation ($R^2=0.66$; and $R^2=0.80$ without the two outliers). Other details as in Figure 2.

Figure 5. Chromium isotope composition of bulk sediment (circles) and leach fractions stars) from the Cariaco Basin top core samples. Numbers on the left of sample names refer to sample locations on Figure 1b. The light blue bands represent the range of Atlantic seawater values reported by Bonnand et al. (2013) and Scheiderich et al. (2015) and the ranges of published data for bulk sediment (pink) and leach fractions (purple) from Cariaco Basin are also shown (Reinhard et al., 2014). Other details as in Figure 2.

Figure 6. Histogram of the Cr isotope values measured in global oxic marine sediments. Also shown are ranges for bulk silicate Earth (BSE; Schoenberg et al., 2008; Farkaš et al., 2013), the bulk Earth model estimate from Moynier et al. (2011), and the range for modern seawater (Bonnand et al., 2013; Scheiderich et al., 2015).

Table captions:

Table 1a. Peru Margin bulk sediment sample data.

Table 1b. Cr/Ti ratios in Peru Margin sediment leachates.

Table 2. Cariaco Basin bulk sediment sample data.

Table 3. Oxic global marine core-top sediment sample data.

Table 1a: Peru Margin bulk sediment sample data.

Sample name	Units	1H1-023	1H1-042	1H1-062	1H1-082	1H1-102	1H1-122	1H1-142	1H2-010	1H2-030	1H2-050	1H2-070	1H2-090	1H2-110	1H2-130	1H3-002
Depth	cmbsf	23	42	62	82	102	122	142	160	180	200	220	240	260	280	302
Age	ka	1.69	3.09	4.57	6.04	7.52	8.99	10.46	11.79	13.26	14.99	16.96	18.93	20.90	22.87	25.04
$\delta^{15/14}\text{N}$	‰	5.23	NA**	6.14	5.25	5.78	NA	6.06	5.53	4.77	5.12	4.05	6.31	6.64	3.44	0.59
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	0.57	0.59	0.57	0.55	0.63	0.64	0.60	0.59	0.56	0.65	0.72	0.73	0.73	0.64	0.57
$\delta^{53/52}\text{Cr}_{\text{leach}}^*$	‰	0.57	0.59	NA	NA	0.61	0.65	NA	0.60	NA	0.67	0.90	NA	0.82	NA	NA
Cr/Ti	$\mu\text{g}.\mu\text{g}^{-1}$	0.059	0.058	0.067	0.064	0.115	0.070	0.069	0.070	0.057	0.030	0.019	0.055	0.030	0.025	0.019
Cr _{auth}	$\mu\text{g}.\text{g}^{-1}$	66.6	62.9	60.9	149.7	69.1	73.2	81.8	72.7	64.2	0.0	0.0	63.5	0.0	0.0	0.0
f _{auth}	-	0.47	0.46	0.53	0.51	0.73	0.55	0.55	0.55	0.45	0.00	0.00	0.43	0.00	0.00	0.00
TOC	wt%	11.51	12.73	13.29	12.35	10.52	17.63	11.87	12.97	9.30	3.66	0.70	7.39	3.83	0.98	1.15
Mg	$\mu\text{g}.\text{g}^{-1}$	16,402	12,816	14,334	22,595	14,857	14,571	12,929	10,946	11,989	8,470	6,381	9,061	9,264	11,133	6,218
Al	$\mu\text{g}.\text{g}^{-1}$	49,148	48,299	37,659	93,992	17,859	41,903	47,028	38,439	54,439	54,909	61,316	51,367	63,779	112,708	63,912
Mn	$\mu\text{g}.\text{g}^{-1}$	227	221	185	421	92	186	215	187	223	291	294	269	319	497	291
Ba	$\mu\text{g}.\text{g}^{-1}$	273	460	244	476	243	540	321	807	299	363	414	334	417	1,466	442
Ti	$\mu\text{g}.\text{g}^{-1}$	2,389	2,315	1,714	4,522	825	1,887	2,177	1,889	2,469	2,805	2,623	2,690	3,392	4,759	2,700
Cr	$\mu\text{g}.\text{g}^{-1}$	141	135	115	291	95	132	150	132	141	85	51	148	100	120	52
Fe	$\mu\text{g}.\text{g}^{-1}$	17,346	16,830	13,860	40,285	13,608	14,850	17,038	14,065	20,235	15,270	12,737	22,832	20,279	31,888	13,873
Co	$\mu\text{g}.\text{g}^{-1}$	5.6	5.7	5.1	11.3	3.0	5.7	5.9	5.1	6.1	5.1	4.3	6.5	6.1	8.5	4.7
Ni	$\mu\text{g}.\text{g}^{-1}$	120	126	118	206	93	136	148	135	114	58	23	106	58	44	29
Cu	$\mu\text{g}.\text{g}^{-1}$	95	115	103	148	96	131	118	114	90	34	19	55	39	31	25
Zn	$\mu\text{g}.\text{g}^{-1}$	244	335	100	185	78	117	119	109	117	88	50	97	91	132	59
Mo	$\mu\text{g}.\text{g}^{-1}$	39	39	50	68	83	79	63	41	33	13	4	65	23	16	15
V	$\mu\text{g}.\text{g}^{-1}$	158	147	203	270	177	242	189	173	141	72	51	131	116	107	59
U	$\mu\text{g}.\text{g}^{-1}$	12.9	12.2	10.2	22.6	8.1	13.5	11.3	12.2	11.6	15.4	12.0	13.2	10.6	25.1	11.6
Cd	$\mu\text{g}.\text{g}^{-1}$	30	46	74	58	72	100	72	66	46	29	15	37	26	66	24
Pb	$\mu\text{g}.\text{g}^{-1}$	7.3	9.8	10.7	11.8	5.8	7.8	8.3	8.4	8.3	10.2	10.1	7.9	13.8	27.9	11.7
As	$\mu\text{g}.\text{g}^{-1}$	18.6	17.1	15.2	30.7	19.6	17.1	17.9	15.8	15	16.6	9.7	22.0	20.2	35.7	13.1
Rb	$\mu\text{g}.\text{g}^{-1}$	64	59	50	111	24	56	58	48	64	57	56	66	73	136	61
Sr	$\mu\text{g}.\text{g}^{-1}$	225	201	342	378	346	250	325	313	350	534	510	256	287	747	464
Zr	$\mu\text{g}.\text{g}^{-1}$	45	72	22	71	19	27	25	39	35	47	40	48	55	68	51
W	$\mu\text{g}.\text{g}^{-1}$	1.3	1.4	1.4	2.3	1.3	1.3	1.3	1.2	1.4	1.3	1.1	1.4	1.2	1.7	1.0

*Cr isotope composition measured in the leach fraction.

** NA: not analyzed.

Table

Table 1a: continued

Sample name	Units	1H3-022	1H3-042	1H3-062	1H3-082	1H3-102	1H3-122	1H3-142	1H4-010	1H4-030	1H4-050	1H4-070	1H4-090	1H4-110	1H4-130	1H5-002
Depth	cmbsf	322	342	362	382	402	422	442	460	480	500	520	540	560	580	602
Age	ka	27.01	29.38	32.13	34.88	37.63	40.39	43.14	45.61	48.37	51.12	53.87	56.62	58.86	60.57	62.46
$\delta^{15/14}\text{N}$	‰	1.03	3.48	3.37	2.90	3.90	4.00	3.19	3.91	3.17	3.85	3.54	4.19	3.73	2.97	2.94
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	NA	NA	0.42	NA	0.52	0.53	0.44	NA	NA	0.46	NA	0.52	NA	NA	0.40
$\delta^{53/52}\text{Cr}_{\text{leach}}$	‰	NA	NA	0.48	NA	0.50	NA	NA	NA	NA	0.47	NA	NA	NA	NA	0.48
Cr/Ti	$\mu\text{g} \cdot \mu\text{g}^{-1}$	0.017	0.029	0.033	0.036	0.048	0.055	0.035	0.042	0.041	0.043	0.043	0.059	0.043	0.038	0.037
Cr_{auth}	$\mu\text{g} \cdot \text{g}^{-1}$	0.0	0.0	3.8	11.7	37.0	49.3	11.1	27.4	28.3	27.9	28.3	37.1	26.0	19.5	14.3
f_{auth}	-	0.00	0.00	0.04	0.12	0.35	0.44	0.11	0.26	0.23	0.27	0.28	0.47	0.27	0.17	0.15
TOC	wt%	0.82	4.41	5.67	4.99	6.39	7.20	5.34	5.41	7.35	7.35	5.53	8.67	6.41	5.56	6.31
Mg	$\mu\text{g} \cdot \text{g}^{-1}$	10,287	9,189	10,128	10,502	10,752	9,868	11,060	11,297	11,151	10,427	9,821	8,985	8,885	12,450	8,691
Al	$\mu\text{g} \cdot \text{g}^{-1}$	94,392	56,368	52,617	55,921	46,795	41,556	56,058	52,690	56,770	49,088	46,942	28,146	44,165	63,859	47,107
Mn	$\mu\text{g} \cdot \text{g}^{-1}$	479	313	290	297	271	237	300	284	300	278	248	161	242	326	266
Ba	$\mu\text{g} \cdot \text{g}^{-1}$	623	1,356	316	324	306	276	304	401	305	292	290	219	273	304	268
Ti	$\mu\text{g} \cdot \text{g}^{-1}$	4,118	2,970	2,723	2,765	2,221	2,039	2,919	2,495	2,992	2,390	2,385	1,341	2,286	3,133	2,539
Cr	$\mu\text{g} \cdot \text{g}^{-1}$	72	87	89	98	106	113	102	105	122	103	103	79	97	117	94
Fe	$\mu\text{g} \cdot \text{g}^{-1}$	24,996	22,424	19,240	22,248	18,793	19,010	21,517	20,412	22,670	19,520	17,537	13,249	18,222	23,533	18,043
Co	$\mu\text{g} \cdot \text{g}^{-1}$	7.2	6.3	5.7	6.1	6.2	6.1	6.4	6.4	7.1	6.3	5.9	4.1	5.8	7.9	5.9
Ni	$\mu\text{g} \cdot \text{g}^{-1}$	36	63	57	42	87	94	65	80	79	72	75	78	82	76	70
Cu	$\mu\text{g} \cdot \text{g}^{-1}$	37	65	57	79	121	102	90	64	71	74	63	70	102	65	56
Zn	$\mu\text{g} \cdot \text{g}^{-1}$	89	100	102	121	118	112	115	114	119	107	100	81	115	115	100
Mo	$\mu\text{g} \cdot \text{g}^{-1}$	25	37	28	46	40	44	35	49	42	42	39	48	45	32	28
V	$\mu\text{g} \cdot \text{g}^{-1}$	95	111	113	116	143	135	123	157	151	134	140	121	159	154	118
U	$\mu\text{g} \cdot \text{g}^{-1}$	14.2	9.5	7.7	8.5	9.8	9.5	9.3	8.2	10.8	8.5	9.6	7.1	9.6	10.1	9.3
Cd	$\mu\text{g} \cdot \text{g}^{-1}$	27	36	34	7	47	50	39	37	45	42	44	60	47	18	23
Pb	$\mu\text{g} \cdot \text{g}^{-1}$	16.3	10.4	8.2	11.8	9.9	7.6	9.9	11.9	12.5	12.0	9.9	8.3	8.9	11.6	11.1
As	$\mu\text{g} \cdot \text{g}^{-1}$	32.1	24.2	17.1	17.1	15.9	19.0	18.8	16.7	18.9	18.2	11.8	14.6	14.0	12.3	11.0
Rb	$\mu\text{g} \cdot \text{g}^{-1}$	84	70	73	80	63	59	71	79	74	66	65	43	60	81	60
Sr	$\mu\text{g} \cdot \text{g}^{-1}$	594	328	298	197	268	218	291	212	336	350	436	273	267	249	346
Zr	$\mu\text{g} \cdot \text{g}^{-1}$	67	53	40	30	42	28	38	29	44	41	30	15	30	40	42
W	$\mu\text{g} \cdot \text{g}^{-1}$	1.6	1.4	1.1	1.3	13.9	1.5	1.4	1.2	1.4	1.2	1.1	0.7	1.6	1.2	1.4

Table 1a: continued

Sample name	Units	1H5-020	1H5-040	1H5-062	1H5-080	1H5-100	1H5-120	1H5-140	1H6-010	1H6-032	1H6-050	1HCCW-14	2H1-010	2H1-030	2H1-050	2H1-070
Depth	cmbsf	620	640	662	680	700	720	740	760	782	800	825	835	855	875	895
Age	ka	64.00	65.71	67.60	69.14	71.64	74.93	78.22	81.51	85.12	88.08	92.19	93.84	97.12	100.41	103.70
$\delta^{15/14}\text{N}$	‰	3.36	3.80	4.27	3.18	3.35	3.62	3.68	6.12	7.63	7.19	7.51	7.23	4.48	6.99	8.07
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	0.47	NA	NA	0.42	NA	NA	0.55	0.75	0.80	0.75	0.88	0.83	0.67	0.74	NA
$\delta^{53/52}\text{Cr}_{\text{leach}}$	‰	0.44	NA	NA	NA	NA	NA	NA	0.76	NA	NA	0.90	NA	NA	NA	NA
Cr/Ti	$\mu\text{g} \cdot \mu\text{g}^{-1}$	0.057	0.047	0.064	0.037	0.051	0.060	0.046	0.090	0.086	0.087	0.081	0.065	0.049	0.053	0.062
Cr _{auth}	$\mu\text{g} \cdot \text{g}^{-1}$	55.4	33.5	79.2	28.5	51.4	67.3	37.4	117.1	90.5	95.8	61.8	69.4	41.1	47.7	60.9
f _{auth}	-	0.45	0.34	0.51	0.15	0.39	0.48	0.31	0.65	0.64	0.64	0.61	0.52	0.36	0.41	0.50
TOC	wt%	8.27	6.38	9.09	6.68	10.00	11.29	5.45	8.27	10.82	8.57	5.89	10.00	6.83	5.82	5.78
Mg	$\mu\text{g} \cdot \text{g}^{-1}$	9,473	9,370	16,785	17,657	10,157	10,213	9,802	11,042	12,402	11,215	10,359	10,788	9,628	11,801	11,264
Al	$\mu\text{g} \cdot \text{g}^{-1}$	44,529	41,982	50,236	98,651	49,587	46,933	50,138	43,240	38,075	38,708	26,458	44,465	47,090	49,111	42,722
Mn	$\mu\text{g} \cdot \text{g}^{-1}$	240	235	261	508	250	242	278	277	225	230	181	271	264	289	264
Ba	$\mu\text{g} \cdot \text{g}^{-1}$	251	252	478	572	314	299	311	413	403	436	9,185	369	314	432	2,165
Ti	$\mu\text{g} \cdot \text{g}^{-1}$	2,152	2,069	2,391	5,143	2,621	2,338	2,602	2,007	1,645	1,719	1,242	2,053	2,359	2,189	1,954
Cr	$\mu\text{g} \cdot \text{g}^{-1}$	123	98	154	189	133	140	119	180	142	150	101	134	115	116	122
Fe	$\mu\text{g} \cdot \text{g}^{-1}$	16,541	15,886	18,722	36,321	17,604	17,471	17,241	17,038	15,712	15,240	10,959	17,470	17,297	19,728	17,547
Co	$\mu\text{g} \cdot \text{g}^{-1}$	5.4	5.2	6.8	12.7	6.0	5.7	5.9	7.2	7.4	6.2	4.4	6.6	6.0	7.0	6.2
Ni	$\mu\text{g} \cdot \text{g}^{-1}$	96	77	157	152	105	122	88	162	141	153	86	112	95	95	79
Cu	$\mu\text{g} \cdot \text{g}^{-1}$	70	60	109	116	72	60	59	91	124	81	63	67	99	106	98
Zn	$\mu\text{g} \cdot \text{g}^{-1}$	102	117	162	208	111	149	99	94	95	91	80	90	102	104	99
Mo	$\mu\text{g} \cdot \text{g}^{-1}$	41	44	82	56	31	43	33	62	86	99	75	54	50	55	65
V	$\mu\text{g} \cdot \text{g}^{-1}$	142	151	243	264	137	152	118	255	261	318	241	230	156	272	266
U	$\mu\text{g} \cdot \text{g}^{-1}$	11.2	9.5	17.4	19.7	14.7	12.4	15.7	15.6	15.7	14.0	6.4	13.0	12.6	12.7	13.6
Cd	$\mu\text{g} \cdot \text{g}^{-1}$	35	43	110	48	28	63	44	71	72	77	77	61	40	44	69
Pb	$\mu\text{g} \cdot \text{g}^{-1}$	9.9	11.0	16.6	21.6	10.7	10.6	11.2	8.0	10.5	12.1	12.3	9.1	39.5	11.7	10.2
As	$\mu\text{g} \cdot \text{g}^{-1}$	13.2	13.4	20.5	19.6	11.2	12.2	12.3	12.0	13.7	16.8	12.2	14.7	12.9	16.7	16.4
Rb	$\mu\text{g} \cdot \text{g}^{-1}$	60	56	72	116	64	61	58	53	44	47	39	61	57	60	54
Sr	$\mu\text{g} \cdot \text{g}^{-1}$	313	392	839	518	440	360	513	305	416	353	613	368	382	418	412
Zr	$\mu\text{g} \cdot \text{g}^{-1}$	23	21	38	72	41	30	40	27	39	33	24	28	44	32	45
W	$\mu\text{g} \cdot \text{g}^{-1}$	1.1	12.4	1.4	2.4	1.2	1.2	1.1	1.8	0.7	0.8	0.9	0.9	1.0	1.3	1.1

Table

Table 1a: continued

Sample name	Units	2H1-090	2H1-110	2H1-130	2H2-002	2H2-020	2H2-040	2H2-060	2H2-080	2H2-100	2H2-120	2H2-140	2H3-010	2H3-030	2H3-050	2H3-070	2H3-090	2H3-110	2H3-130
Depth	cmbsf	915	935	955	977	995	1015	1035	1055	1075	1095	1115	1135	1155	1175	1195	1215	1235	1255
Age	ka	106.99	110.27	113.56	117.18	120.14	123.42	126.71	130.00	133.00	136.00	139.00	142.00	145.00	148.00	151.00	154.00	157.00	160.00
$\delta^{15/14}\text{N}$	‰	8.30	8.80	9.17	9.34	8.74	6.95	8.06	7.03	7.03	6.00	3.83	4.82	4.77	4.82	4.99	3.59	4.36	3.33
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	NA	0.91	NA	NA	0.75	NA	0.82	NA	0.75	NA	NA	0.62	NA	0.50	NA	NA	0.47	0.44
$\delta^{53/52}\text{Cr}_{\text{leach}}$	‰	NA	0.95	NA	NA	NA	NA	NA	NA	0.89	NA	NA	NA	NA	NA	NA	NA	NA	0.46
Cr/Ti	$\mu\text{g}.\mu\text{g}^{-1}$	0.053	0.060	0.057	0.045	0.070	0.034	0.041	0.033	0.032	0.027	0.046	0.088	0.080	0.052	0.058	0.041	0.045	0.037
Cr _{auth}	$\mu\text{g}.\text{g}^{-1}$	48.9	56.2	44.1	37.9	126.7	10.6	29.2	6.2	4.9	0.0	42.5	82.9	147.8	65.8	126.0	32.1	38.0	21.8
f _{auth}	-	0.41	0.47	0.45	0.31	0.55	0.08	0.24	0.05	0.03	0.00	0.32	0.65	0.61	0.40	0.46	0.23	0.31	0.16
TOC	wt%	7.98	7.75	7.63	8.16	5.59	4.08	5.70	4.87	4.42	3.51	3.84	8.34	9.90	9.80	9.41	7.99	6.56	4.55
Mg	$\mu\text{g}.\text{g}^{-1}$	11,408	11,328	10,564	11,332	14,219	13,067	13,891	13,788	21,888	11,853	11,319	14,757	12,342	11,921	20,827	12,461	13,618	12,470
Al	$\mu\text{g}.\text{g}^{-1}$	47,407	44,369	38,930	58,201	73,263	77,842	69,526	77,055	132,728	73,182	54,159	31,472	67,070	68,757	108,278	76,328	57,193	75,915
Mn	$\mu\text{g}.\text{g}^{-1}$	282	260	230	319	389	354	380	375	696	381	314	201	320	288	533	346	328	338
Ba	$\mu\text{g}.\text{g}^{-1}$	376	387	325	430	367	389	351	492	685	408	847	160	309	316	499	365	255	339
Ti	$\mu\text{g}.\text{g}^{-1}$	2,256	1,990	1,746	2,712	3,305	3,836	2,970	3,551	6,091	3,603	2,905	1,458	3,030	3,119	4,649	3,460	2,742	3,666
Cr	$\mu\text{g}.\text{g}^{-1}$	119	118	99	123	230	131	122	117	195	98	133	129	243	163	271	140	124	136
Fe	$\mu\text{g}.\text{g}^{-1}$	18,804	18,309	16,488	23,138	49,123	30,575	25,624	28,424	53,974	26,876	27,001	13,555	37,704	24,846	51,264	27,931	24,629	29,804
Co	$\mu\text{g}.\text{g}^{-1}$	7.0	6.5	5.8	7.6	9.7	7.5	9.9	10.3	14.9	8.0	7.4	4.7	7.7	7.9	19.8	7.7	7.1	8.5
Ni	$\mu\text{g}.\text{g}^{-1}$	78	78	73	72	83	26	69	65	70	41	110	116	126	113	362	62	84	70
Cu	$\mu\text{g}.\text{g}^{-1}$	52	95	98	79	75	55	69	62	83	55	65	87	91	95	188	72	68	60
Zn	$\mu\text{g}.\text{g}^{-1}$	95	87	101	115	157	126	128	184	218	131	150	86	146	148	317	149	129	158
Mo	$\mu\text{g}.\text{g}^{-1}$	64	72	79	59	73	68	48	49	54	24	47	46	66	73	101	46	23	30
V	$\mu\text{g}.\text{g}^{-1}$	242	219	222	218	258	171	192	166	224	122	122	190	298	294	465	200	161	161
U	$\mu\text{g}.\text{g}^{-1}$	9.6	8.6	7.2	8.2	9.9	6.6	8.3	6.8	13.7	9.5	22.3	10.7	22.0	16.1	29.2	14.1	10.5	11.5
Cd	$\mu\text{g}.\text{g}^{-1}$	85	77	62	30	51	1	43	52	35	23	28	45	35	33	189	10	45	14
Pb	$\mu\text{g}.\text{g}^{-1}$	15.8	13.2	10.8	16.7	24.1	22.5	26.3	27.1	36.9	21.4	10.3	8.4	13.8	21.0	29.4	25.9	12.8	20.5
As	$\mu\text{g}.\text{g}^{-1}$	19.8	16.6	14.5	16.1	31.2	17.2	16.4	17.3	35.7	18.9	29.5	10.1	28.5	17.9	47.1	20.6	23.4	17.4
Rb	$\mu\text{g}.\text{g}^{-1}$	64	55	52	76	96	111	101	109	151	91	68	42	88	89	131	106	78	92
Sr	$\mu\text{g}.\text{g}^{-1}$	509	396	315	249	276	202	291	217	393	274	400	301	249	194	342	197	241	217
Zr	$\mu\text{g}.\text{g}^{-1}$	35	33	25	72	61	76	55	83	104	76	42	31	52	57	92	66	53	76
W	$\mu\text{g}.\text{g}^{-1}$	1.0	0.9	1.0	1.1	1.3	1.4	1.1	1.3	3.0	1.3	1.1	0.7	1.5	1.3	2.3	1.8	1.1	1.4

Table 1b.

Sample name	Cr/Ti
	$\mu\text{g} \cdot \mu\text{g}^{-1}$
1H2-110	0.382
1H2-130	0.330
1H3-002	0.384
1H3-062	0.315
1H3-102	0.329
1H3-122	0.359
1H3-142	0.292
1H4-050	0.313
1H4-090	0.344

Table 2: Cariaco Basin bulk sediment sample data.

Sample name	Units	PL07-22BX	PL07-89BX	PL07-82BX	PL07-105BX	PL07-67BX	PL07-69BX	PL07-111BX
Sample number	-	1	2	3	4	5	6	7
Water depth	m	656	1342	818	1296	400	545	411
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	0.31	0.25	0.28	0.17	0.29	0.29	0.17
$\delta^{53/52}\text{Cr}_{\text{leach}}^*$	‰	0.42	0.35	0.43	0.28	0.37	0.41	0.39
Cr/Ti	$\mu\text{g}.\mu\text{g}^{-1}$	0.036	0.033	0.035	0.033	0.034	0.034	0.034
Ti	$\mu\text{g}.\text{g}^{-1}$	2418	3412	2966	3307	3282	3648	3975
Cr	$\mu\text{g}.\text{g}^{-1}$	88	113	105	109	112	125	135
Fe	$\mu\text{g}.\text{g}^{-1}$	26762	42679	33537	42490	35291	39210	43608
Co	$\mu\text{g}.\text{g}^{-1}$	9	13	11	14	12	12	14
Ni	$\mu\text{g}.\text{g}^{-1}$	59	79	72	72	81	78	79
Cu	$\mu\text{g}.\text{g}^{-1}$	29	36	33	37	35	35	41
Zn	$\mu\text{g}.\text{g}^{-1}$	96	155	129	136	136	136	157
Mo	$\mu\text{g}.\text{g}^{-1}$	16.0	33.7	50.4	28.5	57.4	89.3	22.3
V	$\mu\text{g}.\text{g}^{-1}$	192	260	226	266	282	265	293
U	$\mu\text{g}.\text{g}^{-1}$	4.4	6.1	7.7	6.0	7.8	10.4	5.4
Nb	$\mu\text{g}.\text{g}^{-1}$	7.9	10.7	9.4	10.5	10.5	12.3	12.5
Cd	$\mu\text{g}.\text{g}^{-1}$	1.0	3.2	2.7	3.3	3.4	3.1	2.3
La	$\mu\text{g}.\text{g}^{-1}$	24.2	32.2	29.0	30.6	33.0	35.9	36.1
Ce	$\mu\text{g}.\text{g}^{-1}$	47.6	64.5	56.9	60.5	63.9	70.2	70.3
Tl	$\mu\text{g}.\text{g}^{-1}$	0.4	0.5	0.5	0.5	0.5	0.6	0.7
Pb	$\mu\text{g}.\text{g}^{-1}$	34.0	40.6	37.2	36.0	41.9	40.6	40.1
Th	$\mu\text{g}.\text{g}^{-1}$	8.4	8.0	9.6	11.1	10.8	12.1	13.5

*Cr isotope composition measured in the leach fraction.

Table 3: Oxic global marine core-top sediment sample data.

Sample name	Units	AII31-2PG	AII93-24PG	AII93-36PG	CHN115-48PG	CHN57-2PG	CHN75-2-PG	CHN75-9PG	EN066-17GGC
Latitude	deg	10.5833	-6.6950	-13.0067	-26.8533	20.0933	19.4917	14.2333	5.3667
Longitude	deg	-44.8500	130.1117	112.5750	-27.3900	-64.5750	-60.7750	-55.7867	-21.0883
Water depth	m	5106	5467	5222	5933	5808	5262	5141	3014
Depth in the sediment	cmbsf	0-2	0-1.5	0-1	1-2	0-2	23-24	10-11	12-13
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	-0.06	0.06	-0.06	-0.06	-0.01	-0.05	-0.07	-0.08
$\delta^{53/52}\text{Cr}_{\text{leach}}$ *	‰	NA**	NA	NA	NA	0.02	NA	NA	NA
Cr/Ti	$\mu\text{g}.\mu\text{g}^{-1}$	0.017	0.018	0.012	0.012	0.025	0.019	0.017	0.016
Ti	$\mu\text{g}.\text{g}^{-1}$	3053	4242	6285	5062	3643	3887	4342	1137
Cr	$\mu\text{g}.\text{g}^{-1}$	51	77	74	59	89	72	74	18
Ba	$\mu\text{g}.\text{g}^{-1}$	276	563	1068	442	263	311	342	431
Mn	$\mu\text{g}.\text{g}^{-1}$	1305	282	7228	8951	2093	2999	1471	639
Fe	$\mu\text{g}.\text{g}^{-1}$	33124	48534	58117	57381	45132	45434	45271	10247
Co	$\mu\text{g}.\text{g}^{-1}$	15.8	18.1	63.2	94.5	32.5	37.7	20.7	6.9
Ni	$\mu\text{g}.\text{g}^{-1}$	43.8	100.3	410.6	192.9	76.8	80.9	52.0	33.6
Cu	$\mu\text{g}.\text{g}^{-1}$	75.9	93.6	432.3	162.9	86.8	85.5	78.5	33.9
Zn	$\mu\text{g}.\text{g}^{-1}$	73.8	130.6	187.2	134.2	75.5	95.3	104.8	5.0
Mo	$\mu\text{g}.\text{g}^{-1}$	2.0	0.5	23.3	19.2	3.8	3.7	2.1	<DL
V	$\mu\text{g}.\text{g}^{-1}$	89.8	194.2	133.1	138.7	120.6	119.8	128.2	28.3
U	$\mu\text{g}.\text{g}^{-1}$	1.07	1.95	1.60	1.96	1.43	1.50	1.69	0.45
Nb	$\mu\text{g}.\text{g}^{-1}$	10.4	10.1	15.1	14.0	10.4	12.3	15.0	4.7
Cd	$\mu\text{g}.\text{g}^{-1}$	<DL***	<DL	0.6	0.9	<DL	<DL	<DL	<DL
La	$\mu\text{g}.\text{g}^{-1}$	27.6	25.4	54.6	40.5	30.6	33.8	35.0	13.4
Ce	$\mu\text{g}.\text{g}^{-1}$	54.4	56.8	77.4	115.5	70.9	79.4	75.9	21.4
Tl	$\mu\text{g}.\text{g}^{-1}$	0.27	0.29	0.99	0.99	0.49	0.66	0.50	0.08
Pb	$\mu\text{g}.\text{g}^{-1}$	15.39	20.25	35.67	35.82	17.97	23.12	21.97	4.30
Th	$\mu\text{g}.\text{g}^{-1}$	7.19	8.77	14.88	14.66	8.80	10.31	9.55	2.54

*Cr isotope composition measured in the leach fraction.

** NA: not analyzed.

*** <DL: below detection limit.

Table

Table 3: continued

Sample name	Units	EN066-20GGC	EN066-30GGC	EW9302-30GGCEW9302-GGC03	KNR102-1PG	KNR102-2PG	KNR102-4PG	KNR110-19JGC	KNR110-19JGC	
Latitude	deg	5.0833	2.3583	62.7505	49.9020	28.9133	28.9567	30.1717	6.2883	6.2883
Longitude	deg	-20.9867	-19.7150	-20.6775	-44.4642	-70.9450	-71.1033	-69.7733	-44.0750	-44.0750
Water depth	m	2756	5228	1188	4082	5370	5365	5300	4576	4576
Depth in the sediment	cmbsf	2-4	2-4	0-3	2-4	0-2	0-2	3-4	2-3	2-3
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	-0.08	-0.13	-0.14	-0.13	-0.08	-0.06	-0.02	-0.03	-0.03
$\delta^{53/52}\text{Cr}_{\text{leach}}$	‰	NA	NA	NA	NA	NA	NA	NA	0.01	0.01
Cr/Ti	μg.μg ⁻¹	0.015	0.018	0.002	0.016	0.011	0.014	0.023	0.017	0.017
Ti	μg.g ⁻¹	1105	1602	17107	2915	4235	5112	4322	3363	3363
Cr	μg.g ⁻¹	17	28	37	47	47	71	100	58	58
Ba	μg.g ⁻¹	260	147	237	377	333	417	547	317	317
Mn	μg.g ⁻¹	261	2483	1725	801	955	1069	14242	1250	1250
Fe	μg.g ⁻¹	9551	16236	85278	24185	24641	36652	55105	36311	36311
Co	μg.g ⁻¹	5.4	11.4	36.5	11.4	12.0	17.2	109.2	16.7	16.7
Ni	μg.g ⁻¹	16.0	60.4	28.1	29.6	28.3	40.9	113.4	44.5	44.5
Cu	μg.g ⁻¹	21.2	87.5	55.3	20.3	20.0	27.5	141.4	68.1	68.1
Zn	μg.g ⁻¹	22.1	44.9	120.1	40.1	44.4	74.1	245.1	90.8	90.8
Mo	μg.g ⁻¹	0.5	2.2	1.3	<DL	<DL	0.8	30.9	1.6	1.6
V	μg.g ⁻¹	28.2	45.9	263.7	60.2	64.7	102.3	195.2	107.3	107.3
U	μg.g ⁻¹	0.48	0.64	0.73	0.82	1.57	1.76	1.93	1.25	1.25
Nb	μg.g ⁻¹	4.7	6.9	27.3	7.8	12.6	15.8	14.7	11.3	11.3
Cd	μg.g ⁻¹	<DL	<DL	<DL	<DL	<DL	<DL	0.8	<DL	<DL
La	μg.g ⁻¹	11.5	16.5	21.6	19.1	26.5	23.5	40.7	28.4	28.4
Ce	μg.g ⁻¹	18.7	33.0	48.4	38.7	58.0	54.1	93.1	57.0	57.0
Tl	μg.g ⁻¹	0.09	0.26	0.03	0.14	0.21	0.38	1.98	0.38	0.38
Pb	μg.g ⁻¹	6.10	7.88	5.52	9.64	11.34	16.81	24.75	15.33	15.33
Th	μg.g ⁻¹	0.78	3.70	2.15	4.20	6.72	6.01	11.05	5.70	5.70

Table

Table 3: continued

Sample name	Units	KNR-110-79GGC	KNR140-GGC21	KNR140-2-48GGC	KNR159-51GGC	KNR159-5-54GGC	KNR176-2-8GGC	RNDBT6-12GGC	RNDBT6-21GGC
Latitude	deg	4.3250	28.2458	32.7462	-25.8823	-29.5362	6.8205	51.0608	51.4150
Longitude	deg	-43.5033	-74.4103	-76.1258	-43.3062	-43.3378	-77.9364	168.0832	167.4067
Water depth	m	2821	4705	2100	2150	4003	2896	3416	2727
Depth in the sediment	cmbsf	4.5-6	0-2	0-2	1-2	5-7	0-2	4-5	1-2
$\delta^{53/52}\text{Cr}_{\text{bulk}}$	‰	-0.07	0.00	0.23	0.02	-0.01	-0.10	-0.11	-0.10
$\delta^{53/52}\text{Cr}_{\text{leach}}$	‰	NA	0.10	NA	NA	NA	-0.21	NA	NA
Cr/Ti	$\mu\text{g}.\mu\text{g}^{-1}$	0.019	0.022	0.023	0.015	0.013	0.039	0.012	0.013
Ti	$\mu\text{g}.\text{g}^{-1}$	1392	3365	2347	2586	3724	4524	2529	3716
Cr	$\mu\text{g}.\text{g}^{-1}$	26	75	55	40	48	177	30	50
Ba	$\mu\text{g}.\text{g}^{-1}$	202	331	226	245	606	233	1947	1132
Mn	$\mu\text{g}.\text{g}^{-1}$	352	1756	479	663	1653	391	1410	622
Fe	$\mu\text{g}.\text{g}^{-1}$	14436	37803	21144	23441	37046	57713	28411	42592
Co	$\mu\text{g}.\text{g}^{-1}$	7.2	22.5	7.5	11.9	19.6	23.5	15.0	17.2
Ni	$\mu\text{g}.\text{g}^{-1}$	17.1	50.5	27.7	23.7	45.3	83.6	33.2	33.6
Cu	$\mu\text{g}.\text{g}^{-1}$	24.6	55.5	20.5	29.2	74.1	76.9	50.0	48.5
Zn	$\mu\text{g}.\text{g}^{-1}$	35.1	93.9	56.2	46.8	85.7	54.3	58.5	115.0
Mo	$\mu\text{g}.\text{g}^{-1}$	<DL	1.6	<DL	0.9	1.7	<DL	<DL	1.2
V	$\mu\text{g}.\text{g}^{-1}$	46.5	100.1	61.9	54.8	88.8	146.9	85.6	109.3
U	$\mu\text{g}.\text{g}^{-1}$	0.79	1.21	2.79	1.14	1.29	1.10	0.63	1.38
Nb	$\mu\text{g}.\text{g}^{-1}$	4.8	10.0	6.6	8.2	9.8	3.8	2.5	7.2
Cd	$\mu\text{g}.\text{g}^{-1}$	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
La	$\mu\text{g}.\text{g}^{-1}$	14.4	29.1	19.9	19.6	24.1	5.9	8.2	18.5
Ce	$\mu\text{g}.\text{g}^{-1}$	24.9	62.7	36.1	36.5	48.2	12.4	17.0	40.7
Tl	$\mu\text{g}.\text{g}^{-1}$	0.15	0.34	0.17	0.20	0.31	-	0.09	0.20
Pb	$\mu\text{g}.\text{g}^{-1}$	6.81	14.69	7.07	9.94	14.06	5.55	8.67	12.73
Th	$\mu\text{g}.\text{g}^{-1}$	3.45	7.17	4.33	5.36	6.93	1.01	1.71	4.62

(a)

(b)

(c)

Figure 1

Peru Margin

Figure 2

Peru Margin

Figure 3

Figure

Figure 4

Figure

Figure 5

Figure