



The isotopic composition of authigenic chromium in anoxic marine sediments: A case study from the Cariaco Basin



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ABSTRACT

Chromium (Cr) isotopes are an emerging proxy for tracking redox processes at the Earth's surface. However, there has been limited exploration of the Cr isotope record of modern and recent marine sediments. The basic inorganic chemistry of Cr suggests that anoxic marine basins should factor prominently in the global Cr cycle and that sediments deposited within anoxic basins may offer a valuable Cr isotope archive throughout Earth's history. Here, we present $\delta^{53}\text{Cr}$ data from sediments of the Cariaco Basin, Venezuela—a 'type' environment for large, perennially anoxic basins with a relatively strong hydrological connection to the global oceans. We document a marked positive shift in bulk $\delta^{53}\text{Cr}$ Cr values following the termination of the Last Glacial Maximum, followed by relative stasis. Based on a suite of independent redox proxies, this transition marks a switch from oxic to persistently anoxic and sulfidic (euxinic) depositional conditions within the basin. We find good agreement between two independent approaches toward estimating the $\delta^{53}\text{Cr}$ Cr composition of authigenic Cr in euxinic Cariaco Basin sediments and that these estimates are very similar to the $\delta^{53}\text{Cr}$ Cr composition of modern open Atlantic Ocean seawater. These data, together with considerations of reaction kinetics and mass balance within the Cariaco Basin, are consistent with the hypothesis that anoxic marine settings can serve as a chemical archive of first-order trends in seawater $\delta^{53}\text{Cr}$ Cr composition. Additionally, the Cariaco Basin data suggest that there has been secular stability in the average $\delta^{53}\text{Cr}$ Cr value of Atlantic seawater over the last ~15 kyr.

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1. Introduction

Over the last decade there has been prolific development of heavy stable isotope techniques for examining a range of questions in low temperature geochemistry, geomicrobiology, and paleoceanography (Johnson and Bullen, 2004; Dauphas and Rouxel, 2006; Anbar and Rouxel, 2007). Recently, the chromium (Cr) isotope system has been explored as a potential proxy for the oxidation–reduction chemistry of Earth surface environments (Frei et al., 2009, 2011, 2013; Døssing et al., 2011; Bonnand et al., 2011; Crowe et al., 2013) and continues to be developed for application to problems in environmental geochemistry (Ellis et al., 2002, 2004; Johnson and Bullen, 2004; Berna et al., 2010;

Basu and Johnson, 2012; Raddatz et al., 2011; Izbicki et al., 2012; Wanner et al., 2012, 2013). Recent efforts also involve laboratory experiments designed to help interpret natural Cr data (Zink et al., 2010; Døssing et al., 2011; Basu and Johnson, 2012; Kitchen et al., 2012; Wang and Johnson, 2012). However, the utility of the Cr isotope system specifically as a paleoceanographic proxy has been less explored, with the global Cr isotope cycle remaining poorly constrained and a number of potentially important geochemical archives still uncharacterized (Schoenberg et al., 2008; Bonnand et al., 2013; Farkas et al., 2013).

Chromium isotope ratios of chemical sedimentary rocks have been proposed as a proxy for atmospheric O_2 abundance during Earth surface weathering (Frei et al., 2009; Crowe et al., 2013). However, work to date on the geologic record of Cr and its isotopes has focused largely on Fe-rich chemical sediments, such as Precambrian iron formations (e.g., Frei et al., 2009, 2013; Konhauser et al., 2011). Though there are reasons to expect that

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these lithologies provide good targets for measuring the Cr isotope composition of contemporaneous seawater (e.g., Frei et al., 2009; Døssing et al., 2011), their deposition throughout Earth's history is sporadic, providing stringent limits on the temporal resolution afforded by such archives and leaving large intervals of Earth surface evolution inaccessible. Recent work is beginning to expand the focus to other lithotypes (Frei et al., 2011; Bonnand et al., 2013), but little groundwork has been done in modern settings to establish the depositional and post-depositional controls on sedimentary Cr isotope archives in diverse sedimentary environments. Deciphering the information contained within additional marine facies may provide more temporally continuous insight into the history of the Earth surface Cr cycle—as connected mechanistically to evolving atmospheric composition and ocean chemistry. In particular, anoxic organic-rich shales provide a potentially powerful target archive for reconstructing the chemical evolution of seawater.

2. Background

2.1. Chromium isotope systematics

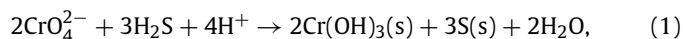
Chromium cycles between two primary redox states in solid phases and aquatic species under Earth surface conditions—Cr(VI) and Cr(III). Rock-forming minerals contain Cr(III) as an octahedrally coordinated constituent of a range of oxide, oxyhydroxide and/or silicate phases (Peterson et al., 1997; Becquer et al., 2003; Fandeur et al., 2009a). Chromium can oxidize to Cr(VI) during weathering predominantly through redox interactions with solid Mn-oxide phases, and subsequently forms tetrahedrally coordinated oxyanions (e.g., CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) that are highly soluble and readily transported in oxidizing aqueous fluids. The chromate anion, CrO_4^{2-} , typically dominates at marine pH values (Bartlett and James, 1979; Fendorf, 1995; Oze et al., 2007; Fandeur et al., 2009b). Chromate, however, is readily reduced by a wide range of reductants including dissolved Fe(II) (Fendorf and Li, 1996; Sedlak and Chan, 1997); structural Fe(II) in many common mineral phases (Eary and Rai, 1989; Bond and Fendorf, 2003); dissolved H_2S (Pettine et al., 1994; Kim et al., 2001); solid Fe–S phases common in sulfidic environments, both amorphous (Patterson et al., 1997; Graham and Bouwer, 2010) and crystalline (Zouboulis et al., 1995); and a variety of organic substrates (Wittbrodt and Palmer, 1996; Bolan et al., 2003). Upon reduction at circumneutral or alkaline pH the majority of resulting Cr(III) will hydrolyze to form $\text{Cr}(\text{OH})_3$, which is sparingly soluble and readily removed from solution.

The Cr isotope composition of high- and low-temperature rocks, reported in delta notation relative to the international standard NIST SRM-979 ($\delta^{53}\text{Cr} = 1000\text{‰} \times [({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{sample}}/({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{SRM-979}} - 1]$), is controlled almost entirely by fractionations imparted by redox transformations (Ellis et al., 2002, 2004; Schauble et al., 2004). This relationship can be rationalized by the theoretical prediction that Cr isotope fractionations between different Cr(VI)- and Cr(III)-containing species with similar coordination environments for Cr should be small (Schauble et al., 2004). Because the dominant valence states of Cr show strong preference for octahedral [Cr(III)] and tetrahedral [Cr(VI)] coordination, it is thus expected that non-redox processes should play a relatively small role in governing Cr isotope fractionation in natural environments. This prediction is in marked contrast to systems such as Fe, Mo and Cu (Schauble et al., 2004), in which coordination changes associated with surface adsorption can induce very large isotope effects, and is supported by experimental work (Ellis et al., 2004).

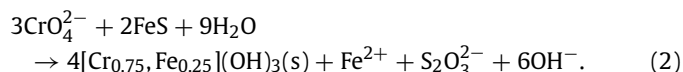
In contrast, differences in Cr redox state impart significant isotope effects. If isotopic equilibrium can be attained, the $\text{Cr}^{(\text{VI})}\text{O}_4^{2-}$ oxyanion is predicted by *ab initio* calculations to be ${}^{53}\text{Cr}$ -enriched by ~6–7‰ relative to a coexisting Cr(III) reservoir (Schauble et al.,

2004). Kinetic fractionations associated with CrO_4^{2-} reduction are also large, with the reduction of Cr(VI) to Cr(III) being characterized by fractionation factors (α) between ~0.9982 and 0.9955, depending on the nature of the reduction process and experimental conditions (Ellis et al., 2002; Sikora et al., 2008; Berna et al., 2010; Døssing et al., 2011; Basu and Johnson, 2012; Kitchen et al., 2012; Zink et al., 2010). Fractionations during Cr(III) oxidation are less well constrained by observations, and limited available data suggest that the isotopic systematics of Cr(III) oxidation cannot be explained by a single kinetic or equilibrium process (Bain and Bullen, 2005; Wang et al., 2010; Zink et al., 2010). A competition between offsetting equilibrium and kinetic Cr(VI)–Cr(III) fractionations, as well as kinetic fractionations occurring during disproportionation of metastable Cr(IV) and Cr(V) intermediates, may lead to a range of isotopic compositions within the mobile Cr(VI) pool (Bain and Bullen, 2005; Zink et al., 2010). Despite these complications, the measured $\delta^{53}\text{Cr}$ values of near-surface groundwaters are in general significantly more ${}^{53}\text{Cr}$ -enriched than the high-temperature crustal Cr source (Izbicki et al., 2008; Raddatz et al., 2011), an observation broadly consistent with the enrichment of ${}^{53}\text{Cr}$ in the more soluble Cr(VI) species as a function of reaction progress during partial reduction.

Iron-rich marine chemical sediments have been proposed previously to capture the Cr isotope composition of ambient seawater (e.g., Frei et al., 2009; Crowe et al., 2013) under the premise that the reduction of Cr(VI) by dissolved Fe(II) and sequestration of insoluble Cr(III) within sediments is quantitative and records the Cr isotope composition of chromate in the local fluid regardless of local fractioning processes. Similar logic can be applied to systems rich in other reductants. For example, dissolved Cr(VI) will also be effectively reduced and precipitated by reaction with hydrogen sulfide (Kim et al., 2001):



or through reaction with Fe–S phases (Patterson et al., 1997):



The kinetics of Cr(VI) reduction on both amorphous and crystalline Fe–S surfaces are extremely rapid and approach or exceed those associated with reaction with aqueous Fe(II) at circumneutral pH under most natural conditions (Graham and Bouwer, 2010). Furthermore, electron microscopy of precipitates produced through reaction of Cr(VI) with dissolved sulfide, as well as synchrotron-based X-ray microanalysis of Cr(VI) reduction by Fe–S phases, indicate that in both cases reduction to Cr(III) is efficient. The resultant Cr(III) is readily incorporated into a solid phase—either directly through co-precipitation as $\text{Cr}(\text{OH})_3(\text{s})$ (Kim et al., 2001), in a solid solution with Fe(III) [$(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3(\text{s})$] (Patterson et al., 1997; Mullet et al., 2004) or within a substituted-type hematite structure ($\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$) (Mullet et al., 2007).

Given the above considerations, we hypothesize that stratified, sulfidic marine basins may quantitatively reduce and capture incoming Cr, and the sediments deposited within may therefore serve as useful repositories for the Cr isotope composition of ambient source waters. Here, we report the Cr isotope composition of sediment samples from a core through sediments deposited below the chemocline within the Cariaco Basin after the Last Glacial Maximum (ca. 19,000 years ago). The Cr isotope composition of the authigenic fraction within bulk sediments is estimated by employing two independent approaches—a mass balance reconstruction based on detrital tracers and a series of acid leaching experiments. The stratigraphic data reveal a positive shift in authigenic $\delta^{53}\text{Cr}$ values to values similar to modern open Atlantic Ocean seawater coincident with a major chemical reorganization of the basin after

the last deglaciation and a shift from oxic to anoxic water column conditions. This shift is followed by relative stasis during an extended period of anoxic and sulfidic (euxinic) deposition within the basin.

These observations are integrated with a discussion of the relative transport-reaction timescales pertaining to the Cariaco Basin and, more broadly, marine environments capable of supporting CrO_4^{2-} reduction. Combined, these considerations suggest a framework for reconstructing the history of the Cr isotope composition of seawater by examining ancient fine-grained siliciclastic sedimentary rocks deposited under anoxic/euxinic conditions and provide a working model for the processes regulating seawater Cr isotope composition. Finally, we briefly explore some potential implications of these results for global Cr isotope mass balance and the use of Cr isotopes in anoxic sediments and sedimentary rocks as an ancient Earth surface redox proxy.

2.2. The Cariaco Basin

The Cariaco Basin is one of the largest anoxic marine basins on the modern Earth (second only to the Black Sea), covering an approximate area of 7000 km² within a structural depression on the continental shelf north of Venezuela. The basin consists of two sub-basins of ~1400 m depth separated by a ~900-m-deep saddle and is bordered by a series of shallow sills along its western and northern margins (reviewed in [Scranton et al., 2001](#); [Alvera-Azcárate et al., 2009](#)). Restricted horizontal exchange with the open Caribbean Sea over the sills, combined with the microbial respiratory decay of sinking organic matter from highly productive surface waters, leads to stable anoxia, the accumulation of hydrogen sulfide below ~300 m depth and deep waters that are often at or above saturation with respect to FeS phases (e.g., [Percy et al., 2008](#)).

During glacial intervals, limited nutrient exchange over the sills due to lower eustatic sea level resulted in comparatively low rates of primary and export production and thus decreased the oxygen demand in deeper waters ([Haug et al., 1998](#); [Yarincik et al., 2000a](#)). Following sea level rise during the last deglaciation, more intense exchange of nutrients with thermocline waters of the Caribbean led to increased primary production, export of carbon from surface waters and the development of euxinic conditions in the deep basin ([Dean et al., 1999](#); [Lyons et al., 2003](#)). The result of this hydrographically forced increase in deep-water oxygen demand following the last deglaciation was the inception and subsequent temporal persistence of euxinic conditions below the basin chemocline after ~14.5 ka. Thereafter, geochemical signatures of microlaminated sediments deposited in the deep basin attest to predominantly anoxic deposition and elevated levels of dissolved hydrogen sulfide (see below).

3. Samples and analytical procedures

Samples for this study were obtained from Site 1002 of Leg 165 of the Ocean Drilling Program ([Fig. 1](#)). Detailed location information and core descriptions are available from Shipboard Scientific Party (1997), and detailed sedimentological and age relationships can be found in [Lyons et al. \(2003\)](#). Briefly, in the upper ~6.5 m below the seafloor (mbsf; deposited between ~14.5 ka to the present), sediments consist of a dark olive grey, organic-rich silty clay undisturbed by bioturbation that grades downward into laminated diatomaceous clayey mud with abundant calcareous microfossils. An abrupt transition occurs at ~6.5 mbsf from the upper microlaminated sediments into an underlying bioturbated (massive) light grey clay. This massive clay layer transitions downward at ~7.3 mbsf into an interval of massive reddish-brown clay—a transition that is confined to a roughly 1–2 cm interval—and this

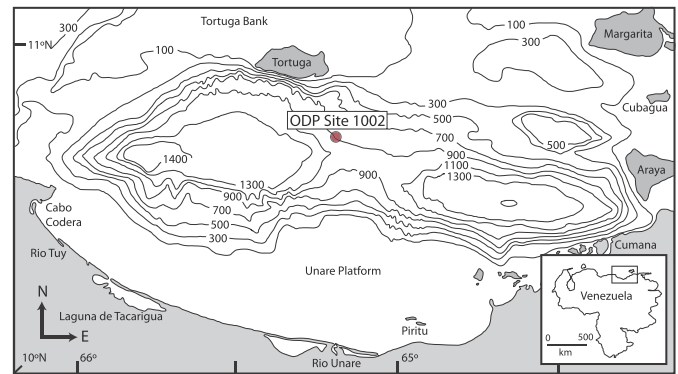


Fig. 1. Bathymetric map of the Cariaco Basin, offshore Venezuela (inset). Red circle shows ODP Site 1002. Note sill depths between Cabo Codera and Isla Tortuga (to the west) and between Isla Tortuga and Isla Margarita (to the east). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reddish-brown clay extends to the base of the sediment interval examined here. The extent of bioturbation and sediment geochemistry of both massive clay intervals, including the relatively low organic carbon content relative to the overlying euxinic interval, attest to oxic depositional conditions ([Lyons et al., 2003](#)). Details of sample treatment and analytical protocols for solid phase data generated previously can be found in [Lyons et al. \(2003\)](#) but are reviewed here for context.

Dried sediment samples for Cr isotope analysis were ashed overnight at 450 °C to remove organic phases. Ashed sediment powders were then completely digested with a combined HF–HNO₃–HCl procedure. In an effort to isolate the authigenic Cr fraction from the presumably less soluble detrital component, a subset of samples (not ashed) was additionally treated with trace-metal-grade HNO₃. Specifically, splits of dried sediment were leached at a variety of acid strengths overnight at room temperature while being agitated on a shaking table. Acid splits for bulk and partial digests were then processed through our analytical protocol for Cr isotope analysis ([Berna et al., 2010](#); [Basu and Johnson, 2012](#); [Kitchen et al., 2012](#)), which is based on the method of [Schoenberg et al. \(2008\)](#). Briefly, acid splits were first spiked with a ⁵⁰Cr–⁵⁴Cr double spike, in Cr(III) form, to obtain a constant spike/sample ratio (⁵⁴Cr_{spike}/⁵²Cr_{sample} ~ 0.5). Samples were allowed to equilibrate with the added double spike, dried down, reconstituted in 1 N HCl and diluted with nanopure H₂O. This sequence was followed by the addition of 0.2 M (NH₄)₂S₂O₈ to all samples, after which solutions were heated for two hours at ~130 °C in order to oxidize all Cr present to Cr(VI).

After cooling, samples were centrifuged to remove precipitates formed during oxidation. The supernatants were loaded directly onto columns with a 2 ml bed volume of AG1x8 anion exchange resin (100–200 mesh) pre-cleaned with 2 ml distilled 5 N HNO₃ and 20 ml 6 N HCl and preconditioned with 5 ml 0.025 N HCl. Matrix elements were then eluted with 16 ml 0.2 N and 4 ml 2 N HCl, after which Cr(VI) retained on the resin was reduced to Cr(III) by adding 1 ml 2 N HNO₃ (with 2 wt% H₂O₂). After waiting 30 min to allow for complete reduction, Cr(III) was eluted with 6 ml 2 N HNO₃ (with 2 wt% H₂O₂). Samples were then dried down and reconstituted in 6 N HCl, after which Fe was removed on an AG1x8 anion exchange column with 6 N HCl ([Frei et al., 2009](#)). Titanium and vanadium were removed using an AG50x8 cation exchange column following a HNO₃–HF–HCl procedure ([Yamakawa et al., 2009](#); [Moynier et al., 2011](#)). Final samples were then reconstituted in 2% HNO₃ for isotopic analysis.

Chromium isotope compositions were measured using a Nu Plasma MC-ICP-MS coupled to a DSN-100 desolvating nebulizer system (Nu Instruments) at the University of Illinois at Urbana-

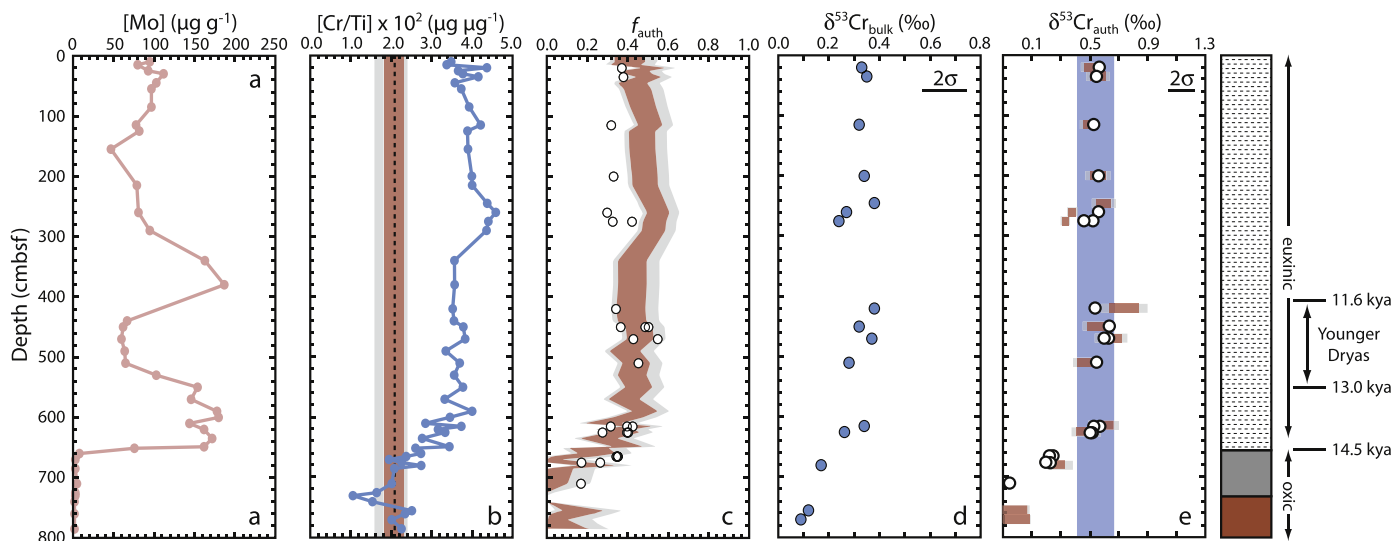


Fig. 2. Bulk and reconstructed sediment geochemical data for sediments deposited at ODP Site 1002 since the Last Glacial Maximum. Core stratigraphy at right and data for Mo in (a) are from Lyons et al. (2003). Grey field in (b) denotes the range of Cr/Ti values for upper continental crust (UCC), while the black dotted line and red field denote the mean and 95% confidence interval for sediments deposited under oxic conditions. Values for the authigenic Cr fraction (f_{auth} ; c) are calculated based on measured [Cr/Ti] values assuming the resampled mean and 95% confidence interval of oxic sediments as the detrital background (red field) or a range of estimates for UCC (grey field; Gao et al., 1998; McLennan, 2000; Rudnick and Gao, 2003). Also shown in (c) are values calculated based on leachate [Cr] data (open circles). The Cr isotope composition of bulk sediments is shown in (d). In (e), the isotopic composition of the reconstructed authigenic component ($\delta^{53}\text{Cr}_{\text{auth}}$) is shown, according to calculations using the UCC composite range (grey bars), the mean and 95% confidence interval for oxic sediments (red bars), and the sediment leaches (open circles). The blue shaded region denotes the range for modern open Atlantic seawater (Bonnand et al., 2013). Error bars in (d, e) show external reproducibility (uniform 2σ) of $\pm 0.09\%$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Champaign according to methods described by Schoenberg et al. (2008). The ^{50}Cr – ^{54}Cr double spike served to correct for isotopic fractionation during sample preparation and for the mass bias of the mass spectrometer (Ellis et al., 2002). Analysis was performed using a high-mass-resolution method (Weyer and Schweiters, 2003) to avoid polyatomic interferences from $^{40}\text{Ar}^{12}\text{C}^+$, $^{40}\text{Ar}^{14}\text{N}^+$ and $^{40}\text{Ar}^{16}\text{N}^+$. We corrected for trace amounts of ^{54}Fe , ^{50}Ti and ^{50}V not removed during the chemical purification procedure by monitoring ^{56}Fe , ^{49}Ti and ^{51}V . Standard solutions were analyzed at multiple concentrations and it was confirmed that no significant offset occurred between them. Sets of three samples were bracketed by unprocessed NIST SRM-979 standards in order to monitor stability of the instrument and results were normalized to the mean SRM-979 value for each session (Schoenberg et al., 2008). A NIST SRM-3112a standard, as well as a procedural blank and the geostandard SDO-1, were processed during each preparation via the same procedures used for all samples. Blank Cr (typically less than 2 ng) is negligible compared to the Cr (typically 1 µg) contained in our samples. Chromium isotope compositions are reported here as $\delta^{53}\text{Cr}$ values according to conventional delta (δ) notation, where $\delta^{53}\text{Cr} = [(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{SRM-979}} - 1] \times 1000$. External reproducibility was $\pm 0.09\%$ (2σ), evaluated as the modified root mean square difference of 16 pairs of duplicate samples/geostandards taken through the entire procedure during sample preparation and analysis:

$$\sigma = \sqrt{\sum_{i=1}^n (i_1 - i_2)^2 \cdot [2n]^{-1}}, \quad (3)$$

where $i_{1,2}$ are two duplicate analyses of sample/standard i and n is the number of procedural duplicates. Variability among replicate analyses of SRM-3112a was below external reproducibility ($-0.05 \pm 0.08\%$, $n = 5$).

4. Results and discussion

4.1. Estimating the isotopic composition of authigenic Cr in Cariaco Basin sediments

The sedimentary geochemistry subsequent to ~ 14.5 ka is strongly indicative of persistently euxinic deposition within the deep basin (Dean et al., 1999; Yarincik et al., 2000a; Lyons et al., 2003). Enrichments and burial rates of sulfide-sensitive trace metals (typified in Fig. 2a by Mo) are elevated well above those typical of oxic sediments or organic-rich sulfidic sediments deposited beneath oxic or suboxic bottom waters (Scott and Lyons, 2012). Sulfur isotope ratios of sedimentary pyrite ($\delta^{34}\text{S}_{\text{pyrite}}$) are largely invariant and closely mirror the isotopic composition of dissolved sulfide in the modern deep basin (Lyons et al., 2003)—a pattern typical of pyrite formation dominated by syngenetic precipitation within a sulfidic water column (e.g., Lyons, 1997). These observations stand in marked contrast to sediments deposited during the glacial interval, which show a broader range of $\delta^{34}\text{S}_{\text{pyrite}}$ values and are generally much more ^{34}S -enriched (Lyons et al., 2003), suggesting microbial sulfate reduction in a more closed (pore-water) system with respect to sulfate exchange.

Because the bulk sedimentary Cr content of a siliciclastic sediment will represent an admixture of detrital and authigenic Cr—typically with detrital inputs much larger than those characteristic of other redox-sensitive elements (for example, Mo)—we normalized sedimentary Cr content to the insoluble detrital tracer Ti (Fig. 2b). Elevated authigenic Cr fractions (e.g., f_{auth} , see below) are evident as Cr/Ti values in excess of the average Cr/Ti of underlying oxic sediments, which are in turn very similar to bulk upper continental crust (UCC; see below). The pattern of Cr enrichment mirrors that of Mo and other redox-sensitive metals within the deep basin sediments. Samples deposited beneath oxic water during the last glacial episode are not noticeably enriched above typical upper crustal material, but authigenic enrichments become apparent with the onset of euxinia and remain elevated throughout

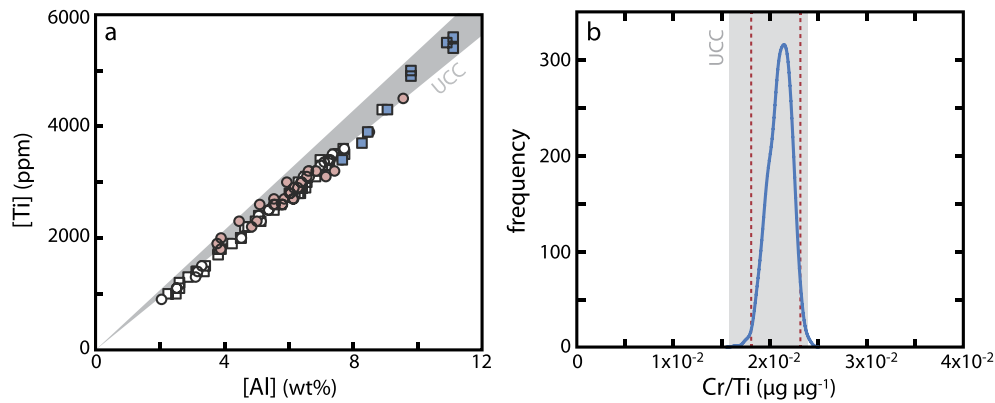


Fig. 3. Detrital background of Cariaco Basin sediments. Shown in (a) are Ti and Al concentrations for samples deposited under oxic conditions during the last glaciation (blue squares), samples deposited under euxinic conditions during the current interglacial (red circles) and data for samples collected in modern time-series sediment traps (open symbols; [Martinez et al., 2007](#)). Also shown is the field for upper continental crust (UCC) using a range of estimates ([Gao et al., 1998](#); [McLennan, 2000](#); [Rudnick and Gao, 2003](#)). Shown in (b) are results from bootstrapping (1000 resamplings) of Cr and Ti data for samples deposited under oxic conditions. Blue curve shows the smoothed frequency distribution of resampled mean values, and red dashed lines denote the 95% confidence interval. Grey field shows a range of estimates for upper continental crust (UCC), as in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the upper interval ([Fig. 2b](#)). Sedimentary Cr isotope values are uniformly positive ([Fig. 2d](#)) and show a distinct shift in average values from $\delta^{53}\text{Cr}_{\text{bulk}} = 0.13 \pm 0.08\text{‰}$ (2SD) to $\delta^{53}\text{Cr}_{\text{bulk}} = 0.32 \pm 0.09\text{‰}$ (2SD) with the inception of stable euxinic conditions at ~ 14.5 ka. Variability among samples within each subset is thus comparable to or less than external reproducibility.

It is important to consider the effect of dilution of authigenic Cr within sediments by a detrital fraction that has a different isotopic composition, most likely ^{53}Cr -depleted relative to potential authigenic sources (e.g., [Schoenberg et al., 2008](#); [Frei et al., 2009](#)). Comparison of the detrital tracers Ti and Al in sediments deposited before and after the last deglaciation, combined with modern sediment trap data, suggests that in general the geochemistry of the detrital component of Cariaco Basin sediments during the deposition of the sampled interval has been relatively invariant ([Fig. 3a](#)). It is important to note that clear variations in provenance have been demonstrated to be associated with glacial–interglacial changes to local hydrology, in addition to some changes linked to oscillatory movement of the Intertropical Convergence Zone and associated dust fluxes (ITCZ) ([Yarincik et al., 2000b](#)). However, these changes are relatively small in comparison to the estimated ranges for the Ti, Al and Cr contents of average upper continental crust (UCC). Indeed, analyses of sediments deposited under oxic conditions yield an average Cr/Ti value that is indistinguishable from estimates of UCC ([Fig. 2b](#); [Fig. 3b](#)) but yields a statistically more precise error envelope on Cr/Ti than the range inherent in using typical UCC composites ([Fig. 3b](#)). We thus use this range as a ‘best estimate’ for the detrital background in what follows, while also propagating the full range of values estimated for UCC.

We estimate authigenic Cr concentrations ($[\text{Cr}]_{\text{auth}}$) using the $[\text{Cr}/\text{Ti}]$ value of an assumed detrital component (either the underlying oxic sediments in our core, OxSed, or UCC composite values) and the measured Cr and Ti concentrations in each sample according to:

$$[\text{Cr}]_{\text{auth}} = [\text{Cr}]_{\text{total}} - ([\text{Ti}]_{\text{total}} \cdot [\text{Cr}/\text{Ti}]_{\text{UCC, OxSed}}). \quad (4)$$

This estimate of the authigenic fraction of sedimentary Cr ($f_{\text{auth}} = [\text{Cr}]_{\text{auth}}/[\text{Cr}]_{\text{total}}$; [Fig. 2c](#)) is then used to estimate the isotopic composition of the authigenic sedimentary pool by mass balance according to:

$$\delta^{53}\text{Cr}_{\text{auth}} = (\delta^{53}\text{Cr}_{\text{bulk}} - [(1 - f_{\text{auth}})\delta^{53}\text{Cr}_{\text{det}}])f_{\text{auth}}^{-1}, \quad (5)$$

where $\delta^{53}\text{Cr}_{\text{bulk}}$ denotes the bulk Cr isotope composition, and $\delta^{53}\text{Cr}_{\text{auth}}$ and $\delta^{53}\text{Cr}_{\text{det}}$ denote the isotopic compositions of the authigenic and detrital pools, respectively. The latter was taken as the

average bulk isotope composition of the underlying oxic sediments ($\delta^{53}\text{Cr}_{\text{det}} = 0.13\text{‰}$). Though this value is slightly ^{53}Cr -enriched relative to mafic igneous rocks ([Schoenberg et al., 2008](#)), the Cr isotope composition of detrital sediment in a given environment may well be isotopically distinct from any presumed igneous source given the isotopic fractionations associated with chemical alteration during soil formation and subsequent sediment processing and it is important to emphasize that the values obtained through acid leaching of sediments are entirely independent of any assumed detrital end-member.

The results of our mass balance approach are shown in [Fig. 2e](#), along with data derived from bulk sediment leaching experiments ($\delta^{53}\text{Cr}_{\text{leach}}$). The authigenic correction enhances the stratigraphic shift to more positive $\delta^{53}\text{Cr}$ values observed in bulk composition, with authigenic Cr isotope values subsequent to the inception of euxinic deposition from both methods being very similar to the published $\delta^{53}\text{Cr}$ range of open Atlantic seawater ([Bonnand et al., 2013](#))—and thus the inferred source waters feeding the Cariaco Basin. The authigenic $\delta^{53}\text{Cr}$ values as obtained from acid leaches on samples deposited after the onset of euxinic deposition are remarkably homogeneous [$\delta^{53}\text{Cr}_{\text{leach}} = 0.58 \pm 0.10\text{‰}$ (2SD)], with variability among samples that is comparable to external reproducibility. Values for $\delta^{53}\text{Cr}_{\text{auth}}$ as obtained through detrital correction are more uncertain as a result of the variability in UCC composites and some uncertainty in the Cr/Ti background of underlying oxic sediments ([Fig. 2e](#)). However, the average value for $\delta^{53}\text{Cr}_{\text{auth}}$ for samples deposited after the onset of euxinic deposition, using the average Cr/Ti value of underlying oxic sediments as a detrital background [$\delta^{53}\text{Cr}_{\text{auth}} = 0.53 \pm 0.21\text{‰}$ (2SD)], is statistically indistinguishable from that obtained from leachate data. These mean values can be compared with an average value for open Atlantic seawater of $0.53 \pm 0.18\text{‰}$ (2SD) ([Bonnand et al., 2013](#)), which is similar across four major Atlantic Ocean water masses. It is important to note that the observed variability seen among water masses in Atlantic seawater is well above the measurement uncertainty reported by [Bonnand et al. \(2013\)](#), which may reflect oceanographic processes still to be determined. That said, there is clearly a strong correspondence between the two independent estimates of $\delta^{53}\text{Cr}_{\text{auth}}$ and the $\delta^{53}\text{Cr}$ range of open Atlantic seawater. The data provide a notable contrast to the few oxic/anoxic sediment data published to date from the Arabian Sea ([Schoenberg et al., 2008](#)), which instead suggest isotopic fractionation during partial Cr(VI) reduction (see below).

Chromium concentrations and $\delta^{53}\text{Cr}$ values from a subset of sediment samples obtained by leaching at a range of acid strengths

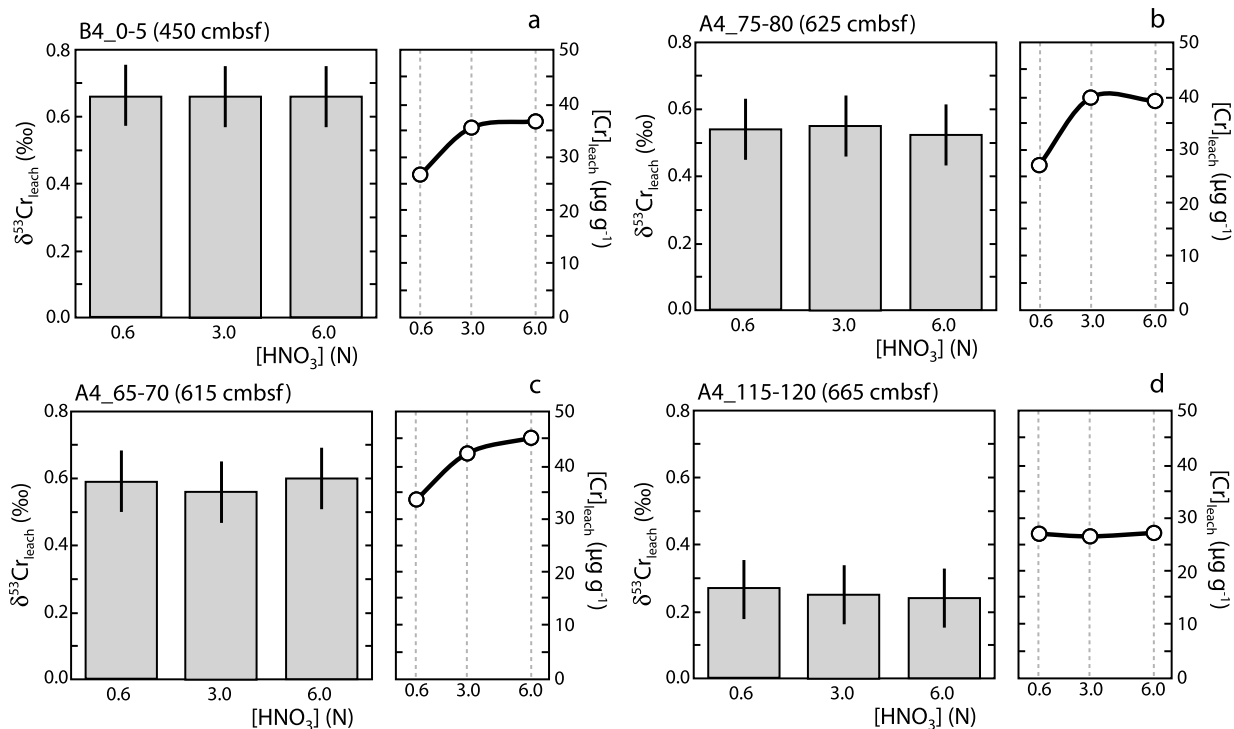


Fig. 4. The Cr content and isotopic composition of sediment leachates. Each panel shows the measured $\delta^{53}\text{Cr}$ values for leachate samples ($\delta^{53}\text{Cr}_{\text{leach}}$; left) and the Cr concentration of acid splits ($[\text{Cr}]_{\text{leach}}$; right) for a range of HNO_3 strengths. Error bars in the left portion of each panel denote external reproducibility of 0.09‰ (uniform 2σ).

are shown in Fig. 4. Although variable acid strengths mobilize different absolute quantities of Cr from the host sediment in most cases, the isotopic composition of all leachates for a given sample are analytically indistinguishable. For many samples, particularly those in the upper portions of the core with higher calculated f_{auth} values (Fig. 2c), our leaching procedure does not appear to have quantitatively mobilized all authigenic Cr within the sediment. Nevertheless, the leachate values for each sample remain indistinguishable within error and are very similar to the $\delta^{53}\text{Cr}_{\text{auth}}$ values calculated according to detrital correction. In cases where there does not appear to be residual authigenic Cr, $\delta^{53}\text{Cr}$ values from the leachates and calculated $\delta^{53}\text{Cr}_{\text{auth}}$ values also match well. Thus, in no case does there appear to be Cr mobilized by the acid leach that is significantly in excess of that calculated via detrital correction.

The agreement between the mass-balance corrected $\delta^{53}\text{Cr}_{\text{auth}}$ values and the estimates via sediment leaching (Fig. 2e) supports the notion that our detrital corrections provide a good estimate of the authigenic Cr isotope composition of the sediments, despite the uncertainty inherent in any correction for an incompletely known and potentially varying detrital background. In addition, the lack of any notable effect of acid strength on measured leachate Cr isotope composition (Fig. 4a–d) suggests that authigenic Cr in Cariaco Basin sediments is hosted within an isotopically homogeneous pool that is mobilized congruently (albeit sometimes non-quantitatively) upon leaching. We hypothesize that the most likely host phase is $\text{Cr}(\text{OH})_3$ or $[\text{Cr}_x\text{Fe}_{1-x}](\text{OH})_3$ coprecipitated with sedimentary Fe–S phases.

However, given the operational nature of the extraction method employed here and the possibility that seawater is isotopically heterogeneous with respect to Cr (see below), it is important to consider whether the $\delta^{53}\text{Cr}$ values measured on leachate samples might represent mixing between an authigenic Cr component and a recalcitrant detrital component and may thus underestimate the isotope composition of the true sedimentary authigenic pool. Under this alternative scenario: (1) the source waters feeding

the Cariaco are significantly heavier than open Atlantic seawater, (2) the calculated $\delta^{53}\text{Cr}_{\text{auth}}$ values are spuriously light as a result of inaccuracies in our background correction and (3) the leaching technique underestimates true $\delta^{53}\text{Cr}_{\text{auth}}$ values due to admixture between an authigenic ^{53}Cr -enriched phase and a more recalcitrant ^{53}Cr -depleted detrital phase.

Such an admixture model would require that both sedimentary pools, detrital and authigenic, are mobilized in constant proportions regardless of sediment type, Cr content and acid strength (Fig. 4)—and that this proportionality is consistent regardless of the absolute quantity of Cr extracted during leaching. Furthermore, these values would need to fortuitously match the values obtained independently through detrital correction, and this correspondence would again need to be independent of sediment type, depositional environment and the absolute quantity of Cr extracted during each leaching procedure. Consequently, we consider the interpretation of our combined data by admixture between two phases unlikely. We emphasize that future work should seek to refine wet chemical methods designed to isolate the authigenic component of sedimentary Cr in siliciclastic marine sediments and that the reconstruction of authigenic $\delta^{53}\text{Cr}$ values in sediments and sedimentary rocks with a significant detrital component must be pursued with caution. However, in this case it is far more parsimonious to attribute the correspondence between both methods of $\delta^{53}\text{Cr}_{\text{auth}}$ reconstruction and between reconstructed $\delta^{53}\text{Cr}_{\text{auth}}$ and Atlantic seawater to effectively quantitative capture of source water $\delta^{53}\text{Cr}$ composition in a euxinic sedimentary system.

4.2. Authigenic Cr in anoxic marine sediments as a seawater $\delta^{53}\text{Cr}$ archive

Previous paleoredox studies involving Cr isotopes have assumed that in reducing environments the timescales of CrO_4^{2-} reduction will be much more rapid than transport/exchange timescales, with the result that CrO_4^{2-} will in effect be quantitatively reduced and removed from solution (e.g., Frei et al., 2009). Though this is a

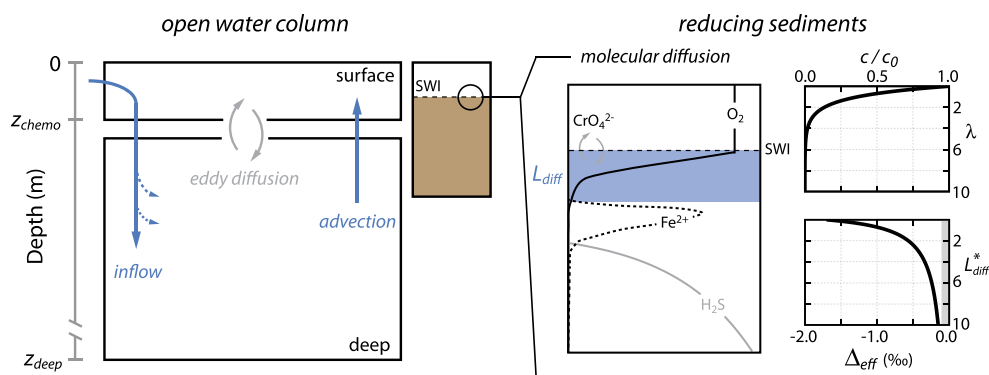


Fig. 5. Transport-reaction scenarios for CrO_4^{2-} reduction and isotopic fractionation in reducing marine environments. Shown schematically are the end-member systems discussed in the text. In the anoxic open water column case (left), water column transport occurs through external inflow/advection (blue arrows) and turbulent diffusion (grey arrows). In a reducing sediment system (right), transport occurs through molecular diffusion and a non-reactive diffusive zone may exist between the sediment–water interface (SWI) and a deeper zone of reduction, through which CrO_4^{2-} diffuses but does not react. The length scale of this zone is given by L_{diff} . Shown in the far right panels are (top) normalized CrO_4^{2-} concentration (c/c_0) as a function of e -folding depth below the top of the reaction zone (in units of $\lambda = \sqrt{D_{Cr}/k}$) and (bottom) isotopic offset from overlying water (Δ_{eff}) as a function of dimensionless depth ($L_{diff}^* = L_{diff}/\lambda$; see text). The greatest potential for isotopic fractionation from source water values exists in diffusion-dominated systems, unless rates of advection are very rapid.

defensible notion it is not yet clear whether such reasoning can be inclusively applied to anoxic marine systems in general, and we consider it worthwhile to explore whether one might expect from first principles that the authigenic Cr in Cariaco Basin sediments captures the $\delta^{53}\text{Cr}$ signature of source water values. More broadly, an explicit delineation of the conditions that promote/inhibit fractionation during partial reduction and thus enhance/minimize offset from ambient fluid $\delta^{53}\text{Cr}$ values in reducing marine environments will be useful both for reconstructing the primary controls on modern Cr isotope mass balance and interpreting signals from the rock record.

In the case of a silled marine basin such as the Cariaco, the system-scale isotopic offset from ambient source water $\delta^{53}\text{Cr}$ values will be modulated by the relationship between the residence time of deep waters within the basin and a characteristic reaction timescale as governed by prevailing water column chemistry. In essence, the isotopic fractionation occurring at the microscopic scale results in a system-scale isotopic offset only if partially reacted, isotopically fractionated Cr(VI) escapes back to the open ocean. If partially reduced Cr(VI) escapes only in very small amounts or not at all, then Cr(VI) is in effect quantitatively reduced and the $\delta^{53}\text{Cr}$ of the reaction product must match that of the influx.

In this light, it is important to emphasize that half-lives for CrO_4^{2-} reduction with dissolved H_2S or Fe(II) are exceptionally short at the conditions typically pertaining to modern reducing marine settings. Using kinetic rate laws for reaction with H_2S and Fe(II) (Pettine et al., 1994; Sedlak and Chan, 1997), and considering ambient temperature and water column chemistry within the Cariaco Basin (Jacobs et al., 1987; Scranton et al., 1987, 2001; Zhang and Millero, 1993), reduction half-lives below the chemocline are on the order of ~ 5 – 10 days (for reaction with H_2S) and ~ 1 – 2 h (for reaction with Fe(II)), even neglecting the possibility of reduction by amorphous solid Fe–S phases (which can be very rapid; Graham and Bouwer, 2010). These timescales can be compared to bottom water residence times of ~ 50 – 150 years for the Cariaco Basin (Scranton et al., 1987; Piper and Dean, 2002), showing that, for a simple model in which a water mass becomes reducing as a whole and remains largely intact, CrO_4^{2-} reduction in the basin should be essentially quantitative.

A complication to this scenario is presented by the possibility of more sporadic or chaotic transport processes that can sometimes influence the ventilation of silled marine basins. In the Cariaco, convective injection of surface waters followed by plume breakdown at terminal depths below the chemocline (Samodurov et al.,

2013) or periodic entrainment of surface waters into the reducing zone during chemocline shoaling (e.g., Astor et al., 2003) could potentially result in water masses that undergo partial CrO_4^{2-} reduction and are exhumed more rapidly than the basin-average deep water residence time. However, significant isotopic offset can be achieved only if the timescales of exhumation through turbulent diffusion and/or vertical advection are comparable to, but less than, characteristic reaction timescales below the chemocline. Given typical rates of upward advection [~ 8 m yr^{-1} ; Ho et al. (2004)] for the Cariaco, transport back across the chemocline on a length scale of ~ 50 – 150 m should require on the order of ~ 5 – 20 years. When compared to the reaction timescales given above, it seems unlikely that a substantial fraction of the Cr(VI) exposed to reducing conditions escapes prior to complete reduction to become mixed back into the oxic layer and transported out of the basin. Accordingly, we assert that known transport processes should not be expected to lead to significant isotopic fractionation from source waters in the Cariaco Basin.

This relationship can be contrasted against reducing marine sediments overlain by relatively oxygenated bottom waters, in which transport of CrO_4^{2-} is controlled largely by molecular diffusion with reaction occurring at some depth below a diffusive boundary layer (Fig. 5). Clark and Johnson (2008), building on the analysis of Johnson and DePaolo (1994) and following the approach of Bender (1990) and Brandes and Devol (1997), demonstrated that in this type of system (e.g., a reducing sediment overlain by oxygenated bottom waters and neglecting bioturbation/bioirrigation by benthic fauna) the primary factor controlling the system-scale isotopic offset from overlying water values is the length scale of the reactively neutral diffusive zone (i.e., the zone through which a reactive solute must diffuse before participating in the fractionating reaction). As this zone becomes smaller, fractionation from overlying water values increases to a maximum “effective” fractionation factor ($^{53}\alpha_{eff}$) defined by:

$$^{53}\alpha_{eff} = \sqrt{^{53}\alpha_{int}} \left[\frac{1 + \left(\frac{L_{diff}}{\lambda}\right)}{1 + \left(\frac{L_{diff}}{\lambda}\right)\sqrt{^{53}\alpha_{int}}} \right], \quad (6)$$

where $^{53}\alpha_{int}$ is the intrinsic isotopic fractionation factor (the local factor operating at a microscopic scale); L_{diff} is the length scale of the nonreactive zone and λ defines the diffusion–reaction length scale, which is governed by the sediment diffusion coefficient of the reactant species and the rate constant for a first-order reduction reaction (Clark and Johnson, 2008).

For our purposes, two important points emerge from this relationship. The first is that as $L_{diff} \rightarrow \infty$ (for example, very deep O_2 penetration into the sediment column), the system-scale isotopic offset from overlying water values approaches zero (Fig. 5). However, we would not expect such systems to be responsible for significant reductive mass fluxes of Cr (Clark and Johnson, 2008). The second is that factors conspiring to change the width of the nonreactive diffusive zone and the diffusion–reaction length scale, such as bottom water chemistry, organic carbon flux to the sediment–water interface or unsteady sediment accumulation, can have significant effects on the system-scale isotopic offset of sedimentary Cr from overlying water values. The latter factors are likely to be particularly important for many modern and ancient continental margin settings with relatively well-oxygenated bottom waters, and it is possible that these factors provide significant isotopic leverage for internal Cr isotope mass balance within the ocean.

4.3. Implications for the Earth surface Cr cycle

The residence time of dissolved Cr in the modern ocean is estimated to be ~ 9 – 10 kyr (Reinhard et al., 2013), which is markedly longer than timescales of ocean mixing. However, this value is not particularly well constrained and even if accurate would not preclude the possibility that seawater $\delta^{53}\text{Cr}$ values are spatially heterogeneous, particularly given that seawater $\delta^{53}\text{Cr}$ data are few in number at present. That being said, available data for seawater $\delta^{53}\text{Cr}$ (Bonnand et al., 2013) represent four major water masses within the Atlantic Ocean with a range of mean ages between ~ 0 and 600 yr (Khatriwala et al., 2012) and include data for a water mass dominated by North Atlantic Deep Water (NADW) that has aged considerably subsequent to downward convective transport in the North Atlantic and has been admixed with ~ 20 – 30% Antarctic Bottom Water (AABW, Johnson, 2008). Isotopic data from other ocean regions, in particular eastern boundary current systems that may support partial CrO_4^{2-} reduction in the water column (Rue et al., 1997) and open ocean surface waters that show evidence for dynamic seasonal Cr transformations (Connelly et al., 2006), will be essential for full evaluation of the controls on seawater $\delta^{53}\text{Cr}$. However, it seems at present that open Atlantic seawater is not characterized by marked isotopic heterogeneity on a basin scale.

In any case, it is important to emphasize that sediments being deposited from perennially anoxic marine systems such as the Cariaco Basin would be expected to capture ambient regional source water values independent of spatial heterogeneity in seawater $\delta^{53}\text{Cr}$ at a global scale. Although additional work is needed to confirm that this observation is widespread, negligible isotopic offset from source waters in such systems would have important but relatively straightforward ramifications for global Cr isotope mass balance. Many of the isotopic fluxes in the Earth surface Cr cycle are poorly constrained at present (e.g., Bonnand et al., 2013), but it is nonetheless self-evident that mechanisms that remove Cr from the ocean will either capture the isotopic composition of ambient source waters or they will be isotopically offset. Isotope mass balance for Cr within the ocean can thus be generally formulated as:

$$\frac{d\delta_{sw}^{53}}{dt} = \left[J_{in}(\delta_{in}^{53} - \delta_{sw}^{53}) - \sum_i J_i \Delta_i^{53} \right] M_{sw}^{-1}, \quad (7)$$

where J_{in} denotes the combined input flux integrated across all sources, δ_{sw}^{53} and δ_{in}^{53} denote the $\delta^{53}\text{Cr}$ composition of seawater (in a globally integrated sense) and the $\delta^{53}\text{Cr}$ composition of combined inputs to the ocean, respectively, and M_{sw} denotes the mass of Cr in seawater. The last term in brackets represents the combined effects of removal fluxes (J_i) that are isotopically offset

from seawater by a factor Δ_i^{53} that depends on the governing removal process. If we assume steady state ($d\delta_{sw}^{53}/dt = 0$), and specify $f_i = J_i/J_{in}$, we arrive at a conventional steady state expression for oceanic Cr isotope mass balance:

$$\delta_{sw}^{53} = \delta_{in}^{53} - \sum_i f_i \Delta_i^{53}. \quad (8)$$

As in Eq. (7), removal fluxes that are not isotopically offset from seawater do not explicitly appear in the isotope mass balance expression but are important through their role in modulating the value of f_i .

It is possible that very little net fractionation is expressed within the oceans, in which case the globally integrated $\delta^{53}\text{Cr}$ composition of the seawater reservoir would track δ_{in}^{53} and could represent a relatively direct tracer of regolith processing and aqueous-particulate Cr transport at Earth's surface—and in particular atmospheric gas composition as linked to coupled Mn–Cr redox cycling. However, given that the primary removal process of Cr from seawater should be the reduction of CrO_4^{2-} and subsequent removal as Cr(III), an equally viable null hypothesis is that the globally integrated Cr isotope composition of seawater is ^{53}Cr -enriched relative to the combined input flux. Regardless, it is clear from inspection of Eqs. (7) and (8) that an increase in the burial of Cr in anoxic environments such as the Cariaco Basin relative to environments that are isotopically offset from local seawater (i.e., $f_i \rightarrow 0$) would be expected to shift the globally integrated $\delta^{53}\text{Cr}$ of the ocean toward the isotopic composition of the combined input flux—and this analysis is valid independent of any assumptions regarding internal oceanic fractionation mechanisms, material fluxes or isotope compositions. Considered in the context of the second null hypotheses above we might thus expect, perhaps counterintuitively, that increased removal into anoxic environments such as the Cariaco Basin would cause a transient decrease in seawater $\delta^{53}\text{Cr}$ values toward δ_{in}^{53} , unless offset by changes in the isotope composition of combined inputs and/or increased removal into sediments supporting partial CrO_4^{2-} reduction.

In sum, we suggest that the authigenic component of sedimentary Cr in anoxic marine systems may preserve negligible isotopic fractionation from source water values, largely as a result of extremely rapid CrO_4^{2-} reduction kinetics at even modest dissolved H_2S and Fe(II) concentrations. If confirmed through further study of modern perennially anoxic marine systems, this would greatly simplify global Cr isotope mass balance and would provide a new sedimentary archive for tracking the evolving Earth surface Cr cycle. Additionally, as discussed above, reducing sediments overlain by oxygenated waters—where transport of CrO_4^{2-} is controlled by molecular diffusion—may lead to significant isotopic offset from overlying seawater $\delta^{53}\text{Cr}$ values. In this light, the offset between globally integrated seawater $\delta^{53}\text{Cr}$ and δ_{in}^{53} , a potentially important process tracer of the global Cr cycle, may be governed to a significant extent by the balance between burial fluxes of authigenic Cr in anoxic settings and reducing sediments overlain by oxygenated waters.

5. Conclusions

We present new $\delta^{53}\text{Cr}$ data from Cariaco Basin sediments deposited over the past ~ 15 kyr. There is an increase in authigenic Cr content and in the $\delta^{53}\text{Cr}$ of the sediments associated with a change from oxic to anoxic and sulfidic (euxinic) conditions at roughly 14.5 ka, but our estimates of the magnitude of authigenic Cr enrichment and its Cr isotope composition have remained essentially constant for the last ~ 14.5 kyr. Furthermore, our estimates of the $\delta^{53}\text{Cr}$ value of the authigenic Cr pool from a reactive Cr leach and as obtained through detrital correction of bulk sediment $\delta^{53}\text{Cr}$ values are internally consistent and match current estimates for the

Cr isotope composition of open Atlantic seawater. These results along with consideration of reaction/transport timescales for CrO_4^{2-} in reducing marine systems allow us to draw several key conclusions: (1) sediments deposited under an anoxic water column can potentially be used to track the evolution of ambient seawater Cr isotope values, (2) larger isotopic offsets from ambient source waters are expected for reducing sediments overlain by oxygenated waters and (3) the Cr isotope composition of Cariaco source waters (and potentially global seawater) has not changed markedly over the last 14.5 kyr, a time period longer than current estimates of the marine residence time of Cr. The latter result suggests the possibility that the Cr cycle has been broadly at steady state since the Last Glacial Maximum.

These results set the stage for construction and refinement of global Cr isotope mass balance and for consideration of the main factors driving seawater Cr isotope variability in the geologic past—specifically, more comprehensive temporal records than those afforded by the sporadic distribution of Fe-rich chemical sediments will now require the development of a more detailed understanding of the mechanisms driving transient and steady state behavior of seawater $\delta^{53}\text{Cr}$. In addition, these results suggest that fine-grained anoxic siliciclastic sediments and sedimentary rocks can capture ambient seawater $\delta^{53}\text{Cr}$ values and that these values have the potential to closely track inputs to the marine system during periods of widespread oceanic anoxia. If so, the Cr isotope composition of anoxic marine sediments and sedimentary rocks has the unique potential to serve as both an atmospheric paleobarometer and a proxy for the marine redox landscape in deep time.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.09.024>.

References

- Alvera-Azcárate, A., Barth, A., Weisberg, R.H., 2009. A nested model of the Cariaco Basin (Venezuela): description of the basin's interior hydrography and interactions with the open ocean. *Ocean Dyn.* 59, 97–120.
- Anbar, A.D., Rouxel, O., 2007. Metal stable isotopes in paleoceanography. *Annu. Rev. Earth Planet. Sci.* 35, 717–746.
- Astor, Y., Muller-Karger, F., Scranton, M.I., 2003. Seasonal and interannual variation in the hydrography of the Cariaco Basin: implications for basin ventilation. *Cont. Shelf Res.* 23, 125–144.
- Bain, D., Bullen, T.D., 2005. Chromium isotope fractionation during oxidation of Cr(III) by manganese oxides. *Geochim. Cosmochim. Acta* 69, S212.
- Bartlett, R.J., James, B., 1979. Behavior of chromium in soils: III. Oxidation. *J. Environ. Qual.* 8, 31–35.
- Basu, A., Johnson, T.M., 2012. Determination of hexavalent chromium reduction using Cr stable isotopes: isotopic fractionation factors for permeable reactive barrier materials. *Environ. Sci. Technol.* 46, 5353–5360.
- Beccquer, T., Quantin, C., Sicot, M., Boudot, J.P., 2003. Chromium availability in ultramafic soils from New Caledonia. *Sci. Total Environ.* 301, 251–261.
- Bender, M.L., 1990. The $\delta^{18}\text{O}$ of dissolved O_2 in seawater: a unique tracer of circulation and respiration in the deep sea. *J. Geophys. Res.* 95, 22243–22252.
- Berna, E.C., Johnson, T.M., Makdisi, R.S., Basui, A., 2010. Cr stable isotopes as indicators of Cr(VI) reduction in groundwater: a detailed time-series study of a point-source plume. *Environ. Sci. Technol.* 44, 1043–1048.
- Bolan, N.S., Adriano, D.C., Natesan, R., Koo, B.-J., 2003. Effects of organic amendments on the reduction and phytoavailability of chromate in mineral soil. *J. Environ. Qual.* 32, 120–128.
- Bond, D.L., Fendorf, S., 2003. Kinetics and structural constraints of chromate reduction by green rusts. *Environ. Sci. Technol.* 37, 2750–2757.
- Bonnand, P., James, R.H., Parkinson, I.J., Connelly, D.P., Fairchild, I.J., 2013. The chromium isotopic composition of seawater and marine carbonates. *Earth Planet. Sci. Lett.* 382, 10–20.
- Bonnand, P., Parkinson, I.J., James, R.H., Karjalainen, A.M., Fehr, M.A., 2011. Accurate and precise determination of stable Cr isotope compositions in carbonates by double spike MC-ICP-MS. *J. Anal. At. Spectrom.* 26, 528–535.
- Brandes, J.A., Devol, A.H., 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. *Geochim. Cosmochim. Acta* 61, 1793–1801.
- Clark, S.K., Johnson, T.M., 2008. Effective isotopic fractionation factors for solute removal by reactive sediments: a laboratory microcosm and slurry study. *Environ. Sci. Technol.* 42, 7850–7855.
- Connelly, D.P., Statham, P.J., Knap, A.H., 2006. Seasonal changes in speciation of dissolved chromium in the surface Sargasso Sea. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 53, 1975–1988.
- Crowe, S.A., et al., 2013. Atmospheric oxygenation three billion years ago. *Nature* 501, 535–538.
- Dauphas, N., Rouxel, O., 2006. Mass spectrometry and natural variations of iron isotopes. *Mass Spectrom. Rev.* 25, 515–550.
- Dean, W., Piper, D.Z., Peterson, L.C., 1999. Molybdenum accumulation in Cariaco basin sediment over the past 24 k.y.: a record of water-column anoxia and climate. *Geology* 27, 507–510.
- Døssing, L.N., Dideriksen, K., Stipp, S.L.S., Frei, R., 2011. Reduction of hexavalent chromium by ferrous iron: a process of chromium isotope fractionation and its relevance to natural environments. *Chem. Geol.* 285, 157–166.
- Eary, L.E., Rai, D., 1989. Kinetics of chromate reduction by ferrous ions derived from hematite and biotite at 25 °C. *Am. J. Sci.* 289, 180–213.
- Ellis, A., Bullen, T.D., Johnson, T.M., 2002. Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* 295, 2060–2062.
- Ellis, A.S., Johnson, T.M., Bullen, T.D., 2004. Using chromium stable isotope ratios to quantify Cr(VI) reduction: lack of sorption effects. *Environ. Sci. Technol.* 38, 3604–3607.
- Fandeur, D., et al., 2009a. Synchrotron-based speciation of chromium in an Oxisol from New Caledonia: importance of secondary Fe-oxyhydroxides. *Am. Mineral.* 94, 710–719.
- Fandeur, D., et al., 2009b. XANES evidence for oxidation of Cr(III) to Cr(VI) by Mn-oxides in a lateritic regolith developed on serpentinized ultramafic rocks of New Caledonia. *Environ. Sci. Technol.* 43, 7384–7390.
- Farkas, J., et al., 2013. Chromium isotope variations ($\delta^{53/52}\text{Cr}$) in mantle-derived sources and their weathering products: implications for environmental studies and the evolution of $\delta^{53/52}\text{Cr}$ in the Earth's mantle over geologic time. *Geochim. Cosmochim. Acta* 123, 74–92.
- Fendorf, S.E., 1995. Surface reactions of chromium in soils and waters. *Geoderma* 67, 55–71.
- Fendorf, S.E., Li, G., 1996. Kinetics of chromate reduction by ferrous iron. *Environ. Sci. Technol.* 30, 1614–1617.
- Frei, R., Gaucher, C., Døssing, L.N., Sial, A.N., 2011. Chromium isotopes in carbonates – a tracer for climate change and for reconstructing the redox state of ancient seawater. *Earth Planet. Sci. Lett.* 312, 114–125.
- Frei, R., Gaucher, C., Poulton, S.W., Canfield, D.E., 2009. Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461, 250–253.
- Frei, R., Gaucher, C., Stolper, D., Canfield, D.E., 2013. Fluctuations in late Neoproterozoic atmospheric oxidation – Cr isotope chemostratigraphy and iron speciation of the late Ediacaran lower Arroyo del Soldado Group (Uruguay). *Gondwana Res.* 23, 797–811.
- Gao, S., et al., 1998. Chemical composition of the continental crust as revealed by studies in east China. *Geochim. Cosmochim. Acta* 62, 1959–1975.
- Graham, A.M., Bouwer, E.J., 2010. Rates of hexavalent chromium reduction in anoxic estuarine sediments: pH effects and the role of acid volatile sulfides. *Environ. Sci. Technol.* 44, 136–142.
- Haug, G.H., et al., 1998. Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr. *Paleoceanography* 13, 427–432.
- Ho, T.Y., et al., 2004. Vertical and temporal variability of redox zonation in the water column of the Cariaco Basin: implications for organic carbon oxidation pathways. *Mar. Chem.* 86, 89–104.
- Izbicki, J.A., Ball, J.W., Bullen, T.D., Sutley, S.J., 2008. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA. *Appl. Geochem.* 23, 1325–1352.
- Izbicki, J.A., Bullen, T.D., Martin, P., Schroth, B., 2012. Delta Chromium-53/52 isotopic composition of native and contaminated groundwater, Mojave Desert, USA. *Appl. Geochem.* 27, 841–853.
- Jacobs, L., Emerson, S., Huested, S.S., 1987. Trace metal geochemistry in the Cariaco Trench. *Deep-Sea Res., A, Oceanogr. Res. Pap.* 34, 965–981.
- Johnson, G.C., 2008. Quantifying Antarctic Bottom Water and North Atlantic Deep Water volumes. *J. Geophys. Res.* 113.

- Johnson, T.M., Bullen, T.D., 2004. Mass-dependent fractionation of selenium and chromium isotopes in low-temperature environments. In: *Geochemistry of Non-Traditional Stable Isotopes*, vol. 55, pp. 289–317.
- Johnson, T.M., DePaolo, D.J., 1994. Interpretation of isotopic data in groundwater-rock systems: model development and application to Sr isotope data from Yucca Mountain. *Water Resour. Res.* 30, 1571–1587.
- Khatiwal, S., Primeau, F., Holzer, M., 2012. Ventilation of the deep ocean constrained with tracer observations and implications for radiocarbon estimates of ideal mean age. *Earth Planet. Sci. Lett.* 325–326, 116–125.
- Kim, C., Zhou, Q., Deng, B., Thornton, E.C., Xu, H., 2001. Chromium(VI) reduction by hydrogen sulfide in aqueous media: stoichiometry and kinetics. *Environ. Sci. Technol.* 35, 2219–2225.
- Kitchen, J.W., Johnson, T.M., Bullen, T.D., Zhu, J., Raddatz, A., 2012. Chromium isotope fractionation factors for reduction of Cr(VI) by aqueous Fe(II) and organic molecules. *Geochim. Cosmochim. Acta* 89, 190–201.
- Konhauser, K.O., et al., 2011. Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event. *Nature* 478, 369–373.
- Lyons, T.W., 1997. Sulfur isotopic trends and pathways of iron sulfide formation in upper Holocene sediments of the anoxic Black Sea. *Geochim. Cosmochim. Acta* 61, 3367–3382.
- Lyons, T.W., Werne, J.P., Hollander, D.J., Murray, R.W., 2003. Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela. *Chem. Geol.* 195, 131–157.
- Martinez, N.C., et al., 2007. Modern climate forcing of terrigenous deposition in the tropics (Cariaco Basin, Venezuela). *Earth Planet. Sci. Lett.* 264, 438–451.
- McLennan, S.M., 2000. Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochim. Geophys. Geosyst.* 2.
- Moynier, F., Yin, Q.Z., Schauble, E.A., 2011. Isotopic evidence of Cr partitioning into Earth's core. *Science* 331, 1417–1420.
- Mullet, M., Boursiquot, S., Ehrhardt, J.J., 2004. Removal of hexavalent chromium from solutions by mackinawite, tetragonal FeS. *Colloids Surf. A, Physicochem. Eng. Asp.* 244, 77–85.
- Mullet, M., Demoisson, F., Humbert, B., Michot, L.J., Vantelon, D., 2007. Aqueous Cr(VI) reduction by pyrite: speciation and characterisation of the solid phases by X-ray photoelectron, Raman and X-ray absorption spectroscopies. *Geochim. Cosmochim. Acta* 71, 3257–3271.
- Oze, C., Bird, D.K., Fendorf, S.E., 2007. Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proc. Natl. Acad. Sci. USA* 104, 6544–6549.
- Patterson, R.R., Fendorf, S., Fendorf, M., 1997. Reduction of hexavalent chromium by amorphous iron sulfide. *Environ. Sci. Technol.* 31, 2039–2044.
- Percy, D., Li, X., Taylor, G.T., Astor, Y., Scranton, M.I., 2008. Controls on iron, manganese and intermediate oxidation state sulfur compounds in the Cariaco Basin. *Mar. Chem.* 111, 47–62.
- Peterson, M.L., Brown Jr., G.E., Parks, G.A., Stein, C.L., 1997. Differential redox and sorption of Cr(III/VI) on natural silicate and oxide minerals: EXAFS and XANES results. *Geochim. Cosmochim. Acta* 61, 3399–3412.
- Pettine, M., Millero, F.J., Passino, R., 1994. Reduction of chromium(VI) with hydrogen sulfide in NaCl media. *Mar. Chem.* 46, 335–344.
- Piper, D.Z., Dean, W.E., 2002. Trace-element deposition in the Cariaco Basin, Venezuela Shelf, under sulfate-reducing conditions – a history of the local hydrography and global climate, 20 ka to the present. *U.S. Geol. Surv. Prof. Pap.* 1670, 1–41.
- Raddatz, A., Johnson, T.M., McLing, T.L., 2011. Cr stable isotopes in Snake River Plain aquifer groundwater: evidence for natural reduction of dissolved Cr(VI). *Environ. Sci. Technol.* 45, 502–507.
- Reinhard, C.T., et al., 2013. Proterozoic ocean redox and biogeochemical stasis. *Proc. Natl. Acad. Sci. USA* 110, 5357–5362.
- Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In: Holland, H.D., Turekian, K.K. (Eds.), *Treatise on Geochemistry*. Elsevier, pp. 1–64.
- Rue, E.L., Smith, G.J., Cutter, G.A., Bruland, K.W., 1997. The response of trace element redox couples to suboxic conditions in the water column. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 44, 113–134.
- Samodurov, A.S., et al., 2013. Modeling vertical exchange of heat, salt, and other dissolved substances in the Cariaco Basin. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 71, 61–72.
- Schauble, E.A., Rossman, G.R., Taylor, H.P.J., 2004. Theoretical estimates of equilibrium chromium-isotope fractionations. *Chem. Geol.* 205, 99–114.
- Schoenberg, R., Zink, S., Staubwasser, M., von Blanckenburg, F., 2008. The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* 249, 294–306.
- Scott, C., Lyons, T.W., 2012. Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: refining the paleoproxies. *Chem. Geol.* 324–325, 19–27.
- Scranton, M.I., Astor, Y., Bohrer, R., Ho, T.Y., Muller-Karger, F., 2001. Controls on temporal variability of the geochemistry of the deep Cariaco Basin. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 48, 1605–1625.
- Scranton, M.I., Sayles, F.L., Bacon, M.P., Brewer, P.G., 1987. Temporal changes in the hydrography and chemistry of the Cariaco Trench. *Deep-Sea Res., A, Oceanogr. Res. Pap.* 34, 945–963.
- Sedlak, D.L., Chan, P.G., 1997. Reduction of hexavalent chromium by ferrous iron. *Geochim. Cosmochim. Acta* 61, 2185–2192.
- Sikora, E.R., Johnson, T.M., Bullen, T.D., 2008. Microbial mass-dependent fractionation of chromium isotopes. *Geochim. Cosmochim. Acta* 72, 3631–3641.
- Wang, D.T., Fregoso, D.C., Ellis, A.S., Johnson, T.M., Bullen, T.D., 2010. Stable isotope fractionation during chromium(III) oxidation by δ -MnO₂. In: *Fall Meeting 2010*. American Geophysical Union. Abstract #H53F-1109.
- Wang, X., Johnson, T.M., 2012. Isotope exchange rates and equilibrium fractionation between Cr(III) and Cr(VI). *Mineral. Mag.* 76, 2516.
- Wanner, C., Zink, S., Eggenberger, U., Maeder, U., 2012. Assessing the Cr(VI) reduction efficiency of a permeable reactive barrier using Cr isotope measurements and 2D reactive transport modeling. *J. Contam. Hydrol.* 131, 54–63.
- Wanner, C., Zink, S., Eggenberger, U., Maeder, U., 2013. Unraveling the partial failure of a permeable reactive barrier using a multi-tracer experiment and Cr isotope measurements. *Appl. Geochem.* 37, 125–133.
- Weyer, S., Schweiters, J.B., 2003. High precision Fe isotope measurements with high mass resolution MC-ICPMS. *Int. J. Mass Spectrom.* 226, 355–368.
- Wittbrodt, P.R., Palmer, C.D., 1996. Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. *Environ. Sci. Technol.* 30, 2470–2477.
- Yamakawa, A., Yamashita, K., Makishima, A., Nakamura, E., 2009. Chemical separation and mass spectrometry of Cr, Fe, Ni, Zn, and Cu in terrestrial and extraterrestrial materials using thermal ionization mass spectrometry. *Anal. Chem.* 81, 9787–9794.
- Yarincik, K.M., Murray, R.W., Lyons, T.W., Peterson, L.C., Haug, G.H., 2000a. Oxygenation history of bottom waters in the Cariaco Basin, Venezuela, over the past 578,000 years: results from redox-sensitive metals (Mo, V, Mn, and Fe). *Paleoceanography* 15, 593–604.
- Yarincik, K.M., Murray, R.W., Peterson, L.C., 2000b. Climatically sensitive eolian and hemipelagic deposition in the Cariaco Basin, Venezuela, over the past 578,000 years: results from Al/Ti and K/Al. *Paleoceanography* 15, 210–228.
- Zhang, J., Millero, F.J., 1993. The chemistry of anoxic waters in the Cariaco Trench. *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* 40, 1023–1041.
- Zink, S., Schoenberg, R., Staubwasser, M., 2010. Isotopic fractionation and reaction kinetics between Cr(III) and Cr(VI) in aqueous media. *Geochim. Cosmochim. Acta* 74, 5729–5745.
- Zouboulis, A.I., Kydros, K.A., Matis, K.A., 1995. Removal of hexavalent chromium anions from solutions by pyrite fines. *Water Res.* 29, 1755–1760.