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Fractionation Behavior of Chromium Isotopes during the Sorption of Cr (VI) on Kaolin and its Implications for Using Black Shales as a Paleoredox Archive

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Abstract Chromium stable isotope variations in marine black shales are increasingly used to constrain redox changes though time. However, how well black shale $\delta^{53}Cr$ values represent ambient seawater $\delta^{53}Cr$ values is difficult to assess as black shales contain both detrital and authigenic mineral phases, of which only authigenic phases are expected to mirror seawater, while detrital silicate phases are expected to show igneous $\delta^{53}Cr$ values. In order to correct for detrital contamination, it is thus imperative to know whether detrital minerals are in fact characterized by igneous $\delta^{53}Cr$ values. To investigate this further, three sets of Cr (VI) batch sorption experiments were conducted, reacting kaolin with (1) with a synthetic Cr (VI) solution, (2) with Cr (VI) doped river water, and (3) with Cr (VI) doped seawater. Further, sequential leaches were applied to reacted kaolin to evaluate how well sorbed Cr (VI) can be leached. The experiments revealed that Cr (VI) readily sorbs on kaolin, changing its Cr concentration and isotopic composition. In river water, kaolin sorbed up to 36 μg of Cr (VI) per gram of kaolin and recorded a negative offset in bulk $\delta^{53}Cr$ of up to 0.26‰ relative to unreacted kaolin, while no sorption was observed in seawater. Our leaching experiments revealed that already a weak acid leach (0.5M HCl) readily mobilizes some of the sorbed Cr from kaolin, which when applied to black shales will likely contaminate leachates designed to release authigenic Cr. This has major implications for the application of Cr stable isotopes in black shales as marine paleoredox archives.

1. Introduction

It has been suggested that the emergence of metazoans and diversification of animal life during the Phanerozoic was closely linked to increases in atmospheric oxygen (Berner et al., 2007; Butterfield, 2009). To better understand the connection between biological evolution and oxygen, it is crucial to reliably constrain the spatial and temporal evolution of atmospheric oxygen levels over Earth's history. Chromium stable isotopes are emerging as a powerful proxy for reconstructing and constraining redox changes at the Earth's surface through time (e.g., Canfield et al., 2018; Crowe et al., 2013; Frei et al., 2009; Planavsky et al., 2014; Reinhard et al., 2014; Wei et al., 2018). Cr occurs in the environment as two stable oxidation states, Cr (III) and Cr (VI) (e.g., Qin & Wang, 2017). The delivery of isotopically fractionated Cr to the oceans is realized through the oxidation of Cr (III) to Cr (VI) and subsequent back reduction of Cr (VI), such that differences in the degree of fractionation between marine sedimentary rocks and the continental source material or the lack thereof can be used as a sensitive proxy for surface oxygenation (e.g., Frei et al., 2009; Holmden et al., 2016).

Cr is commonly present in its reduced form, Cr (III), in igneous rocks with a narrow range of chromium isotope ($\delta^{53}Cr$) values averaging -0.124 ± 0.101‰ (2σ; Schoenberg et al., 2008). The oxidation of Cr (III) to Cr (VI) depends on the presence of manganese oxide (MnO_2), which acts as a catalyzing agent (Fendorf, 1995; Fendorf & Zasoski, 1992; Oze et al., 2016, 2007). MnO_2 is only stable under surface conditions where atmospheric oxygen concentrations are above a critical threshold value, estimated to be between 0.03% and 1% of present atmospheric oxygen level based on kinetic constraints (Crowe et al., 2013; Planavsky et al., 2014). Oxidized Cr (VI) is present as the highly soluble and mobile chromate (CrO_4^{2-}) and bichromate ($HCrO_4^{-}$) anions, which are transported to the ocean via riverine and groundwater transport (Ellis et al., 2002; Zink et al., 2010). During transport Cr (VI) can be immobilized by back reduction to Cr (III) through

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natural reductants, such as aqueous Fe (II) and dissolved humic acid (Ellis et al., 2002). The reduction of Cr (VI) to Cr (III) prefers lighter isotopes, so that the partial back reduction of mobile Cr (VI) to immobile Cr (III) results in a range of negative fractionation factors and thus results in a net flux of isotopically heavy Cr (VI) into the oceans (Frei et al., 2009; Holmden et al., 2016; Oze et al., 2007; Zink et al., 2010). This is supported by positively fractionated δ^{53}Cr values of modern seawater, which show a range of fractionation between 0.1‰ and 1.7‰ (Bonnand et al., 2013; Bruggmann et al., 2019; Frei et al., 2018; Goring-Harford et al., 2018; Moos & Boyle, 2018; Paulukat et al., 2016; Scheiderich et al., 2015). Isotopically heavier δ^{53}Cr values have also been reported for river waters (D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015; Sun et al., 2019 ; Wu et al., 2017) and their particle loads (Sun et al., 2019; Wu et al., 2017) as well as for altered mafic and ultramafic rocks (Farkaš et al., 2013; Shen et al., 2015), while paleosols and modern weathering profiles are generally characterized by negatively fractionated δ^{53}Cr values (Berger & Frei, 2014; Crowe et al., 2013; D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015). The positively fractionated Cr pool reaching the ocean can be buried in marine sediments by rapid and efficient back reduction to insoluble Cr (III) via dissolved or particulate inorganic reductants (e.g., Fe (II) or Fe-S mineral phases), which has the potential to quantitatively capture the ambient seawater Cr composition (Frei et al., 2009; Gueguen et al., 2016; Reinhard et al., 2014). Further, Cr (VI) can be reduced by organic reductants (Qin & Wang, 2017, and references therein). The resulting Cr (III) can be stabilized in solution by organic ligands (Saad et al., 2017) or removed from surface seawater by phytoplankton through extracellular adsorption and direct cellular incorporation (Semeniuk et al., 2016). As the reduction of Cr (VI) prefers light Cr (e.g., Kitchen et al., 2012; Zink et al., 2010), the latter is likely to contribute negatively fractionated Cr compared to the surface water to the sediment via organic particles sinking (Semeniuk et al., 2016).

Marine sedimentary archives targeted by Cr isotope studies constraining redox conditions are iron-rich sedimentary rocks (e.g., Frei et al., 2013, 2009; Wei et al., 2018), carbonates (e.g., Caxito et al., 2018; Gilleaudeau et al., 2016; Wei, Frei, Gilleaudeau, et al., 2018), and black shales (e.g., Canfield et al., 2018; Cole et al., 2016; Planavsky et al., 2014). The Cr isotopic composition of the authigenic phases of these sedimentary rocks is assumed to mirror the Cr composition of seawater at the time of deposition (Gilleaudeau et al., 2016; Planavsky et al., 2014). The application of black shales as a paleoredox archive represents a particular challenge as they are primarily detrital sediments, which at the same time contain a variety of authigenic mineral phases (e.g., carbonates, phospates, and pyrite) of potential interest to paleoenvironmental studies. Detrital clays in particular are known to host Cr derived from weathered continental rocks and are assumed to introduce a large unfractionated Cr pool to marine black shales, potentially masking the δ^{53}Cr value of the authigenic mineral phases. Due to their temporal and spatial abundance, black shales offer an important paleoredox archive with the potential to better constrain past redox fluctuations during time periods, which are not covered by iron formations or carbonates. A recent study suggested that detrital phases in cherts could carry positively fractionated δ^{53}Cr values of up to 0.20‰ (Huang et al., 2018), which challenges the fundamental assumption that siliciclastic detritus exclusively carries unfractionated δ^{53}Cr values and indicates that the Cr composition of detrital mineral phases might have been altered during their transport into the oceans. Cr sorption on sediments has been suggested as a process with the potential to shift the Cr composition of weatherable detrital sediments toward positively fractionated δ^{53}Cr values (Huang et al., 2018). This is supported by generally positively fractionated δ^{53}Cr values reported for the bulk suspended particle load of the Connecticut River (Sun et al., 2019; Wu et al., 2017).

Clay minerals can remove pollutants from solution through adsorption mechanisms and cation exchange (Acharya et al., 2017; Bhattacharyya & Sen Gupta, 2006; Rosales-Landeros et al., 2013). They are very fine particles that have the chemical properties of colloids (Sharma et al., 2009), and their high chemical and mechanical stability, high specific surface area, and consequential high cation exchange capacity make them excellent adsorbents (Ajouyed et al., 2011; Bhattacharyya & Sen Gupta, 2006). They are known to readily sorb trace metals, including Cr, which could potentially alter their original composition. The sorption of Cr (both as Cr (III) and Cr (VI)) on natural and modified clays has been well described in numerous environmental remediation studies (e.g., Ajouyed et al., 2011; Bhattacharyya & Sen Gupta, 2006; Deng et al., 2014; Fritzen et al., 2006; Göde et al., 2010; Khan et al., 1995; Parthasarathy et al., 2003). However, thus far, it is unknown whether the sorption of Cr onto clay minerals is associated with an isotopic fractionation. Cr (VI) readily adsorbs on clay minerals through electrostatic attraction between the positively charged surface areas and negatively charged Cr (VI) species (CrO_4^{2-} and $HCrO_4^-$; Acharya et al., 2017; Covelo

et al., 2007). At neutral and alkaline pH, however, clay minerals commonly have a negatively charged surface area resulting in a rather low adsorption capacity for Cr (VI) at naturally occurring pH ranges (Acharya et al., 2017; Marjanović et al., 2011; Taylor, 2000). Alternatively, Cr (VI) can be reduced to Cr (III) by natural reducing agents (e.g., Fe (II) or organic matter) and subsequently sorbed through cation exchange (Brookshaw et al., 2014; Covelo et al., 2007; Koppelman, 1980). For example, clay minerals rich in Fe (II) have been shown to remove Cr (VI) from solution by a coupled reduction/adsorptionmechanism (Brookshaw et al., 2014; He et al., 2005; Taylor, 2000) and humic acid can catalyze the adsorption of Cr (VI) on kaolin (Li et al., 2010). Hence, it is tenable to assume that the bulk Cr isotope signature of detrital clays might not fall within the narrow igneous baseline of $\delta^{53}Cr = -0.124 \pm 0.101‰$ (Schoenberg et al., 2008) but that their Cr isotope compositions might be significantly affected by adsorption/desorption induced compositional changes during weathering, transport, sedimentation, and postdepositonal diagenesis.

Cr stable isotopes in marine black shales are a promising tool to reconstruct past seawater redox, but the high proportions of detrital clays in black shales are likely to dominate, or at least contaminate and dilute any present ambient seawater Cr isotopic composition potentially captured in authigenic mineral phases, such as carbonates and phosphates. This study aims to evaluate clay mineral sorption as a process that could potentially alter the bulk $\delta^{53}Cr$ values of detrital clays. We performed a series of batch adsorption experiments using synthetic Cr (VI) brine and kaolin and measured the Cr concentration and isotope composition of the reacted solution and kaolin phase to investigate the potential adsorption capacity and fractionation potential of Cr (VI) adsorption on clay. Additionally, kaolin was reacted with Cr (VI) doped natural river and ocean water to determine (1) at which stage during the Cr cycle sorption mechanisms could be encountered, (2) what the effects of different water matrices on the sorption capacities are, and (3) whether or not sorbed Cr fractions have the potential to reflect authigenic signatures of contemporaneous seawater. Finally, a sequential leach method using 0.5M HCl, 6M HCl, HF, and *aqua regia* was applied to the reacted kaolin phase, to evaluate the retention potential of Cr (VI) on clays and to determine if Cr isotopes were sorbed homogeneously.

2. Materials and Methods

2.1. Materials and Preparation

The kaolin (china clay) used in this study was provided by English China Clays and was mined in the open pits at Saint Austell in Cornwall, United Kingdom. Kaolin was chosen as the adsorbing material to constrain the sorption experiments to surface processes, as kaolinite's sorption and exchange capacity is primarily confined to the surface, in contrast to other clays, such as smectite or illite, where sorption processes also involve interior lattice exchange site reactions (Rosales-Landeros et al., 2013). A piece of kaolin was powdered using an agate mortar and pestle and washed three times with 6M HCl in order to enhance surface reactivity. Subsequently, the substrate was rinsed with ultrapure Milli-Q water (mq) and dried down on a hot plate.

A Cr (VI) stock solution was prepared by dissolving analytical grade $K_2Cr_2O_7$ in MilliQ ™ 18 MΩ ultrapure water. Several Cr (VI) solutions of various concentration (0.1 to 10 μg/ml) were prepared from the stock solution by diluting with mq. $NaNO_3$ was used as a background electrolyte at a concentration of 0.01M. Further, the pH of the solutions was adjusted to a pH of 8 using NaOH, which is characteristic for ocean waters.

Additionally, a seawater series and a river water series was doped with Cr (VI) solution to Cr (VI) concentrations between 0.1 and 10 μg/ml. The Cr (VI) stock solution was prediluted before mixing into the seawater and river water series to achieve the same dilution factor for the background matrix of all Cr (VI) concentrations applied in this study. For the seawater matrix series a standard low nutrient Atlantic seawater from Ocean Scientific International Ltd (Batch: LNS23) was used for the experiments. The river water matrix was a water sample from the Olewiger Creek in Trier, Germany. The concentrations of the major anions competing with Cr (VI) for sorption in the seawater and river water samples were measured at the University of Copenhagen and are listed in Table 1. The pH of the seawater and river water sample was determined using a Consort multiparameter analyzer (C5020) as 7.9 and 7.4, respectively.

Table 1

Concentrations (μg/ml) of the Major Competing Anions in the Seawater and River Water Samples That Were Used as a Background Matrix for the Cr (VI) Sorption Experiments

Setup	Cl	NO_3	SO_4
Seawater	20391.00	54.50	2857.36
River water	32.52	14.82	23.30

2.2. Batch Adsorption

The batch experimental setup was based on the method used by Ajouyed et al. (2011) with some modifications. In all the adsorption experiments, 200 mg of kaolin was reacted with 20 ml Cr (VI) solution in 50 ml-polypropylene tubes. The Cr (VI) solutions varied in concentration (0.1–10 μg/ml) and matrix (mq, seawater and river river, respectively). Additionally, a blank was run for each series by reacting 200 mg of kaolin with 20 ml matrix solution containing no Cr. The polypropylene tubes were placed in an overhead shaker at room temperature for 24 hr. Subsequently, the suspensions were centrifuged at 4,000 rpm for 10 min. The supernatants were pipetted off and filtered using 0.45 μm syringe filters. The kaolin phase was rinsed with mq before it was transferred into Teflon beakers and dried down at 120 °C on a hot plate. A complete dissolution of the kaolin was achieved by adding HF and placing the beakers with closed lids at 120 °C on a hot plate overnight. Afterward the lids were removed from the beakers and the suspensions were dried down at 120 °C. The final residues were redissolved in 20 ml mq for later analysis. To ensure reproducibility, all batch experiments were run in duplicate.

2.3. Leaching

Two additional batch adsorption experiments were run at a low (0.1 μg/ml) and a high (5 μg/ml) Cr (VI) concentration. The kaolin phase of these runs was separated by centrifuging and pipetting the respective supernatants off. Next, the kaolin was rinsed using mq and dried down. To achieve a complete dissolution and Cr recovery, the kaolin was leached in four sequential acid attacks: I) 0.5M HCl, II) 6M HCl, III) HF, and IV) aqua regia. The reacted kaolin was exposed to the leaching acid for 2 hr in the first two leach steps, while the last two leaches were conducted overnight. After each leach step, the samples were centrifuged, the respective supernatants were pipetted off and dried down, while the respective kaolin residues were washed with mq before the next leaching acid was added. The final residues of each leach step were redissolved in 20 ml mq for Cr analyses. The leaching experiments were also run in duplicate to ensure reproducibility.

2.4. Analytical Methods

The pH of the starting solutions was measured using a Consort multiparameter analyzer (C5020), which was calibrated at room temperature using pH 4, pH 7, and pH 10 buffer solutions. The Cr (VI) concentration of the solutions before and after reaction was determined using a DR 2800 Spectrophotometer from Hach. Thermal ionization mass spectrometry was used to determine the total Cr concentration and Cr isotope signatures ($\delta^{53}Cr$) of the initial solutions, supernatants, and kaolin phases. For that Cr of the different samples was separated using a two-step chromatographic column separation consisting of an anion and a cation exchange column (supporting information). The thermal ionization mass spectrometer (TIMS) used for the Cr isotope analyses was an IsoProbe T from IsotopX Ltd. Detailed information on the chromium separation procedure and TIMS analyses is presented in the supporting information.
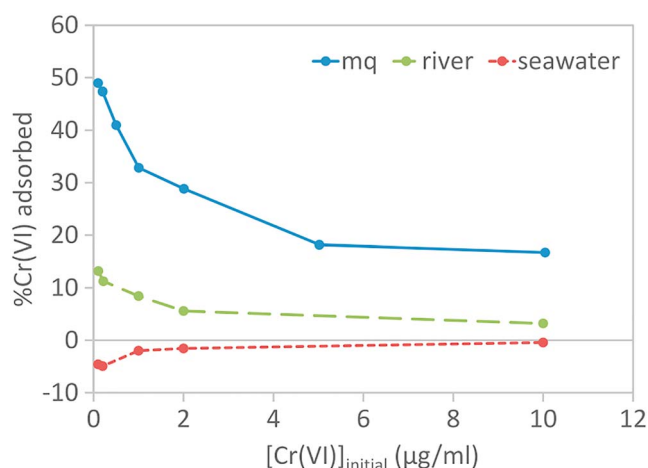
3. Results and Discussion

3.1. Chromium Sorption on Kaolin

The percent of total Cr (VI) sorbed on kaolin in a mq, river, and seawater matrix as a function of initial Cr (VI) concentration is shown in Figure 1. Cr (VI) readily sorbs onto kaolin, increasing its initial bulk Cr concentration and likely altering its bulk Cr isotope composition. The extent of Cr sorption is dependent on the solution composition and decreases from mq to river to seawater, with no evidence for Cr (VI) sorption in seawater. This is likely due to differences in anion concentrations between the different water matrices which compete with Cr (VI) for sorption sites. Due to the alkaline pH of approximately 8 at which the experiments were performed, Cr (VI) competes with OH^- in all experimental setups (~1.7 μg/ml). This competition with OH^- is likely the reason why only

Figure 1. Percentage of total Cr (VI) removed from solution and sorbed on kaolin in a mq (blue), river (green), and seawater matrix (red) as a function of initial Cr (VI) concentration in solution.

40% to 50% of the total Cr (VI) was sorbed in the low concentration mq experiments, despite the high concentration experiment (10 μg/ml) showing a possible concentration drop of up to 1.68 μg/ml. In the river water setup Cr (VI) competes not only with OH^- but also with significant amounts of chloride, sulfate, and nitrate (Table 1), resulting in a decrease in Cr (VI) sorption capacity of approximately 35% at low initial Cr (VI) concentrations and approximately 15% at high initial Cr (VI) concentrations relative to the sorption capacities in mq. However, the fact that Cr (VI) can sorb onto kaolin in a river water matrix suggests that the original Cr isotope composition of clay minerals can potentially be altered during riverine transport. The sorption efficiency of Cr increased with decreasing Cr (VI) concentration in the reactive solutions, with a maximum of 13% of the total dissolved Cr (VI) being sorbed in the 0.1 μg/ml solution experiment. Naturally observed dissolved Cr concentrations in river waters are only as high as 1.5 μg/l, which is significantly lower than the concentrations used in our experiments (D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015; Sun et al., 2019; Wu et al., 2017). Hence, the increasing Cr sorption efficiency of kaolin with decreasing Cr concentration in solution suggests that in a natural runoff, a substantial amount of Cr could be sorbed on suspended kaolinite and potentially other clay minerals as well. In the seawater experimental setup on the other hand, no evidence of Cr sorption was observed, which is likely due to the overwhelming presence of Cl^- (>20,000 μg/ml), which competes with Cr (VI) for sorption sites on kaolin. Hence, we deem it unlikely that Cr (VI) sorbs on clay minerals in a marine setting. Consequently, clay minerals are unlikely to record ambient seawater Cr isotope compositions.

3.2. Langmuir and Freundlich Isotherms

The Langmuir and Freundlich isotherm models were applied to the mq and river water experiments to characterize the sorption of Cr (VI) onto kaolin under these conditions. The Langmuir isotherm model assumes single layer adsorption on a finite number of homogeneous adsorption sites and is expressed in the following equation (Acharya et al., 2017; Ajouyed et al., 2011):

$$\frac{C_e}{q_e} = \frac{1}{(Q_m \times b)} + \frac{C_e}{Q_m}$$

where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the equilibrium amount adsorbed on unit mass of adsorbent, Q_m (mg/g) is the adsorption maximum, and b is the Langmuir bonding energy coefficient.

The Freundlich isotherm model assumes multilayer adsorption onto a heterogeneous surface and is expressed in the following equation (Acharya et al., 2017; Ajouyed et al., 2011):

$$\log q_e = \log K_f + \frac{1}{n} \times \log C_e$$

where K_f (mg/g) and n are the empirical Freundlich constants characterizing the adsorption process.

The linearized Langmuir and Freundlich isotherm plots for the mq and river water experiments are shown in Figure 2, and the Langmuir and Freundlich coefficients calculated from the slope and intercept are given in Table 2. Cr (VI) sorption in a mq matrix fits both adsorption isotherm models well, with a slightly better fit observed for the Freundlich isotherm model ($R^2 = 0.990$). This suggests that Cr (VI) sorbs heterogeneously on kaolin. In the river water matrix the Freundlich isotherm model ($R^2 = 0.991$) returned a significantly better fit than the Langmuir isotherm model ($R^2 = 0.547$), further supporting that kaolin sorbs Cr (VI) on sorption sites with variable adsorption energies. The decreased applicability of the Langmuir isotherm model between the mq and river water matrix experiments is likely due to a higher competition for energetically favorable sorption sites, as not only Cr (VI) but also other anions, such as sulfate, likely sorb on kaolin as well. Hence, the introduction of several competing anions with the river water matrix forced Cr (VI) to sorb more on energetically variable adsorption sites. The empirical Freundlich constants K_f and n can be used to assess the adsorption capacity and favorability of adsorption (Acharya et al., 2017; Ajouyed et al., 2011). Cr (VI) sorption is favorable in both setups as indicated by the Freundlich constants n being >1. However, larger values of K_f and n suggest a higher adsorption capacity, which supports that Cr (VI) sorption in the river matrix was hindered.
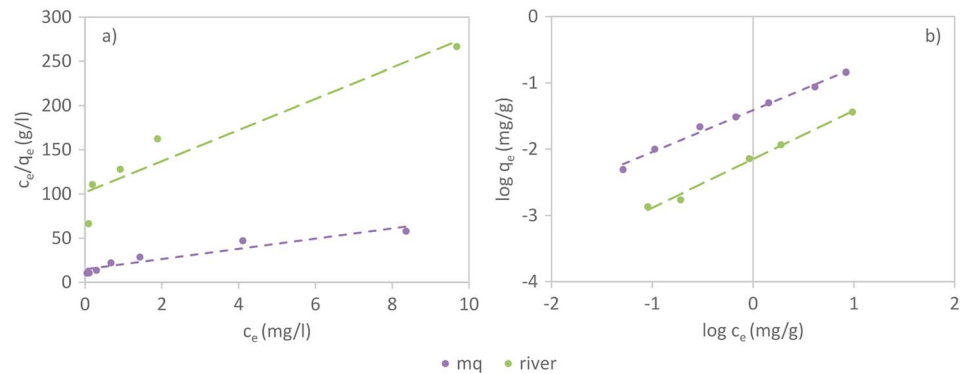
Figure 2. Linearized Langmuir (a) and Freundlich isotherm plots (b) for the sorption of Cr (VI) onto kaolin in a mq (purple) and river water (green) matrix.

3.3. Cr Isotope Fractionation during Sorption

The Cr isotope compositions of the reacted and unreacted liquid and solid phase of the mq and river water batch adsorption experiments are shown in Figure 3. In the mq experiments the δ^{53}Cr values of the reacted solution and kaolin vary significantly at low initial Cr (VI) concentrations, but plateau at initial solution concentrations $\geq 2\,\mu g/ml$, suggesting that Cr isotope fractionation reached equilibrium. At that point no offset can be observed for the δ^{53}Cr value of the reacted Cr solution compared to the unreacted solution, which is characterized by a δ^{53}Cr value of $-0.035‰$. The fact that no offset was observed suggests that either no fractionation occurred or that the amount of Cr removed from the solution was too low to significantly alter the solutions δ^{53}Cr value. The latter is supported by the observation that the reacted kaolin records a δ^{53}Cr value that is ~0.07‰ higher than the unreacted kaolin (with a δ^{53}Cr value of 0.028‰) and ~0.13‰ higher than the unreacted solution. Hence, at high initial Cr (VI) concentrations the reacted kaolin recorded a Cr isotope composition that was significantly different from that of the unreacted Cr solution. The highest potential Cr (VI) sorption capacity of the kaolin was observed at the highest initial Cr (VI) concentration and was approximately 144 μg/g, which is equal to almost 30 μg of Cr being sorbed onto the 200 mg of kaolin used in the experiments (Table 3). This emphasizes the importance of clay minerals as a Cr host in siliciclastic sediments and their potential to remove isotopically light Cr from an ambient freshwater. The fact that the amount of sorbed Cr (VI) still increased between the two highest initital Cr (VI) solution concentrations suggests that Cr (VI) sorption did not reach equilibrium within the concentration range chosen in this study and that the maximum possible Cr (VI) sorption capacity of the kaolin might be even higher than 144 μg/g. At initial solution Cr concentrations lower than 2 μg/ml a positive fractionation was observed for the reacted solution compared to the unreacted solution blank, with the greatest offset of ~0.14‰ observed for an initial Cr concentration of 0.2 μg/ml. This suggests a preferred sorption of isotopically light Cr, probably due to a kinetically favored more rapid reaction of light isotopes relative to heavy ones (Fry, 2006; Watkins et al., 2017). Compared to the unreacted kaolin, the reacted kaolin showed a lower δ^{53}Cr value in the experiments with initial Cr concentrations lower than 2 μg/ml, with a maximal offset of $-0.10‰$ at an initial solution Cr concentration of 0.2 μg/ml. In the experiment with the lowest initial Cr (VI) solution concentration of 0.1 μg/ml, the Cr concentration of the reacted kaolin increased by 4.9 μg/g, more than doubling its initial bulk Cr concentration of ~4 μg/g. Hence, it is not surprising that although only ~50% of the initial Cr (VI) was sorbed, the addition of ~1 μg of Cr (VI) in this experimental setup was sufficient to completely overprint the initial δ^{53}Cr value of the kaolin. Compared to the isotopic composition of the unreacted solution, the δ^{53}Cr values of the reacted kaolin are slightly lower in the 0.2 and 0.5 μg/ml solution experiments, but higher in experiments using a Cr (VI) solution with a concentration $\geq 1\,\mu g/ml$. This suggests a shift in Cr uptake from dominantly light Cr to a mix of isotopically light and heavy Cr from solution, likely because the increased initial Cr (VI) concentration of the solution resulted in a shift from a kinetically driven reaction toward an equilibrium reaction. Kinetic fractionation reactions describe an

Table 2

Freundlich and Langmuir Coefficients for the Sorption of Cr (VI) on Kaolin in a mq and River Water Matrix

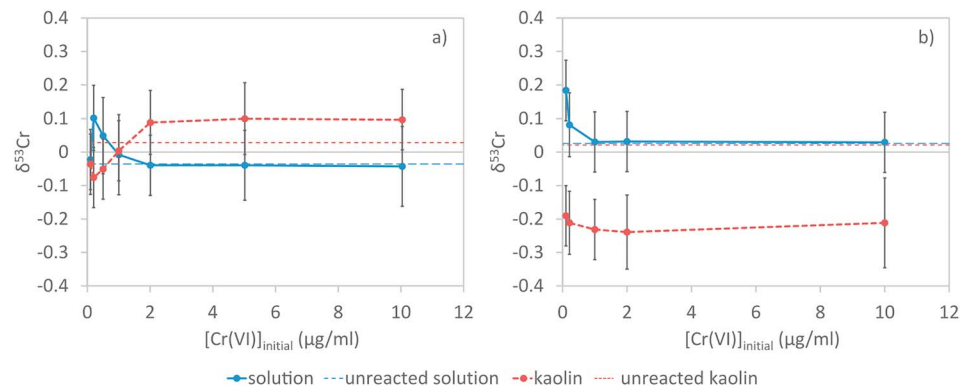| Setup	Langmuir			Freundlich		
	Q_m	b	R^2	K_f	n	R^2
mq	0.173	2.546	0.908	0.039	1.580	0.990
River	0.168	17.099	0.547	0.009	1.178	0.991

Figure 3. Bulk Cr isotopic composition of the reacted solutions (blue) and reacted kaolin (red) as a function of initial Cr (VI) concentration for the mq water (a) and river water (b) experiments. The thin dashed lines mark the bulk Cr isotopic composition of the unreacted mq and river solution (blue) and unreacted kaolin (red).

incomplete isotopic exchange and result in an accumulation of the more reactive, usually lighter isotopes in the product, while equilibrium reactions result in an accumulation of heavier isotopes where bonds are strongest (e.g., Fry, 2006; Schauble, 2004). As surface site bonds are strong, it is unsurprising that the shift to equilibrium conditions with increased initial solution Cr (VI) concentrations resulted in an increased uptake of isotopically heavier Cr. In the experiment with the lowest initial Cr (VI) concentration (0.1 μg/ml), the reacted kaolin showed no isotopic offset compared to the δ^{53}Cr value of the unreacted solution. The fact that the negative δ^{53}Cr offset between the reacted kaolin and unreacted solution decreases below initial Cr (VI) concentrations of 0.2 μg/ml suggests that at low dissolved Cr (VI) concentrations, the kaolin can record the Cr composition of the ambient solution as was observed for the experiment using a 0.1 μg/ml Cr (VI) solution. Considering that naturally occurring dissolved Cr concentrations in rivers are commonly 2 orders of magnitude lower than the lowest initial solution Cr (VI) concentration used in our experiments, this suggests that Cr (VI) sorption onto kaolinite and potentially other clay minerals can record the Cr isotope composition of a respective ambient water. However, we want to emphasize that our experiments, compared to potential natural processes, only ran for short time periods of 24 hr. Longer equilibration periods might result in isotopic fractionations that are unaccounted for by our experimental setup.

The use of a competing river water matrix, instead of mq, reduced the maximum observed adsorption capacity of Cr (VI) on kaolin by more than 100 μg/g to ~36 μg/g (Table 3). The relationship between the chromium isotopic composition of the reacted river water solutions and their initial Cr concentration appears to follow the same trend as the reacted mq solutions but is shifted to lower δ^{53}Cr values (Figure 3). The isotopic composition of the reacted river waters shows no isotopic offset compared to the unreacted river water, which is characterized by a δ^{53}Cr value of 0.025‰, at initial solution Cr (VI) concentrations of 1 μg/ml or higher. This suggests that Cr fractionation reached equilibrium. At lower initial solution Cr (VI)

Table 3
Change in Cr Concentration in the Solution (μg/ml) and Kaolin (μg/g) As Well As the Corresponding Mass of Cr (μg) Removed From the 20 ml of Solution and Added to the 200 mg Kaolin Used in the Experiments Are Given for the Different Initial Cr (VI) Concentration Experiments of the mq and River Water Experimental Setups

Phase	Cr (VI)	0.1 μg/ml	0.2 μg/ml	0.5 μg/ml	1 μg/ml	2 μg/ml	5 μg/ml	10 μg/ml
mq water setup								
Cr (VI) solution	Δ concentration (μg/ml)	−0.05	−0.10	−0.21	−0.33	−0.58	−0.91	−1.68
	Δ mass (μg)	−0.98	−1.90	−4.12	−6.60	−11.58	−18.26	−33.62
Kaolin phase	Δ concentration (μg/g)	4.90	9.99	21.72	30.65	50.05	87.27	144.24
	Δ mass (μg)	0.98	2.00	4.34	6.13	10.01	17.45	28.85
River water setup								
Cr (VI) solution	Δ concentration (μg/ml)	−0.01	−0.02		−0.08	−0.11		−0.32
	Δ mass (μg)	−0.27	−0.48		−1.69	−2.23		−6.39
Kaolin phase	Δ concentration (μg/g)	1.36	1.73		7.17	11.63		36.32
	Δ mass (μg)	0.27	0.35		1.43	2.33		7.26

concentrations, a positive shift in the δ^{53}Cr value was observed, reaching a maximum offset of 0.16‰ in the experiment with the lowest initial Cr (VI) concentration (0.1 µg/ml), supporting the preferred sorption of isotopically lighter Cr (VI). The reacted kaolin recorded an average offset of −0.24‰ compared to both the unreacted solution (0.025‰) and the unreacted kaolin (0.021‰). This demonstrates that even a small increase in Cr concentration of 1.4 µg/g in the kaolin can completely overprint the δ^{53}Cr value of the unreacted kaolin, which had an initial Cr concentration of ~4 µg/g. Further, this supports that kaolin also sorbs isotopically light Cr preferentially in a matrix with competing anions, such as provided by the river water in our experiment. This supports that the bulk Cr isotope composition of particulate kaolin can be shifted by Cr (VI) sorption during riverine transport. The smallest isotopic offset was observed in the experiment conducted with an initial solution Cr (VI) concentration of 0.1 µg/ml, while the largest offset resulted from the experiment with an initial concentration of 2 µg/ml in solution. However, the offsets between the reacted kaolin and unreacted solution of the different Cr (VI) concentration experiments range only from −0.21‰ to −0.26‰ and are therefore within analytical error from each other. The significant increase in observed negative δ^{53}Cr offset between the reacted kaolin and the unreacted solution from the mq to the river water experiment is likely due to an increased competition for sorption sites in the river water compared to mq. The introduction of significant amounts of chloride, sulfate, and nitrate (Table 1) probably resulted in a very selective sorption of lighter Cr isotopes, which react faster than heavier Cr isotopes. At the applied initial solution Cr (VI) concentrations the river water experiments did not provide any evidence that kaolin can record the δ^{53}Cr value of the water in which sorption took place. However, as natural rivers show a wide range in δ^{53}Cr with values of up to 1.68‰ (D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015; Sun et al., 2019; Wu et al., 2017), detrital clay particles sorbing Cr (VI) with the maximal observed offset would still record positively fractionated values of over 1‰. Further, as Cr concentrations in rivers are commonly 2 orders of magnitudes lower than the lowest initial Cr concentration used in the experiments, it is likely that under natural conditions, a higher percentage of the total Cr (VI) could be sorbed, which could result in smaller or even no detectable isotope offsets between kaolin particulates and ambient river water.

3.4. Leaching of Cr from Kaolin

A bulk dissolution and a four step leach method were applied to a reacted kaolin of the 0.1 and 5 µg/ml experimental setups using mq. The δ^{53}Cr values and total Cr mass of the bulk unreacted kaolin, bulk reacted kaolin, and different leach steps are plotted in Figure 4. To compare the results from the sequential leach method to the bulk dissolutions of the reacted kaolin, bulk Cr masses, and bulk δ^{53}Cr values were calculated from all four leach steps by summing up their respective Cr masses and calculating the weighted sum of the δ^{53}Cr values of the leaches with respect to their Cr masses. The calculated bulk isotope signatures and bulk Cr masses match the Cr mass and δ^{53}Cr value of the measured bulk kaolin in both setups, indicating that a complete removal of any Cr present in the solid phase was achieved by the leaches. The experiments yielded similar leaching and fractionation patterns for the experimental setups using 0.1 and 5 µg/ml Cr mq solutions, but with higher released amounts of Cr and greater isotopic offsets observed for the 5 µg/ml setup. The last two leach steps using HF and aqua regia yielded similar amounts of Cr regardless of the initial solution Cr (VI) concentration of the experimental setup. The δ^{53}Cr values of the last two leach steps further returned statistically indistinguishable δ^{53}Cr values. Combined, the released Cr mass and δ^{53}Cr values of the HF and aqua regia steps match the Cr mass and δ^{53}Cr value of the unreacted kaolin well (0.84 µg; 0.028‰ ± 0.09‰), suggesting that these acids mobilized Cr from the kaolin lattice. Hence, the Cr sorbed during the experiment was likely completely removed in the first two leach steps. The initial leach step using 0.5M HCl removed most Cr from the kaolin, yielding 38% (0.72 µg) and 60% (11.17 µg) of the bulk Cr for the leachates of the 0.1 and 5 µg/ml Cr setups, respectively. Further, 0.5M HCl preferentially leached isotopically heavy Cr resulting in a positive isotopic offset of 0.15‰ compared to the δ^{53}Cr value of the unreacted kaolin for the 0.1 µg/ml Cr setup which increased to a δ^{53}Cr value of 0.73‰ for the 5 µg/ml Cr setup. The leachates of the second leach using 6M HCl contained 22% (0.42 µg) and 34% (6.18 µg) Cr in the 0.1 µg/ml Cr and 5 µg/ml Cr experiment, respectively. Their Cr isotopic composition was dominated by isotopically lighter Cr resulting in a negative offset compared to the unreacted kaolin of −0.29‰ and −0.93‰ for the 0.1 and 5 µg/ml experiments, respectively. The significant difference in isotopic offset between the first and second leach step is likely indicative of different sorption mechanism. Metal
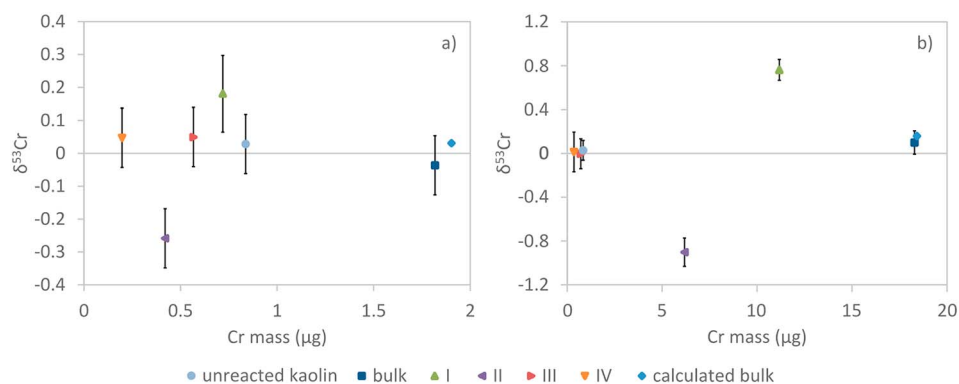
Figure 4. $\delta^{53}Cr$ (‰) values versus the total released Cr mass (µg) for the bulk and leach dissolutions of the reacted kaolin of the experimental setups using an initial solution Cr (VI) concentration of 0.1 (a) and 5 µg/ml (b). $\delta^{53}Cr$ and the released Cr mass were measured for (1) the bulk dissolution of the unreacted kaolin, (2) the bulk dissolution of the reacted kaolin, and (3) the sequential leaches I to IV of the reacted kaolin. Further, a bulk $\delta^{53}Cr$ value and Cr mass was calculated from leach I-IV. The leaching acids used were 0.5M HCl, 6M HCl, HF, and aqua regia for leach step I to IV, respectively.

sorption on a sorbent is commonly fast initially and then significantly slows down with progress of the sorption (Covelo et al., 2004; Strawn et al., 1998). While the fast initial sorption is likely through electrostatic attraction, the following slower sorption can be due to diffusion and sorption in porous media, sorption on sites characterized by lower reactivity, and/or surface precipitation (Covelo et al., 2004; Fuller et al., 1993; Strawn et al., 1998). We therefore hypothesize that the initial 0.5M HCl leach likely recovered the electrostatically bound Cr. As metal sorption on kaolinite is mainly limited to the surface (Rosales-Landeros et al., 2013) and as the mq solution does not support significant surface precipitation due to a limited ion availability, the 6M HCl leach likely mobilized Cr bound to sorption sites of lower reactivity.

3.5. Implications for Using Cr Stable Isotopes in Black Shales as a Paleoredox Archive

Shale standards show a wide range in Cr concentration (e.g., 40–280 µg/g in Govindaraju, 1994), of which based on our data, a large proportion may be hosted in the clay mineral phase. It is unclear to what extent the Cr pool of clays consists of Cr incorporated in the mineral structure during clay mineral formation or later during cation exchange and Cr sorbed onto inner and outer sorption sites. Considering that the acid washed kaolin used in this study only had a Cr concentration of ~4 µg/g, Cr in the mineral structure seems to make up a rather low proportion. The sorbed Cr on the other hand can potentially make up a large proportion of the clay hosted Cr pool, as the sorbed Cr concentrations were up to 36 (~144 µg/g) and 9 (~36 µg/g) times higher than the incorporated Cr concentrations in the mq and river water experiments, respectively (Table 3). This suggest that a large proportion of the clay hosted Cr in black shales might not be sourced from weathered igneous rocks, which complicates the use of black shales as a paleoredox archive. However, the sorption capacity of the kaolin used in this study was artificially enhanced through acid washing. In a natural setting many sorption sites would likely be occupied, reducing the total Cr sorption capacity. Cr (VI) adsorption experiments on clays showed a marginal increase of ~8% in the cation exchange capacity of kaolinite due to acid activation with H_2SO_4 (Bhattacharyya & Sen Gupta, 2006). Low adsorbed Cr concentrations of only up to 1 µg/g reported for the suspended particle load of the Connecticut River (Sun et al., 2019) further support that the natural sorption capacity of clays is likely lower than the 36 µg/g we observed for a riverine setting. However, it is important to note that the composition of the particle load is unknown and therefore likely a poor representative of the natural sorption capacity of clays. Water pH is likely to play an important role when considering the sorption capacity of clays in a natural setting as well. Our experiments only considered a narrow pH range. The Cr (VI) doped mq solutions were adjusted to a pH of 8 to simulate seawater conditions, while the river water Cr (VI) solutions have an only slightly lower pH (7.4). Natural river waters, as well as groundwater and soils, show a wider range in pH, suggesting a variable natural sorption capacity dependant on the environmental conditions, which is supported by an increase

in Cr (VI) sorption on clays with decreasing pH observed in environmental remediation studies (e.g., Ajouyed et al., 2011; Bhattacharyya & Sen Gupta, 2006).

The sorption experiments reveal that not only the Cr concentration but also the isotopic composition of detrital clays can potentially be altered through Cr (VI) sorption. This stands in contrast to the common assumption that δ^{53}Cr values of detrital silicates fall within the unfractionated igneous baseline. However, Cr (VI) sorption is unlikely to result in the recording of the δ^{53}Cr value of ambient seawater in clays as no evidence for Cr (VI) sorption was observed in an ocean water setting. Instead, the igneous baseline δ^{53}Cr value might be overprinted during riverine transport. River waters analyzed to date show a wide range in δ^{53}Cr values between $-0.33‰$ and $1.7‰$ (D'Arcy et al., 2016; Frei et al., 2014; Paulukat et al., 2015; Sun et al., 2019 ; Wu et al., 2017). Particulate clays suspended in rivers are likely to record part of this variability through sorption processes. This is supported by a wide range in δ^{53}Cr value measured for the suspended particle load of the Connecticut river of $-0.11‰$ to $0.20‰$ (Sun et al., 2019; Wu et al., 2017). Hence, the δ^{53}Cr values of detrital clay washed into the oceans by riverine transport is not expected to show a homogeneous, igneous-like Cr isotope signature, which complicates detrital corrections and renders the use of bulk black shale δ^{53}Cr values to reconstruct the δ^{53}Cr values of past seawater problematic. Further, our experiments reveal that if any Cr is sorbed to clay, it is already partially leached with a weak acid leach (e.g., 0.5M HCl). This asks for caution when applying leaching approaches to attack authigenic Cr hosting mineral phases (such as carbonates and phosphates) in shales as these leached fractions may be severely contaminated by clay-sorbed Cr.

4. Conclusion

The Cr (VI) sorption experiments reveal that kaolin readily sorbs Cr, which changes both its Cr concentration and isotopic composition. This stands in contrast to the common assumption that δ^{53}Cr values of detrital silicates should fall within the unfractionated igneous baseline range. The sorption of Cr (VI) is best described using the Freundlich isotherm model ($R^2 = 0.99$), which reveals that sorption of Cr on kaolin is energetically favorable and that Cr sorbs on energetically heterogeneous sorption sites. At low initial solution Cr (VI) concentrations the sorption of Cr on kaolin is kinetically limited. Cr sorption on kaolin is further reduced through the introduction of a competing matrix from 144 μg Cr/g kaolin in the mq setup to 36 μg Cr/g kaolin in the river setup. In the seawater experiment, however, no evidence for Cr sorption was observed, suggesting that the δ^{53}Cr value of ambient seawater probably cannot be recorded through Cr (VI) sorption. Instead, our experiments reveal that the Cr isotope composition of clay minerals can potentially be altered through sorption processes during riverine transport. Further, mobilized Cr (VI) might sorb on clay minerals in soils and so change the isotopic composition of weatherable detrital material. This renders the use of clay δ^{53}Cr values for the reconstruction of δ^{53}Cr values of past seawater problematic and complicates the use of chromium stable isotopes in black shales to reconstruct seawater redox. Likewise, our results ask for caution when calculating authigenic Cr fractions for shale leaches as detrital corrections thus far commonly use the igneous baseline δ^{53}Cr value to correct for detrital contributions in leaches.

However, it is important to note that we used highly simplified batch experiments to model a complex natural system, leaving several questions unanswered: First, Cr (VI) sorption processes and capacities are likely dependant on the sorbent. Other clays than kaolinite, for example, illite or chlorite, might have a higher capacity to incorporate Cr into their crystal structure as they also include interior sorption sites and might behave differently, both in a riverine and oceanic setting. Second, in this study we only considered Cr (VI) sorption alone. In the presence of a reducing agent for example, Cr (VI) can be reduced to Cr (III), which can potentially be incorporated into respective crystal lattices through cation exchange reactions. Under such circumstances, the sorption capacity of Cr in clays can be drastically increased, even in seawater. For example, Fe-rich sheet silicates, such as biotite or chlorite, have the potential to reduce and sorb Cr (VI) through the release of Fe (II; Brookshaw et al., 2014; He et al., 2005), and humic acids, which are commonly present in natural waters, have been shown to increase the adsorption of Cr (VI) onto kaolinite (Li et al., 2010). Finally, the chromium isotope compositions of detrital silicates can likely be altered by other processes than just sorption, such as recrystallization or diagenetic alteration. Hence, the effect of such processes and the effect of Cr sorption in a natural setting need to be further explored before Cr stable

isotopes in black shales can be safely applied to reconstruct redox changes in the marine realm that ultimately could be linked to climate-induced release patterns on land.

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