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978-1-108-79257-8 — The Chromium Isotope System as a Tracer of Ocean and Atmosphere Redox
Kohen W. Bauer , Noah J. Planavsky , Christopher T. Reinhard , Devon B. Cole
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1 Introduction

There has been significant interest in recent decades in the use of transition metal isotope techniques to track the biogeochemical evolution of Earth's ocean-atmosphere system. In particular, transition metals, with measurable stable isotopic variability that can exist at a variety of redox states under Earth surface conditions (such as Cr, Fe, Mo, Tl, and U) have garnered much interest as potential tracers of the redox state of Earth's surface through geological time. This work has been driven by fundamental unresolved questions about past fluctuations in surface oxygen levels. For instance, surface warming over the next millennium is predicted to result in decreased levels of dissolved oxygen in seawater, potentially dramatically altering global biogeochemical cycles and reducing biological productivity and diversity in the world's oceans (Keeling et al., 2010). However, the extent of ocean deoxygenation during warming is still poorly constrained. Few studies have attempted to quantify the spatial extent of low oxygen and fully anoxic marine conditions on a global scale during past warming events. This has challenged efforts to gauge both the scope of redox-dependent feedbacks during various climatic perturbations, and the extent of future redox shifts. Equally, there is also intense debate about the magnitude and timing of larger redox shifts in deep time, including during all the major mass extinctions in Earth's history. Chromium isotopes are primed to become part of the standard toolkit – coupled with trace metal enrichments, nitrogen (N) isotopes, and other novel metal isotope systems – that we use to push forward our understanding of ocean deoxygenation.

There has also been persistent debate about Earth's long-term oxygenation over the past few decades (Lyons et al., 2014). This debate translates into significant uncertainty in the relative roles that environmental and biological factors have played in driving broad-scale evolutionary trends (Cole et al., 2020). For large, multicellular organisms like animals most of the debate has centered on whether oxygen levels were low enough to have prevented animals from establishing stable populations over million-year time scales (Butterfield, 2009; Erwin et al., 2011; Sperling et al., 2013; Towe, 1970). Quantitative constraints on oxygen levels during the majority of the Proterozoic – that is, the billion-year interval preceding the rise of animals, have been a key piece of information missing from this conversation (Kump, 2008; Lyons et al., 2014). Metal isotope systems – including Cr isotopes – can add to this debate by providing minimum or maximum constraints on oxygen concentrations at Earth's surface. Given that Cr redox cycling induces the largest fractionations in this isotope system, the extent of sedimentary Cr isotopic variability can be used to pinpoint when Cr oxidation "turned on" – locally or globally. The initiation of widespread Cr oxidation can, in principle, be quantitatively linked to a range of minimum atmospheric oxygen levels. The Cr isotope system is thus well-suited to answer questions about Earth's long-term evolution as well as recent oxygen dynamics in Earth's oceans.

Here we outline the basics of the Cr isotope system and the major remaining gaps in our knowledge of how this system works. We explore a few examples of how the Cr isotope system can provide unique insights into past fluctuations in Earth's oxygen levels. Rather than an exhaustive but cursory review of all the Cr isotope work from the past decade, we highlight a few case studies that illustrate how the Cr isotope system is well-suited to address questions regarding recent marine oxygen dynamics, as well as Earth's long-term oxygenation. We also highlight some pitfalls of previous Cr isotope work as a means of shaping future endeavors. The overall message is that although the Cr isotope system is much more complicated than originally envisioned, when applied thoughtfully, Cr isotopes remain an important part of the toolkit being used to track marine and atmospheric oxygen levels.

2 Basics of Cr Speciation and Isotope Fractionations

On the modern Earth's surface, the Cr cycle is largely governed by redox reactions whereby soluble Cr(VI) species are produced via oxidation of reduced Cr(III) species. Chromium is present almost exclusively in rock-forming minerals in igneous rocks containing reduced Cr(III) (Fandeur et al., 2009). Therefore, mobilization of Cr in soil environments necessitates the oxidation of Cr(III) to Cr(VI). However, because the kinetics of Cr(III) oxidation with O_2 are slow (Eary and Rai, 1987; Johnson and Xyla, 1991), Mn(III, IV) (oxyhydr-) oxides are typically considered to be the only environmentally relevant oxidant for Cr(III) at the Earth's surface (Bartlett and James, 1979; Eary and Rai, 1987; Fendorf, 1995). The role of superoxide, which has recently been highlighted as an important oxidant, for other metals has not been thoroughly investigated. Oxidation proceeds through dissolved Cr(III) reaction with solid phase Mn oxides and forms tetrahedrally coordinated oxyanions (e.g., CrO_4^{2-}, $HCrO_4^{-}$, $Cr_2O_7^{2-}$), which are highly soluble and readily transported in oxidizing aqueous fluids. Riverine chromate (CrO_4^{2-}) is thus considered to be the main source of Cr to the modern oceans (Bartlett and James, 1979; Fendorf, 1995; Konhauser et al., 2011; Oze et al., 2007). However, many rivers also contain a significant Cr(III) load (e.g., D'Arcy et al., 2016; Wu et al., 2017), which is likely bound by organic ligands.

In modern oxygenated oceans, Cr is thermodynamically stable and present predominantly as Cr(VI), although significant portions of Cr(III) exist in regions; for example, in some North Pacific water masses (Janssen et al., 2020; Wang et al., 2019). The generally conservative behavior of Cr in oxic waters is in strong contrast to that observed in anoxic systems. In anoxic systems Cr(VI) is quickly reduced by Fe(II), sulfide, solid-phase reduced Fe(II) and S phases and even some organic compounds when these are present at high concentrations (Eary and Rai, 1989; Fendorf, 1995; Patterson et al., 1997; Richard and Bourg, 1991). On reduction at circumneutral or alkaline pH, the majority of resulting Cr(III) will hydrolyze to form $Cr(OH)_3$, which is sparingly soluble and readily removed from solution. Therefore, within any anoxic aquatic system, the Cr reservoir will be largely reduced to Cr(III) and subsequently preferentially partitioned into solid (particulate) phases.

Chromium isotope compositions are reported in delta notation ($\delta^{53/52}$Cr), relative to the international standard NIST SRM-979 (δ^{53}Cr = 1000 x [(^{53}Cr/^{52}Cr)$_{sample}$/(^{53}Cr/^{52}Cr)$_{SRM\text{-}979}$ – 1]). Early work on the Cr isotope system in Cr(VI)-contaminated groundwaters established the view that surface water δ^{53}Cr values were controlled by redox transformations (Johnson and Bullen, 2004). Both theoretical and experimental studies indicate that Cr will undergo limited fractionation during most redox-independent transformations, for example, adsorption processes (Ellis et al., 2004; Johnson and Bullen, 2004; Schauble et al., 2004). The typically limited extent of redox-independent Cr isotope fractionations is largely linked to bonding preferences. Chromium(III) has a very strong preference for octahedral coordination, while Cr(VI) strongly favors a tetrahedral coordination. This is in contrast to other heavy metal isotope systems where, in a given redox state, both tetrahedral and octahedral coordination environments are common (e.g., Fe, Cu). As a result, non-redox-linked coordination changes are less likely to drive isotope fractionations of Cr than in "typical" heavy metal isotope systems (Schauble et al., 2004). Chromium(III) complexation with ligands is the most notable exception to this rule (e.g., Babechuk et al. (2018); Saad et al. (2017)). For instance, chromium(III)-organic ligand complexation can cause large (> 1‰) fractionations, but the exact mechanism driving this fractionation is currently unresolved. Saad et al. (2017) suggested that the isotope fractionation occurs during a back reaction, but additional experimental work and ab initio calculations are needed for a more detailed mechanistic understanding of most redox-independent Cr isotope fractionations (see Babechuk et al., 2018).

In marked contrast to most non-redox processes, the oxidation and reduction of Cr species induce large isotope fractionations. Because there is a narrow range of δ^{53}Cr values observed in igneous systems, with an average value of –0.124 ±0.101‰ (2SD) (Schoenberg et al., 2008), Cr isotope fractionations are often compared to this crustal range, which is canonically referred to as the

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igneous silicate Earth (ISE) composition. At equilibrium, the Cr(VI)O_4^{2-} anion is predicted to be enriched in heavy Cr (^{53}Cr) by over 6‰ relative to the coexisting Cr(III) reservoir (Schauble et al., 2004). However, in natural Earth surface systems it is unlikely that the full equilibrium isotope effect will be expressed. Fractionations resulting from oxidation in natural systems observed thus far are less than 1‰. In contrast, fractionations observed during reduction from Cr(VI) to Cr(III) range between 3‰ and 5.5‰ (Ellis et al., 2002, 2004; Johnson and Bullen, 2004; Schauble et al., 2004; Zink et al., 2010). However, if reduction is quantitative, as would be expected in strongly reducing environments, large fractionations will not be expressed at the system scale (Reinhard et al., 2013).

3 A Global Cr Isotope Mass Balance?

3.1 Marine Cr Input Fluxes

The discharge-weighted riverine input of dissolved Cr to the ocean was estimated by (Reinhard et al., 2013) to be ~6 x 10^8 mol y^{-1}. This estimate is significantly below that of McClain and Maher (2016), who estimated a Cr input flux roughly a factor of two higher (~1.7 x 10^9 mol y^{-1}). However, recent work on catchments with minimal anthropogenic influence revealed anomalously low Cr concentrations (~4 x 10^4 mol y^{-1}) relative to those from similar climate zones in the McClain and Maher (2016) study (roughly an order of magnitude lower Cr concentrations (Wu et al., 2017)). Significant anthropogenic riverine Cr contamination seems likely, with the result that accurately reconstructing the pre-anthropogenic riverine Cr flux is challenging. The potential for anthropogenic Cr contamination in rivers also affects our ability to estimate average pre-anthropogenic riverine δ^{53}Cr values. Nonetheless, it is interesting that riverine δ^{53}Cr values are highly variable, but mostly enriched towards heavy compositions relative to crustal values. Most recently, the average riverine δ^{53}Cr value was estimated to be roughly +0.47 ± 0.39‰ (Toma et al., 2019).

Hydrothermal systems do not appear to be a large Cr source, in contrast to many transition metals. High-temperature hydrothermal fluids may be depleted in Cr relative to seawater due to early mixing of hydrothermal fluids and seawater and the rapid formation of Fe (oxyhydr-)oxides, which remove Cr through co-precipitation and scavenging (German et al., 1991). Furthermore, fluid concentration anomalies combined with estimates of global heat flux associated with axial hydrothermal activity (Elderfield and Schultz, 1996) indicate that these systems amount to a small net sink of Cr from seawater (Reinhard et al., 2013). This is corroborated by low Cr inventories in sediments underlying hydrothermal systems (Bauer et al., 2019). The effect of diffuse-flow hydrothermal systems is poorly constrained, although there is some evidence that low-temperature hydrothermal fluids are only mildly enriched in Cr relative to seawater (Sander and Koschinsky, 2000). However, if these concentration anomalies are extrapolated globally by assuming the entire riverine Mg^{2+} flux is removed in diffuse-flow systems, the estimated Cr flux would be ~3−4 x 10^6 mol y^{-1}, still less than ~1% of the dissolved riverine flux (Reinhard et al., 2013). We also note that measurements to date indicate that the δ^{53}Cr of hydrothermal fluids is close to the ISE value (Bonnand et al., 2013).

3.2 Marine Cr Burial Fluxes and Isotope Mass Balance?

There are four primary marine Cr removal fluxes (Figure 1): (1) burial in sediments deposited within anoxic water columns; (2) burial in reducing continental margin sediments; (3) burial in carbonate depositional environments; and (4) burial in oxic marine sediments. Removal of Cr from seawater in any of

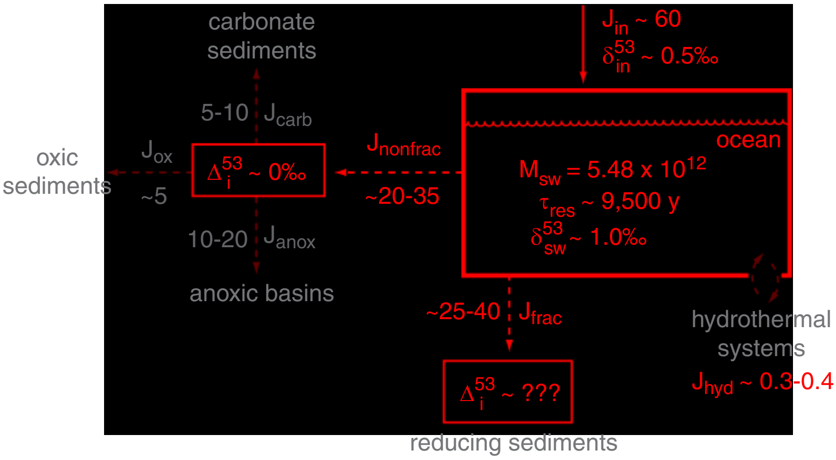

Figure 1 Schematic of the provisional global Cr mass balance discussed in the text and revised from (Reinhard et al., 2013). The magnitude and isotopic composition of the different Cr fluxes have been updated based on Cr studies conducted in the modern oceans (Gueguen et al., 2016; Sander and Koschinsky, 2000; Sander et al., 2003; Scheiderich et al., 2015; Toma et al., 2019). Seawater Cr reservoir mass (M_{sw}), oceanic residence time (τ_{res}), and isotope composition ($\delta^{53}{}_{sw}$) are shown, as are the isotopic offsets from seawater associated with burial in each sink ($\Delta^{53}{}_{i}$ terms). Numbers associated with each flux (J_i) are in units of 10^7 mol y^{-1}. Note that the separation of sink terms into "fractionating" (J_{frac}) and "non-fractionating" ($J_{nonfrac}$) is provisional

these environments could, in principle, be accompanied by an isotopic fractionation – causing seawater δ^{53}Cr values to deviate from the mean time-integrated input value.

3.2.1 Anoxic Sediments

Chromium(VI) may be efficiently scavenged from anoxic water columns, and thus Cr removal in anoxic waters likely represents a significant removal flux despite the small spatial extent of these environments. Work on sediments deposited in the Cariaco Basin, a permanently anoxic marine basin off the coast of Venezuela (Gueguen et al., 2016; Reinhard et al., 2013), suggests that authigenic Cr in euxinic (anoxic, H_2S-rich) sediments is isotopically similar to contemporaneous seawater δ^{53}Cr values (Figure 2). The δ^{53}Cr values are between 0.6‰–0.7‰, which is within error of adjacent Atlantic seawater values (Bonnand et al., 2013). The authigenic Cr isotope composition of Cariaco Basin sediments determined using a detrital element correction (using a Cr/Ti ratio) and a set of weak acid leaches are comparable (Figure 2).

The δ^{53}Cr composition of Cr buried in some anoxic marine sediments may also be influenced by, and record, regional and diagenetic processes. For example, in the Peru margin oxygen minimum zone (POMZ), Cr concentrations and seawater δ^{53}Cr show little variation across the redoxcline (Bruggmann et al., 2019b), contrasting the view that near quantitative Cr(VI) reduction should occur under anoxic conditions. We note, however, that the water column of the POMZ does not accumulate high concentrations of potential Cr(VI) reductants (Scholz et al., 2014), relative to other permanently stratified anoxic ocean basins like the euxinic Cariaco Basin (see above). Bulk and authigenic δ^{53}Cr compositions in shallow POMZ sediments are isotopically heavy (average $\delta^{53}\mathrm{Cr}_{\mathrm{Bulk}}$ signature of 0.77 ± 0.19‰; Bruggmann et al. (2019b)). In the anoxic bottom waters of the POMZ, higher concentrations of ^{53}Cr-depleted Cr are observed, potentially indicating remobilization of Cr on reductive dissolution of reactive Fe (oxyhydr-)oxides in surface sediments. Bruggmann et al. (2019b) also observe covariation between δ^{53}Cr and organic matter contents in the POMZ sediments, which may be indicative of a small yet important authigenic Cr pool delivered to the sediment surface associated with plankton biomass. Furthermore, this organic- and Cr-rich end member has a heavy Cr isotopic composition (1.10 ± 0.08‰). Chromium isotope data from the POMZ thus reveals that even under prevailingly anoxic water column conditions, regional factors such as organic matter loading and the delivery and speciation of Fe may give rise to δ^{53}Cr variations recorded in the sedimentary record.

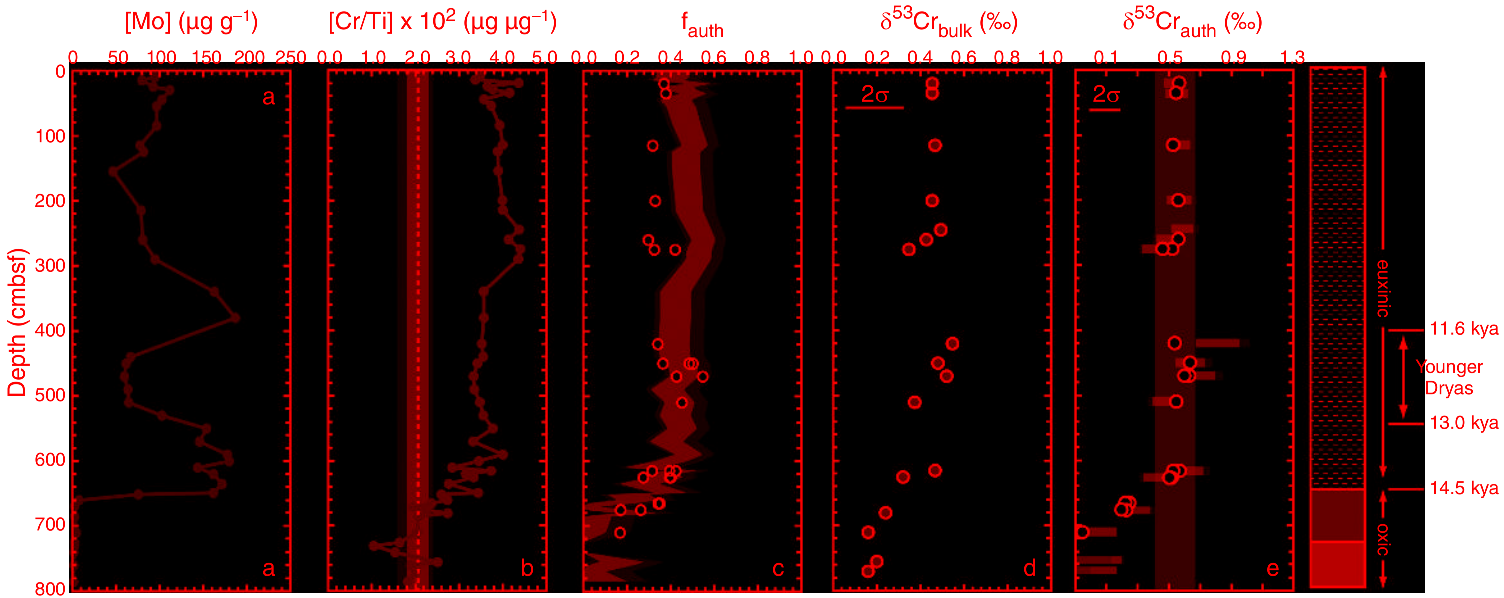

Figure 2 Geochemical data for sediments deposited at ODP Site 1002 since the Last Glacial Maximum (reproduced from Reinhard et al., 2014). Core stratigraphy at right and data for Mo in (**a**) are from Lyons et al. (2003). Gray field in (**b**) denotes the range of Cr/Ti values for upper continental 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 and assuming the resampled mean and 95% confidence interval of oxic sediments as the detrital background (red field) or the range of estimates for UCC (gray field: Rudnick (2003)). 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 ($\delta^{53}Cr_{auth}$) is shown, according to calculations using the UCC composite range (gray 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 deep Atlantic seawater (Bonnand et al., 2013). Error bars in (**d, e**) show external reproducibility (2σ) of ±0.1‰

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3.2.2 Reducing Marine Sediments

There is limited published Cr isotope data from modern reducing marine sediments, however, there are significant fractionations associated with this burial term (Bauer et al., 2018; Bruggmann et al., 2019b; Gueguen et al., 2016). In reducing marine sediments overlain by relatively oxygenated waters, isotope fractionations are often predicted using a simplified diagenetic equation (see Bauer et al. (2018); Clark and Johnson (2008); Johnson and DePaolo (1994); following the approach of Bender (1990) and Brandes and Devol (1997)). In these sedimentary systems, isotope fractionations from overlying water values are tied to the scale of the nonreactive diffusive zone, which for Cr is the oxygen penetration depth. The thinner this zone, the greater the fractionation from overlying water. The rate constant will also strongly affect the fractionation by controlling how close the system is to near quantitative consumption of the porewater Cr reservoir. The "effective" fractionation factor (${}^{53}\alpha_{eff}$) is defined by:

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

where ${}^{53}\alpha_{int}$ is the intrinsic isotope fractionation factor; L_{diff} is the length scale of the nonreactive zone and λ is the diffusion-reaction length scale, which is tied to the sediment diffusion coefficient of the reactant species and the rate constant for a first-order reduction reaction (Clark and Johnson, 2008).

As the diffusive length scale (L_{diff}) increases, driven for example by relatively deep O_2 penetration into the sediment column, the isotopic offset from overlying water decreases, and for strongly oxidizing systems will be near zero (Figure 3) (Clark and Johnson, 2008). Reducing sediments ("suboxic sediments") in contrast should be fractionated from seawater with the magnitude of the fractionation scaling with oxygen penetration depth, which will control L_{diff} and the reaction rate term. In principle, this simple method of quantifying Cr isotope burial fractionations could be coupled with a spatially explicit representation of bottom water oxygen levels and organic carbon fluxes (see Reinhard et al., 2013). Additionally, this framework may lead to a proxy for local oxygen penetration depths in past reducing marine sediments (if coeval seawater values can be independently constrained and authigenic Cr can be reliably reconstructed).

The idealized 1D model has been applied effectively to Cr(VI) reduction in lacustrine-reducing sediments (Bauer et al., 2018), however, its scope has yet to be fully explored in modern marine environments. There is, however, evidence for elevated burial rates of authigenic Cr in reducing continental margin sediments (e.g., Bruggmann et al. (2019b); Brumsack (1989); Shaw et al. (1990))

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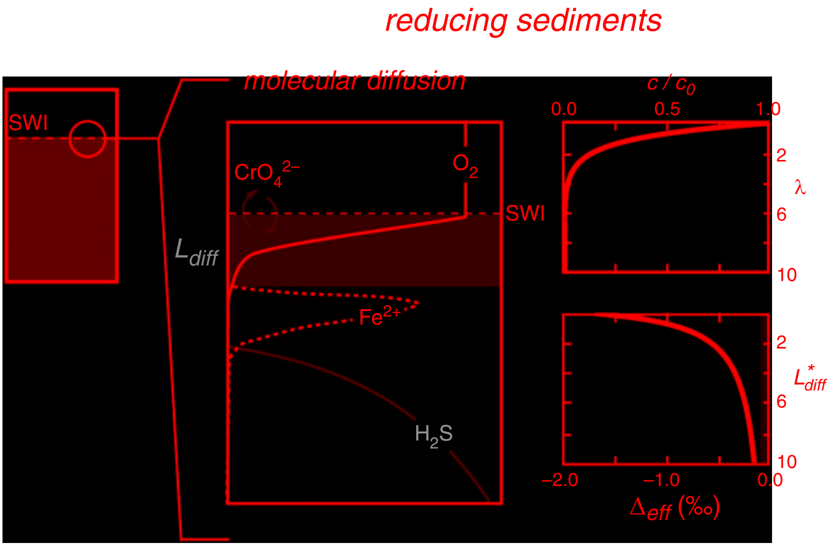

Figure 3 Idealized reaction-transport scenario for Cr redox cycling in reducing marine sediments (after Reinhard et al., 2014). In a reducing sediment system, transport of CrO_4^{2-} occurs through diffusion. A zone may exist between the sediment-water interface (SWI) and a deeper anoxic zone where reduction takes place. Through this zone, CrO_4^{2-} diffuses but does not react. The length scale of this nonreactive zone is given by L_{diff} (blue bar). Shown at right 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 $\lambda = \sqrt{D_{Cr}/k}$, where D_{Cr} is the diffusion coefficient and k is the first-order reaction rate constant) and (bottom) isotopic offset from overlying water (Δ_{eff}) as a function of dimensionless depth ($L_{diff}^* = L_{diff}/\lambda$; see text)

and although these environments are restricted spatially, they likely account for a large portion of the net removal flux of Cr from the ocean. This is important, as we expect that these settings will most readily express the isotopic effects of partial reduction of seawater CrO_4^{2-}. As a result, the mass-weighted isotopic burial flux from the ocean in such regions might be expected to respond dynamically to changes in bottom water chemistry along continental margins – and thus ocean oxygen levels.

3.2.3 Carbonate Sediments

There is currently little Cr isotope data from modern marine carbonate sediments. Sparse results suggest that Bahamian ooids, which typically give

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a mean radiocarbon age of a few thousand years, match Atlantic dissolved seawater δ^{53}Cr values (~0.6‰) (Bonnand et al., 2013). It may be expected that carbonate sediments would be minimally fractionated from contemporaneous seawater δ^{53}Cr values due to the lack of coordination change as the chromate oxyanion is incorporated into the carbonate lattice. However, it is possible that there are vital effects during biogenic carbonate formation. This is consistent with observations on foraminifera and bivalves (Bruggmann et al., 2019a; Pereira et al., 2016; Wang et al., 2017). Chromium concentration and δ^{53}Cr data obtained in foraminiferal shells from modern marine sediments, water columns, and laboratory cultures, furthermore, imply that Cr uptake into the carbonate lattice occurs post-depositionally (Remmelzwaal et al., 2019). This opens the possibility that Cr signatures in foraminiferal shells record bottom and porewater signals, which is contrary to interpretations that these shells are a reliable archive of surface seawater δ^{53}Cr in the geologic past. Although some studies suggest diagenetic effects on carbonate-bound Cr isotope systematics may be important, the precise mechanisms remain poorly constrained. Working out these details in future studies will be of value for the Cr isotope paleoredox proxy.

3.2.4 Oxic Marine Sediments

Currently published data from oxic marine sediments is also limited (Bruggmann et al., 2019b; Gueguen et al., 2016; Wei et al., 2018). A reasonable null hypothesis is that Cr removal in such environments will occur without significant isotopic offset from contemporaneous seawater – given that there is no observed fractionation during Cr sorption to metal (Fe, Al) oxides (Ellis et al., 2004), which is likely the main Cr removal pathway in oxic marine sediments. In addition, sorption efficiency of CrO_4^{2-} on these phases is minimal at typical marine pH values (discussed above), providing an important and potentially very useful contrast to transition metal isotope systems such as molybdenum (Mo). However, δ^{53}Cr values in Fe-Mn crusts are highly variable, likely pointing towards Fe-Mn-induced Cr redox cycling (Wei et al., 2018).

3.3 A Framework for Marine Cr Isotope Mass Balance

Although the material fluxes in the Earth surface Cr cycle can be roughly estimated, the isotopic fluxes are poorly constrained at present. Nevertheless, the mechanisms that remove Cr from the ocean will either capture the isotopic composition of ambient source waters or they will be isotopically offset – with more negative δ^{53}Cr values than seawater. Isotope mass balance for Cr within the ocean can thus be generally formulated according to: