

Using Chromium Stable Isotope Ratios To Quantify Cr(VI) Reduction: Lack of Sorption Effects

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Chromium stable isotope values can be effectively used to monitor reduction of Cr(VI) in natural waters. We investigate effects of sorption during transport of Cr(VI) which may also shift Cr isotopes values, complicating efforts to quantify reduction. This study shows that Cr stable isotope fractionation caused by sorption is negligible. Equilibrium fractionation of Cr stable isotopes between dissolved Cr(VI) and Cr(VI) adsorbed onto γ - Al_2O_3 and goethite is less than 0.04‰ ($^{53}\text{Cr}/^{52}\text{Cr}$) under environmentally relevant pH conditions. Batch experiments at pH 4.0 and pH 6.0 were conducted in series to sequentially magnify small isotope fractionations. A simple transport model suggests that adsorption may cause amplification of a small isotope fractionation along extreme fringes of a plume, leading to shifts in $^{53}\text{Cr}/^{52}\text{Cr}$ values. We therefore suggest that isotope values at extreme fringes of Cr plumes be critically evaluated for sorption effects. A kinetic effect was observed in experiments with goethite at pH 4 where apparently lighter isotopes diffuse into goethite clumps at a faster rate before eventually reaching equilibrium. This observed kinetic effect may be important in a natural system that has not attained equilibrium and is in need of further study. Cr isotope fractionation caused by speciation of Cr(VI) between HCrO_4^- and CrO_4^{2-} was also examined, and we conclude that it is not measurable. In the absence of isotope fractionation caused by equilibrium speciation and sorption, most of the variation in $\delta^{53}\text{Cr}$ values may be attributed to reduction, and reliable estimates of Cr reduction can be made.

Introduction

Chromium is a redox-active metal that is a common anthropogenic contaminant in surface water and groundwater (1–3). The widespread use of chromium in a variety of industrial processes, including electroplating, leather tanning, and wood preservation (4), has resulted in a substantial environmental problem, although natural sources of Cr can be important as well (5). For any remediation design to be effective, it is important to be able to identify the source(s) and to accurately monitor chromium attenuation.

Chromium occurs in nature as Cr(VI) and Cr(III). In natural waters, Cr(VI) exists either as bichromate (HCrO_4^-) or chromate (CrO_4^{2-}). It is highly soluble and extremely mobile, adsorbs only on Fe/Al hydrous oxides, and is a suspected carcinogen. Cr(III), on the other hand, is relatively insoluble, often coprecipitates with Fe(III)-oxyhydroxides (6), adsorbs strongly, is relatively immobile, and has a much lower toxicity. Redox conditions and reactions therefore control the mobility and hence effective toxicity of Cr in aqueous solutions. Most Cr(VI) remediation designs focus on in situ reduction of Cr(VI) to Cr(III), by using reactive barriers (7, 8) or injection of reducing agents (9). Monitoring of Cr(VI) reduction is therefore critical.

Our previous study demonstrated that Cr stable isotope measurements may provide an effective and quick method to monitor Cr(VI) reduction in ground and surface waters (10). Cr(VI) reduction causes an enrichment of the lighter isotopes in the reduced product at any given instant. We monitor this enrichment via the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio, and shifts of 3.5‰ were observed during Cr(VI) reduction by magnetite and sediment slurries. With this enrichment value known, the extent of reduction can be calculated, provided the isotopic composition of the initial source is known. The extent of reduction calculated using this method assumes that in a given system Cr stable isotopes are only fractionated by reduction, and other transport processes can be neglected or accurately accounted for.

Sorption of Cr(VI) likely involves a small isotopic fractionation. It is generally observed that, at equilibrium, heavier isotopes tend to partition preferentially into more strongly bonded environments (11). The bonding environment around adsorbed Cr(VI) may differ slightly from that of Cr(VI) in solution, and thus the heavier and lighter isotopes may fractionate, resulting in slight differences in the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio between the adsorbed and dissolved Cr. If isotope fractionation caused by sorption results in $^{53}\text{Cr}/^{52}\text{Cr}$ shift of roughly 0.5‰ or more in the dissolved Cr(VI), it could complicate attempts to quantify reduction.

Cr(VI), present as the bichromate (HCrO_4^-) form, adsorbs to hydrous oxides of Al and Fe in the pH range from pH 6 to pH 2. Cr(VI) forms an inner sphere complex on goethite and would be similar on γ - Al_2O_3 (2). Both γ - Al_2O_3 and goethite have a net positive surface charge, and Cr(VI) oxyanions have an affinity for such sites. Field studies show adsorption of Cr(VI) is maximum in the pH range of 4–6 and decreasing sharply in the neutral range (12).

Previous studies have examined isotope fractionation of S, Se, and Mo oxyanions during sorption. The S studies were conducted using goethite and soil samples, and Se isotope studies were conducted using Fe hydroxide (13, 14). Both the S and Se studies concluded that their isotopes are not fractionated to a measurable extent by sorption. However, a recent study reports an equilibrium fractionation of Mo isotopes, which can be as large as 2‰ during sorption of Mo on manganese oxides (15).

We expect that small isotopic fractionations induced by sorption to be magnified as advective transport proceeds. Analogous effects have been observed with Fe, Ca, Cu, and Zn isotopes migrating through ion-exchange resins (16–19). An equilibrium isotope fractionation can be equated with ^{53}Cr and ^{52}Cr having different sorption coefficients (K_d 's) and hence different retardation rates (16). During transport, one isotope would be retarded more than the other, causing a change in the relative concentrations of the two isotopes and an isotope ratio difference between the leading edge of the plume and the plume core. This difference would increase

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TABLE 1. Results and Experimental Details^a

solid/pH	pH	hours allowed for equilibration	magnification	total change in $\delta^{53}\text{Cr}(\text{‰})$	fractionation $1000 \ln \alpha^b$	fractionation factor ^b α
alumina	4	6–12	4.5	-0.2 ($n=2$)		1.00000
alumina	6	6–12	4.9	0.0 ($n=2$)		1.00000
goethite	6	6–12	4.8	0.1 ($n=2$)		1.00000
goethite	4	2	4.9	3.5 ($n=3$)	0.7	0.99930
goethite	4	12	4.7–5.1	1.8 ($n=5$)	0.35	0.99965
goethite	4	24	5.1	-0.2 ($n=2$)		1.00000

^a n = number of samples. ^b Fractionation factor α is equal to the isotope ratio of dissolved fraction \div ratio of sorbed fraction and is approximated by the relation $\delta^{53}\text{Cr}_{\text{sorbed}} - \delta^{53}\text{Cr}_{\text{dissolved}} = 1000 \ln \alpha$.

as the plume migrates. Therefore, a variation in $^{53}\text{Cr}/^{52}\text{Cr}$ ratios may result from Cr(VI) transport and sorption in the absence of reduction.

In this study, we measure Cr isotope fractionation during Cr(VI) sorption on $\gamma\text{-Al}_2\text{O}_3$ and goethite in laboratory batch experiments. A sequential enrichment technique was employed to ensure fractionations as small as 0.04‰ (using z -test or t -test) were resolvable given an analytical precision of 0.2‰ (2σ).

Materials and Methods

Experimental Methods. Previous studies have examined reduction of Cr(VI) by organic and inorganic reductants in the presence of mineral surfaces. We modeled our experiments based on the control experiments of these previous studies, wherein no reducing agent was used (20, 21). We determined isotope fractionation caused by Cr(VI) sorption on aluminum oxide, $\gamma\text{-Al}_2\text{O}_3$ (Aluminum Oxid C; Degussa Corporation), and α -goethite (Bayferrox 910, Standard 86; Bayer AG) (20). We chose $\gamma\text{-Al}_2\text{O}_3$ and goethite because sorption of Cr(VI) on the surfaces of these two minerals is well characterized and reduction of Cr(VI) to Cr(III) under similar experimental conditions was not detected by previous studies (2, 20–22). Cr(VI), present as CrO_4^{2-} and HCrO_4^- anions in nature, does not adsorb onto negatively charged surfaces of soils, clays, and sediments (2, 20, 23) but is expected to sorb strongly on Al and Fe hydrous oxides in natural settings. The $\gamma\text{-Al}_2\text{O}_3$ has a BET surface area of 96 m^2/g and a pH_{pzc} (pH where the surface potential is zero) of 8.9. The goethite has a BET surface area of 17.5 m^2/g and a pH_{pzc} of 7.5–7.8. The experiments were conducted aerobically using well-mixed suspensions in 50 mL polypropylene centrifuge tubes at pH 4.0 and pH 6.0. These pH values were chosen based on relevant environmental conditions and covers the pH range of maximum sorption of Cr(VI) on Al and Fe hydrous oxides (2, 12, 22). An acetate solution (1 mM) was used to buffer the pH. Initial adjustments of pH were made by additions of sodium hydroxide. The suspensions were prepared in a 1 mM KCl solution, and initial Cr(VI) concentrations were approximately 200 mg/L.

For Al_2O_3 and goethite, Cr(VI) sorption equilibrium is reached rapidly under these experimental conditions (20). The rate of equilibration was confirmed by performing batch experiments and monitoring dissolved Cr(VI) concentrations (Figure 1). Based on the results of these experiments, the amount of sorbent was chosen such that approximately 50% of the Cr(VI) would be adsorbed. The solids were kept in suspension by shaking on a rotary shaker at 175 oscillations per minute. After equilibration (6–24 h), the solution was decanted and filtered (0.2 μm), and a new batch of sorbent was added to the solution to cause a further sorption of 50% of the remaining Cr(VI).

This process was repeated 10 or 11 times to sequentially shift the isotope ratio in the solution phase. At 50% sorption, each step enriches the solution by one-half of the equilibrium fractionation, and thus the isotopic shift between the final

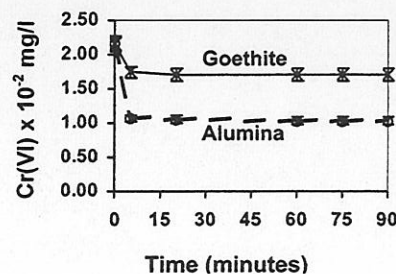


FIGURE 1. Concentration equilibrium curves show an almost instantaneous decrease in dissolved Cr(VI) caused by sorption with no further change.

and initial solution was approximately five times the isotopic fractionation between adsorbed and dissolved Cr(VI). This sequential enrichment process allows for fractionation of 0.04‰ to be detected. The exact amplification factor varied slightly between experiments and is given in Table 1. At each step, dissolved Cr(VI) concentrations were determined, and the penultimate and last steps were analyzed for $\delta^{53}\text{Cr}$ values in duplicate; solutions from earlier steps were also analyzed in some cases to provide additional confirmation of results.

Analytical Methods

Cr Concentration Analysis. Dissolved Cr(VI) concentrations were analyzed spectrometrically at 540 nm using a diphenylcarbazide reagent (24). We monitored matrix interferences by standard additions and none were observed.

Isotope Analysis. Methods for determination of Cr isotope ratios are described in detail elsewhere (10). Briefly, we determine variations in the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio and express results as per mil deviations from a standard

$$\delta^{53}\text{Cr} (\text{‰}) = \frac{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}}\right)_{\text{sam}} - \left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}}\right)_{\text{std}}}{\left(\frac{^{53}\text{Cr}}{^{52}\text{Cr}}\right)_{\text{std}}} \times 1000 \quad (1)$$

where sam and std refer to sample and the NIST SRM 979 standard, respectively. External measurement precision is $\pm 0.2\text{‰}$. We use a double isotope spike technique to account for any isotopic fractionation during sample purification and mass spectrometry. Two stable spike isotopes of ^{50}Cr and ^{54}Cr are added to the sample in known proportions (14, 25, 26), and the $^{54}\text{Cr}/^{50}\text{Cr}$ ratio is monitored to determine the discrimination or measurement bias. The double spike is added before any sample preparation process to correct for any fractionation during the anion exchange purification process as well as during mass spectrometry. The double-spike solution is added in the same valence(s) as the Cr in the sample and passed through anion exchange columns as described previously (10). We elute cations and uncharged species with 0.1 N HCl. The retained Cr(VI) is then reduced to Cr(III) with 0.1 M H_2SO_3 and eluted with 8 mL of 0.1 N HCl.

Some residual SO_3^{2-} in the sample is oxidized to SO_4^{2-} and removed via a second anion exchange column. After purification, the sample, typically 250–500 ng Cr, is mixed with 20 μg of colloidal silica and 0.6 μL of a saturated boric acid solution and loaded onto a rhenium filament. Mass spectrometry is performed on a VG 354 mass spectrometer. Some duplicate isotope analyses were performed on a Finnigan MAT 261 at the U.S. Geological Survey, Menlo Park, CA.

Results and Discussion

Results. Sorption reached equilibrium within the first 5 min. Figure 1 shows the concentrations of the batch experiments used to determine equilibration rates. Within 2–5 min of adding 1.0 g of the solid phase to the solution, Cr(VI) concentrations decreased by approximately 50% for $\gamma\text{-Al}_2\text{O}_3$ and 20% for goethite, and no significant change was measured up to 90 min later. As also observed in previous studies, based on the absence of any decrease in Cr(VI) concentrations after the initial sorption phase, we conclude that no Cr(VI) reduction occurred. The pH did not change within the course of the experiment.

As previously mentioned, the difference in the isotope values of Cr(VI) in the initial solution and that in the leftover Cr(VI) after the 10 steps is a measure of the equilibrium isotope fractionation amplified approximately 5 times. The experiments conducted with $\gamma\text{-Al}_2\text{O}_3$ at pH 4.0 and 6.0 and goethite at pH 6.0 show no significant shifts in $\delta^{53}\text{Cr}$ between the Cr(VI) in the initial solutions and the residual Cr(VI) in the solutions after the 10 sorption steps (Table 1). Therefore, any Cr stable isotope fractionation between Cr(VI) in solution and Cr(VI) adsorbed is less than 0.04‰, the minimum resolvable fractionation. For the experiments with goethite at pH 4.0, the results show a total isotopic shift of 3.5‰ when the experiments were allowed to equilibrate for only 2 h, 1.2‰ when the equilibration time was 12 h, and no fractionation at 24 h. We therefore conclude that sorption of Cr(VI) does not cause any isotope fractionation under equilibrium conditions.

Causes of Kinetic Effects. Given that Cr isotopes are not fractionated during adsorption on $\gamma\text{-Al}_2\text{O}_3$ at pH 4.0 and 6.0 nor on goethite at pH 6.0, we suggest that equilibrium fractionation between adsorbed Cr(VI) and dissolved Cr(VI) is less than 0.04‰. Sorption on goethite at pH 4.0 showed measurable fractionations only for experiments with shorter equilibration times, apparently in response to a kinetic effect. The suspensions at pH 4.0 had visible clumping, unlike the suspensions at pH 6.0. The clumping would increase the time needed for diffusive equilibration and could be responsible for the observed kinetic effects. Lighter isotopes diffuse faster than heavier isotopes in vapor phase (11) and solutions (27). Therefore, ions with the lighter isotopes may diffuse into the clumps at a faster rate, relative to the ions with heavier isotopes. The solution will then be enriched in the heavier isotopes. Eventually, within 24 h, the system reaches isotopic equilibrium, and no measurable isotope fractionation is observed. The observed kinetic effect at pH 4.0 could also be caused by a small reduction of Cr(VI) to Cr(III), followed by oxidation back to Cr(VI). Reduction to Cr(III) may be instantaneous in the presence of Fe^{2+} , followed by a slower oxidation step. If this is the case, within 24 h all the reduced Cr(III) apparently was oxidized back to Cr(VI), as no isotope fractionation was observed. However, as goethite is an Fe^{3+} mineral and the presence of Fe^{2+} in solution was not detected, the possibility of reduction of a small fraction of Cr(VI) followed by oxidation is considered unlikely.

Amplification of Isotopic Fractionation during Transport. A small equilibrium isotope fractionation between adsorbed and dissolved Cr(VI) may result in a relatively large variation in the isotope values in the leading edge of a Cr(VI)

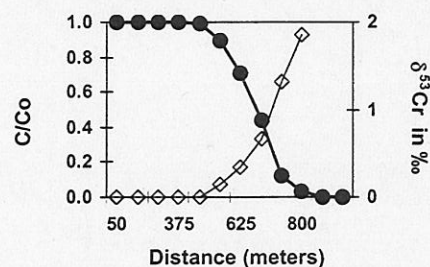


FIGURE 2. Sorbing front. Cr(VI) normalized concentrations (filled circles) and corresponding isotope values (diamonds).

plume as the Cr is transported. As mentioned above, this process is analogous to the transport of elements such as Ca, Fe, Cu, and Zn through an anion exchange column, where a very small isotopic fractionation induced by adsorption results in relatively large isotopic shifts in the column effluent (16–19). The amplification during transport can be modeled using solute transport equations, treating the two isotopes of Cr, ^{53}Cr , and ^{52}Cr as independent solutes. To express the magnitude of the equilibrium isotope fractionation between adsorbed and dissolved Cr(VI), we define a fractionation factor α

$$\alpha = \frac{[^{53}\text{Cr}]_{\text{sorbed}}/[^{52}\text{Cr}]_{\text{sorbed}}}{[^{53}\text{Cr}]_{\text{solution}}/[^{52}\text{Cr}]_{\text{solution}}} \quad (2)$$

where $[^{53}\text{Cr}]$ and $[^{52}\text{Cr}]$ are the concentrations of the individual isotopes and sorbed and solution refer to the sorbed fraction and the fraction in solution, respectively.

For this model, we assume linear sorption isotherms. The sorption coefficients for the two isotopes are

$$K_d^{53} = [^{53}\text{Cr}]_{\text{solution}}/[^{53}\text{Cr}]_{\text{sorbed}} \quad (3)$$

$$K_d^{52} = [^{52}\text{Cr}]_{\text{solution}}/[^{52}\text{Cr}]_{\text{sorbed}} \quad (4)$$

where K_d^{53} and K_d^{52} are the sorption coefficients of ^{53}Cr and ^{52}Cr , respectively.

From eqs 2–4, the equilibrium fractionation can be related to the K_d 's by

$$\alpha = K_d^{53}/K_d^{52} \quad (5)$$

Thus, for a given equilibrium isotope fractionation, the ratio of the retardation factors for the heavy and light isotopes can be obtained. Using the analytical solution of Ogata and Banks (1961) as given in ref 28 for a one-dimensional transport model (first-type boundary condition) we determined the change in $\delta^{53}\text{Cr}$. A groundwater velocity of 1.0 m/day, a dispersion coefficient of 10 m^2/s , and a retardation factor of 5 for one of the isotopes were chosen. The retardation factor for the second isotope was calculated using the relation (5) above for $\alpha = 0.9999$. The relative difference in retardation between the two solutes, ^{53}Cr and ^{52}Cr , is too small to be seen by plotting both transport curves. We therefore show, in Figure 2, a Cr plume concentration front after approximately 1300 days and the corresponding isotope ratios relative to the initial value, along the front. Figure 3 shows the change in the isotope ratio near the leading edge of the plume ($C/\text{Co} = 0.3$) as the front progresses with distance. The rate of change in isotope values is rapid initially and then decreases. Relative differences in advection and retardation of the two solutes, ^{53}Cr and ^{52}Cr , cause the initial rapid rise but eventually dispersive mixing of the plume front tends to lessen isotopic contrasts. The spatial and temporal variation in isotope values calculated with this model is approximately 1.0‰. Therefore, a chromatographic magnification of 10 \times occurred, as the modeled equilibrium isotope fractionation between adsorbed and dissolved Cr(VI) was 0.1‰ ($\alpha = 0.9999$). This example,

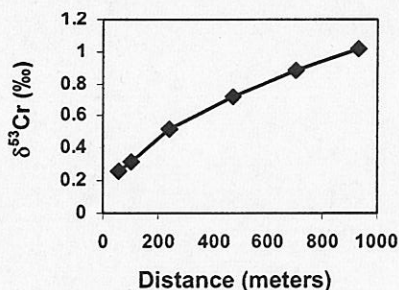


FIGURE 3. Isotope values at the leading edge of the plume ($C/C_0 = 0.3$) as the front progresses with distance.

although not extreme, is relatively conservative with larger magnifications being unlikely. Greater magnifications will occur only in the outermost fringes of plumes, where concentrations are too low to be of consequence.

The kinetic effects observed in the one experiment with goethite at pH 4 may be important in systems that are not under equilibrium. A shift in $\delta^{53}\text{Cr}$ values under such conditions may be possible and would depend on particle size, groundwater velocity, nature of sorbent, time scale of interest, etc. This possible kinetic effect will need to be examined in more detail in the future, especially if systems have equilibration time scales on the order of few days or more. We do advise to critically evaluate isotope values at extreme edges of plumes for equilibrium sorption or kinetic effects before concluding that Cr isotope shifts indicate Cr(VI) reduction.

Equilibrium Isotope Fractionation between Bichromate and Chromate. Equilibrium fractionation of Cr stable isotopes between bichromate and chromate is not apparent in the results. Previous work has suggested, through an indirect analysis of experimental data, the possibility of an equilibrium fractionation of a few per mil between carbonate and bicarbonate (29). The pK_a for the bichromate/chromate equilibrium is 6.4 and at pH 6.0 roughly 40% of the Cr(VI) will be in the bichromate form. Of the two species, bichromate is expected to adsorb. If an equilibrium fractionation between chromate and bichromate does occur, it would result in a difference of the $\delta^{53}\text{Cr}$ values between the adsorbed bichromate and dissolved chromate. However, our experiments at pH 6.0 should show isotope fractionation between dissolved and adsorbed Cr(VI) if such an isotope fractionation existed, yet none was observed. The isotope fractionation caused by speciation is not distinguishable from that caused by sorption. The isotope fractionation caused by one or both mechanisms should also result in differences in the $\delta^{53}\text{Cr}$ values of the initial solution and leftover solution. However, we observed no differences in isotope values. It is remotely possible that the chromate/bichromate fractionation was negated by an equal and opposite sorption effect. However, such a sorption effect is absent in the $\gamma\text{-Al}_2\text{O}_3$ experiment at pH 4.0, where Cr(VI) is present entirely as HCrO_4^- . Therefore, we conclude that isotope fractionation between bichromate and chromate is too small to be detected by this method and will not contribute toward any measurable shift in Cr isotope values.

Environmental Significance. We previously demonstrated that Cr stable isotope values can be used to quantify Cr(VI) reduction in contaminated sites. The results of this study show that sorption, a critical component of solute transport, does not cause a shift in $\delta^{53}\text{Cr}$ values under equilibrium conditions. In the absence of any isotope shift caused by sorption of Cr(VI) and speciation of Cr, reduction of Cr(VI) to reduced products will most likely be the dominant

process causing Cr stable isotope fractionation. Therefore, quantification of the extent of reduction can then be made quickly and with a high degree of confidence. In some systems that have not reached equilibrium, kinetic effects may be important and would need to be examined in more detail.

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