

■ Thermodynamic controls on redox-driven kinetic stable isotope fractionation

C. Joe-Wong, K.L. Weaver, S.T. Brown, K. Maher

■ Supplementary Information

The Supplementary Information includes:

- Methods
- Kinetic Fractionation
- Tables S-1 to S-4
- Figures S-1 and S-2
- Supplementary Information References

Methods

Reduction Experiments

All experiments were performed in an anaerobic glovebox in acid-washed amber HDPE bottles. Solutions were made with doubly deionised water sparged with N₂. Each reactor contained 20 μM Cr(VI), prepared from a 2 mM Na₂CrO₄ stock, and was buffered by 500 μM sodium acetate (pH 4-5.5) or 4-(2-hydroxyethyl)-1-piperazineethanesulfonate (HEPES) (pH 7.3). All experiments with Fe(II)-organic species were conducted at pH 5.5. Fe(II) stocks were prepared from FeCl₂·6H₂O and contained 125 μM Fe(II), 125 μM of the appropriate organic ligand, if any, and 600 μM of the appropriate buffer. A 500 μM Fe(II) stock at pH 7.3 was also prepared.

To ensure that all Cr(VI) was reduced by the intended Fe(II) species, Cr(VI) and Fe(II) were speciated at equilibrium under the reaction conditions using Visual MINTEQ 3.1 (Gustafsson, 2013). Binding constants for the organic ligands were taken from Buerge and Hug (1998). The rate of Cr(VI) reduction by each Fe(II) species present was determined from the speciation of Fe(II) and species-specific rate constants for Cr(VI) reduction by organically ligated Fe(II) (Buerge and Hug, 1998) and inorganic Fe(II) (Pettine *et al.*, 1998). As shown in Table S-1, over 99 % of Cr(VI) is reduced by the intended species under the reaction conditions for each reactor.

Following the method of Kitchen *et al.* (2012), all reactors were constantly stirred. Aliquots of Fe(II) were added to the reservoir of Cr(VI) such that 10–20 % of Cr(VI) reacted, and the reaction was allowed to continue until all the added Fe(II) reacted. An aliquot was then filtered (0.2 μm polyethersulfone), and the concentration of Cr(VI) was measured spectrophotometrically using diphenylcarbazide within 3 % reliability (Environmental Protection Agency, 1992). The fraction of Cr(VI) reduced was calculated from the initial concentration of Cr(VI), the measured concentration of Cr(VI), the mass of the reactor before the addition of Fe(II), the mass of the reactor after the addition of Fe(II), and the mass of the reactor after sampling in order to account for changing solution volumes (Kitchen *et al.*, 2012).



Chromium(VI) Separation

To correct for fractionation due to sample preparation, Cr purification, and instrumental mass bias, a double isotope spike solution (^{50}Cr and ^{54}Cr) was prepared. Purified ^{50}Cr and ^{54}Cr metal was obtained from Isoflex (San Francisco, CA) and gravimetrically prepared into a solution with a target $^{50}\text{Cr}/^{54}\text{Cr}$ of approximately 1 (Rudge *et al.*, 2009). For calibration, the spike was combined with the NIST SRM 979 Cr standard at various spike-sample ratios and the resulting isotopic compositions were measured. Using the accepted values for NIST SRM 979, the exact isotopic composition of the spike was determined. These spike values were used as “knowns” in a system of equations to simultaneously determine an instrumental mass bias factor, the fraction of spike in the spike-sample mixture, and the Cr isotopic composition of the sample. A new batch of the spike was oxidised to Cr(VI) using hydrogen peroxide and ammonium hydroxide for each run, and the oxidised spike added to each sample such that spike Cr:total Cr(VI) = 0.4. The spike was allowed to equilibrate overnight with the sample. Samples from the inorganic Fe(II) reactors were then purified using anion exchange columns (AG1X8 resin, 100-200 mesh, Eichrom) (Ellis *et al.*, 2002; Basu and Johnson, 2012). The anion-exchange resin was pre-cleaned with 2N HNO_3 and flushed with doubly deionised water until the effluent reached circumneutral pH. In brief, cations were eluted with 0.1 N HCl. Sorbed Cr(VI) was then reduced to Cr(III) and eluted with hydrogen peroxide and 2 N HNO_3 . Any remaining Fe was removed by taking samples up in 6 N HCl and putting them through a second anion exchange column (AG1X8 resin, 100–200 mesh, Eichrom). Negatively charged FeCl_4^- was retained on the anion resin, and Cr(III) was eluted with 6 N HCl. Organic residue from the resin was destroyed by repeatedly treating the samples with 30 wt. % hydrogen peroxide and 15 N HNO_3 . Column yields were approximately 70 %.

Samples from Fe(II)-organic reactors required further treatment because the organic ligands form soluble complexes with Cr(III) and Fe(III) and have a high affinity for AG1X8 anion resin, thwarting easy separation of Cr(VI) from Cr(III). After spike equilibration, samples were shaken overnight with pre-cleaned (2 N HNO_3) cation resin (AG50WX8, 200-400 mesh, Bio-Rad). The cation resin was then filtered out, and the samples were purified with anion exchange columns as detailed above. The effectiveness of the separation of Cr(VI) from Cr(III) was evaluated using mass balance equations. For the original, unprocessed sample, the overall isotopic composition of Cr(VI) and Cr(III) must be the same as the original isotopic composition of Cr(VI) prior to reaction:

$$\delta^{53}\text{Cr(VI)}_0 = \frac{\text{Cr(VI)}_{\text{sample}}}{\text{Cr(total)}_{\text{sample}}} \delta^{53}\text{Cr(VI)} + \frac{\text{Cr(III)}_{\text{sample}}}{\text{Cr(total)}_{\text{sample}}} \delta^{53}\text{Cr(III)} \quad (\text{Eq. S-1})$$

In Equation S-1, the original isotopic composition of Cr(VI) prior to reaction ($\delta^{53}\text{Cr(VI)}_0$) was measured for every reactor. The fraction of $\text{Cr(VI)}_{\text{sample}}/\text{Cr(total)}_{\text{sample}}$ was calculated as discussed above, and

$$\frac{\text{Cr(III)}_{\text{sample}}}{\text{Cr(total)}_{\text{sample}}} = 1 - \frac{\text{Cr(VI)}_{\text{sample}}}{\text{Cr(total)}_{\text{sample}}} \quad (\text{Eq. S-2})$$

Thus, the remaining unknowns are $\delta^{53}\text{Cr(VI)}$ and $\delta^{53}\text{Cr(III)}$.

A similar mass balance equation was constructed for the processed, measured sample, where the measured isotopic composition of Cr is the weighted average of the true isotopic composition of Cr(VI) and the isotopic composition of Cr(III), if any Cr(III) remains in the sample:

$$\delta^{53}\text{Cr}_{\text{measured}} = \frac{\text{Cr(VI)}_{\text{measured}}}{\text{Cr(total)}_{\text{measured}}} \delta^{53}\text{Cr(VI)} + \frac{\text{Cr(III)}_{\text{measured}}}{\text{Cr(total)}_{\text{measured}}} \delta^{53}\text{Cr(III)} \quad (\text{Eq. S-3})$$

Here the unknowns are $\delta^{53}\text{Cr(VI)}$, $\delta^{53}\text{Cr(III)}$, and the fraction of Cr(VI)/Cr(total) in the processed sample. The last quantity was calculated by isotope dilution. The amount of Cr(VI) in the sample was determined spectrophotometrically as discussed above, and the amount of spike Cr added to sample was also known from the mass of the spike and its concentration. The amount of Cr(III) was then calculated from the proportion p of the spike in the measured sample (Rudge *et al.*, 2009):

$$p = \frac{\text{Cr}_{\text{spike}}}{\text{Cr(VI)}_{\text{measured}} + \text{Cr(III)}_{\text{measured}}} \quad (\text{Eq. S-4})$$

The fraction of Cr(III) in the processed, measured sample was insignificant except for the Fe(II)-citrate experiments, for which Cr(III) comprised 14 % of the processed, measured samples on average. Thus, ultimately the two mass balance equations can be used to calculate the two remaining unknowns, $\delta^{53}\text{Cr(VI)}$ and $\delta^{53}\text{Cr(III)}$.



Isotopic Analysis

Chromium isotopic ratios were measured at Lawrence Berkeley National Laboratory on a multi-collector inductively-coupled-plasma mass spectrometer (Neptune Plus, Thermo Fisher) in high resolution. Purified samples were taken up in 2 % nitric acid to yield ~2 µg ⁵²Cr/mL. Isotopic compositions are reported in δ notation as deviations from NIST SRM 979:

$$\delta^{53}\text{Cr} = \left(\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{979}} - 1 \right) \quad (\text{Eq. S-5})$$

All measured δ values were corrected for instrumental mass fractionation by deconvoluting the double spike (Rudge *et al.*, 2009). Spiked standard NIST SRM 979 (δ⁵³Cr defined as 0 ‰) was measured between every three samples to assess instrument mass bias drift. The long-term average δ⁵³Cr of the standard was 0.01 ± 0.09 ‰ (2S.D.). Oxidised NIST SRM 979 processed in parallel with samples had an identical δ⁵³Cr of 0.01 ‰. To further estimate the uncertainty associated with these measurements, 13 samples were measured in duplicate, with an almost identical uncertainty of 0.1 ‰ based on twice the root-mean-squared difference.

Fractionation factors were determined using the linearised Rayleigh equation. The linear regression was weighted using uncertainties in both the fraction of Cr(VI) reduced and the measured isotope ratio, and uncertainties for the fractionation factors are two standard deviations of the slope of this regression (York *et al.*, 2004). Weighted and unweighted linear regressions yield identical fractionation factors within uncertainty for all experiments.

As discussed in the main text, the effective fractionation factor ϵ_{eff} for Cr(VI) reduction by aqueous inorganic Fe(II) is the average of the species-specific fractionation factors for all the relevant Fe(II) species (Fe(H₂O)₆²⁺, FeOH⁺, and Fe(OH)₂⁰), weighted by the fraction of Cr(VI) that is reduced by each Fe(II) species. The species-specific fractionation factors can be quantitatively estimated from E° of each species using the linear free energy relationship shown in Figure 1. The fraction of Cr(VI) reduced by each Fe(II) species depends on the amount of each Fe(II) species present and on the species-specific rate constant for Cr(VI) reduction. To determine the amount of each Fe(II) species present, Cr(VI) and Fe(II) were speciated at equilibrium under the reaction conditions using Visual MINTEQ 3.1 (Gustafsson, 2013). Species-specific rate constants for Cr(VI) reduction by Fe(II) were taken from Pettine *et al.* (1998) and Buerge and Hug (1997), and ϵ_{eff} was calculated as below:

$$\epsilon_{\text{eff}} = \frac{k_{\text{H}_2\text{O}} \times [\text{Fe}(\text{H}_2\text{O})_6^{2+}] \times \epsilon_{\text{H}_2\text{O}} + k_{\text{OH}} \times [\text{Fe}(\text{OH})^+] \times \epsilon_{\text{OH}} + k_{2\text{OH}} \times [\text{Fe}(\text{OH})_2^0] \times \epsilon_{2\text{OH}}}{k_{\text{H}_2\text{O}} \times [\text{Fe}(\text{H}_2\text{O})_6^{2+}] + k_{\text{OH}} \times [\text{Fe}(\text{OH})^+] + k_{2\text{OH}} \times [\text{Fe}(\text{OH})_2^0]} \quad (\text{Eq. S-6})$$

where $k_{\text{H}_2\text{O}}$ and $\epsilon_{\text{H}_2\text{O}}$ refer to the rate constant and fractionation factor for Fe(H₂O)₆²⁺, et cetera. As shown in Figure S-2, the reported uncertainties in the rate constants from Pettine *et al.* (1998) propagate to relatively large uncertainties in the modelled ϵ_{eff} . Uncertainties were not propagated for the rate constants of Buerge and Hug (1997) because they are so large (*e.g.*, $k_{\text{H}_2\text{O}} = 0.34 \pm 0.47 \text{ M}^{-1}\text{s}^{-1}$) that they make the model meaningless.

Kinetic Fractionation

Chromium fractionation during Cr(VI) reduction is typically expected to be kinetic because the back-reaction is minimal (Wang *et al.*, 2015; Qin and Wang, 2017). The product Cr(III) generally forms a highly insoluble precipitate that is not easily re-oxidised (Pan *et al.*, 2019), and even aqueous Cr(III) is slow to react (Wang *et al.*, 2015). However, in the experiments presented here where Cr(VI) is reduced by organically ligated Fe(II), the product Cr(III) may complex with the organic ligand (Buerge and Hug, 1998). It is possible that organically ligated Cr(III) may reach isotopic equilibrium with anionic Cr(VI) faster than aqueous inorganic Cr(III) (Cr(H₂O)₆³⁺) or a Cr(III) precipitate. Nevertheless, it is unlikely that the observed fractionation of Cr is equilibrium or even a mixture of kinetic and equilibrium fractionation for several reasons. First, if isotopic exchange between Cr(VI) and Cr(III) is fast in these experiments, this should be reflected in the instrumental mass fractionation factor (β) determined by deconvoluting the ⁵⁰Cr/⁵⁴Cr double spike (Rudge *et al.*, 2009). Despite its name, β in fact reflects all fractionation between the addition of the spike to the sample and measurement of the isotopic ratios, which would include any equilibrium fractionation between Cr(VI) and Cr(III) in the spiked sample. The speciation of the spike was the same as the sample Cr(VI) (*i.e.* HCrO₄⁻/CrO₄²⁻), and the spike was allowed to equilibrate with the sample overnight. Each experiment only lasted a few days, so if the sample Cr(VI) approached isotopic equilibrium with the sample Cr(III) within the experimental timescale, the spike Cr(VI) should also approach isotopic equilibrium with the sample Cr(III) prior to separation. If significant isotopic exchange between the spike Cr(VI) and the sample Cr(III) occurs, then β for samples from the reactors with organically ligated Fe(II) should reflect this as well as fractionation from the ion exchange resins and in the



MC-ICP-MS instrument. Thus, sample β values should differ from β values for the SRM 979 standards, which only reflect fractionation from one ion exchange resin and the MC-ICP-MS instrument. No major differences between sample and standard β values were observed, so significant isotopic exchange between Cr(VI) and Cr(III) is unlikely to have occurred.

Furthermore, it is unlikely that isotopic equilibrium between Cr(VI) and Cr(III) can be approached in these experiments. Reaching isotopic equilibrium implies reaching chemical equilibrium (Beard *et al.*, 2003), but the kinetics of Cr(VI) reduction by these organically ligated Fe(II) species under the conditions of the experiment concentrations can be fit well with a unidirectional reaction (Cr(VI) \rightarrow Cr(III)) and do not show any sign of back-formation of Cr(VI) (Buerge and Hug, 1998). The same lack of back-reaction has been seen for a wide variety of other Cr(VI) reduction reactions, including reduction by other aqueous Fe(II) species, hydrogen sulphide, and Fe(II/III)-bearing clay minerals (Buerge and Hug, 1997; Joe-Wong *et al.*, 2017; Pettine *et al.*, 1994). Isotopic equilibrium between aqueous inorganic Cr(VI) and Cr(III) species is approached on the order of years, with a half-life of nearly 6 years at concentrations more than 1000 times greater than in these experiments (Wang *et al.*, 2015). It is possible that in experiments with organically ligated Fe(II), Cr(III) may complex with the organic ligand (Buerge and Hug, 1998), and isotopic equilibrium between anionic Cr(VI) and organically complexed Cr(III) may be faster than equilibrium with Cr(H₂O)₆³⁺. However, the rate of isotopic exchange for organically ligated Cr(III) would need to be at least six orders of magnitude faster than the rate for Cr(H₂O)₆³⁺ for samples to reach isotopic equilibrium over the course of each experiment, which only lasted a few days and involved micromolar concentrations of Cr. Finally, the observed fractionation is likely too small to be equilibrium. Although there are no theoretical calculations of equilibrium fractionation factors between organically ligated and inorganic Cr(III), typically equilibrium fractionation between organically and inorganically ligated transition metals is smaller than 0.5 ‰ (Jouvin *et al.*, 2009; Morgan *et al.*, 2010; Fujii *et al.*, 2014). Thus, equilibrium fractionation between Cr(VI) and organically ligated Cr(III) would be expected to be roughly between -5.5 and -7.5 ‰ based on estimated equilibrium fractionation factors between Cr(VI) and inorganic Cr(III) (-6 to -7 ‰) (Schauble *et al.*, 2004; Wang *et al.*, 2015). The measured fractionation factors are much smaller than this and likely reflect kinetic fractionation.

The observed fractionation could also potentially be affected by physical heterogeneity in insufficiently mixed reactors, where slow diffusion of the Fe(II) stock may diminish the magnitude of measured fractionation (Kitchen *et al.*, 2012). To minimize such transport limitations, reactors were constantly stirred, and the concentration of the Fe(II) stock was low so that injecting the Fe(II) stock into the reactor would not create temporary zones with extremely high Fe(II) concentrations in which Cr(VI) reduction might be diffusion-limited. The potential for any remaining effects on measured fractionation was investigated for the fast reduction of Cr(VI) by Fe(OH)₂⁰ at pH 7.3 (Buerge and Hug, 1997; Pettine *et al.*, 1998). To enhance heterogeneity immediately after adding the Fe(II) stock, the concentration of the added stock was increased fourfold from 125 μ M to 500 μ M and its volume correspondingly decreased. The measured fractionation decreased from -2.21 ± 0.05 ‰ to -1.89 ± 0.08 ‰ (Fig. S-1, Table S-4). Further increasing transport limitations by both increasing the stock concentration and decreasing the stir speed of the reactor from 900 to 300 rpm caused a slight additional decrease in ϵ to -1.71 ± 0.09 ‰. Although these effects are not insignificant, they are much smaller than the 2 ‰ range in kinetic fractionation observed by changing the ligation of Fe(II), which is more plausibly explained using the Marcus-theory-based model presented in the main text.



Supplementary Tables

Table S-1 Each column shows for a given reactor the predicted rate of Cr(VI) reduction and fraction of Cr(VI) reduced by each Fe(II) species present (Fe(II)-organic, Fe(H₂O)₆²⁺, Fe(OH)⁺, and Fe(OH)₂⁰).

Reactor	Ligand	H ₂ O	Citrate	Nitrilotriacetate	Salicylate	2OH
Rate of Cr(VI) Reduction (μM/s)	Organic	n/a	1.81 × 10 ⁻²	5.45	2.02 × 10 ¹	n/a
	H ₂ O	9.36 × 10 ⁻⁴	1.09 × 10 ⁻⁵	2.43 × 10 ⁻⁷	2.13 × 10 ⁻⁶	4.85 × 10 ⁻⁸
	OH	9.69 × 10 ⁻⁶	3.20 × 10 ⁻⁶	7.16 × 10 ⁻⁸	6.28 × 10 ⁻⁷	2.00 × 10 ⁻³
	2OH	3.48 × 10 ⁻⁷	9.14 × 10 ⁻⁸	2.04 × 10 ⁻⁹	1.79 × 10 ⁻⁸	1.43 × 10 ⁻¹
Fraction of Cr(VI) Reduced	Organic	n/a	1.00	1.00	1.00	n/a
	H ₂ O	0.99	0.00	0.00	0.00	0.00
	OH	0.01	0.00	0.00	0.00	0.01
	2OH	0.00	0.00	0.00	0.00	0.99

Table S-2 Changes in isotopic composition during Cr(VI) reduction by aqueous Fe(II) species. Each pair of columns shows a duplicate reactor.

Reductant	Fraction Cr(VI) Remaining	δ ⁵³ Cr(VI) (‰)	Fraction Cr(VI) Remaining	δ ⁵³ Cr(VI) (‰)
Fe(citrate)	1	-0.02	1	0.01
	0.83	1.33	0.78	1.09
	0.62	2.37	0.57	2.34
	0.40	3.72	0.37	3.63
	0.17	6.55	0.17	6.13
Fe(nitrilotriacetate)	1	0.00	1	-0.02
	0.82	0.71	0.83	0.72
	0.63	1.56	0.62	1.57
	0.43	2.69	0.43	2.67
	0.23	4.29	0.23	4.34
Fe(salicylate)	1	0.18	1	-0.09
	0.83	0.80	0.84	0.83
	0.62	1.85	0.63	1.80
	0.41	3.12	0.42	3.09
	0.20	4.68	0.20	4.64
Fe(OH) ₂	1	0.04	1	0.05
	0.80	0.71	0.83	0.64
	0.61	1.47	0.62	1.36
	0.40	2.44	0.42	2.36
	0.20	4.06	0.21	3.93
	0.04	7.34	0.04	7.11



Table S-3 Changes in isotopic compositions during Cr(VI) reduction by aqueous Fe(II) at different pH values. Each pair of columns shows a duplicate reactor.

pH	Fraction Cr(VI) Remaining	$\delta^{53}\text{Cr(VI)}$ (‰)	Fraction Cr(VI) Remaining	$\delta^{53}\text{Cr(VI)}$ (‰)
4.95	1	0.05	1	0.03
	0.83	0.82	0.83	0.84
	0.61	1.76	0.61	1.76
	0.40	2.98	0.40	2.97
5.22	1	0.18	1	0.01
	0.74	0.80	0.82	0.90
	0.50	1.85	0.58	2.09
	0.27	3.12	0.33	3.51
	--	--	0.11	5.62
5.54	1	0.04	1	0.05
	0.79	0.83	0.78	0.92
	0.57	1.79	0.56	1.98
	0.34	3.06	0.32	3.42

Table S-4 Changes in isotopic compositions during Cr(VI) reduction by aqueous Fe(II) at pH 7.3 under different transport conditions. Each pair of columns shows a duplicate reactor.

Reductant	Fe(II) Stock Concentration (μM)	Stir Speed (rpm)	Fraction Remaining Cr(VI)	$\delta^{53}\text{Cr(VI)}$ (‰)
Fe(OH) ₂	500	900	1	0.08
			0.74	0.59
			0.60	1.27
			0.38	2.05
			0.19	3.44
			0.04	6.22
			1	0.06
Fe(OH) ₂	500	300	0.83	0.55
			0.62	1.12
			0.41	1.89
			0.21	2.91
			0.05	5.40



Supplementary Figures

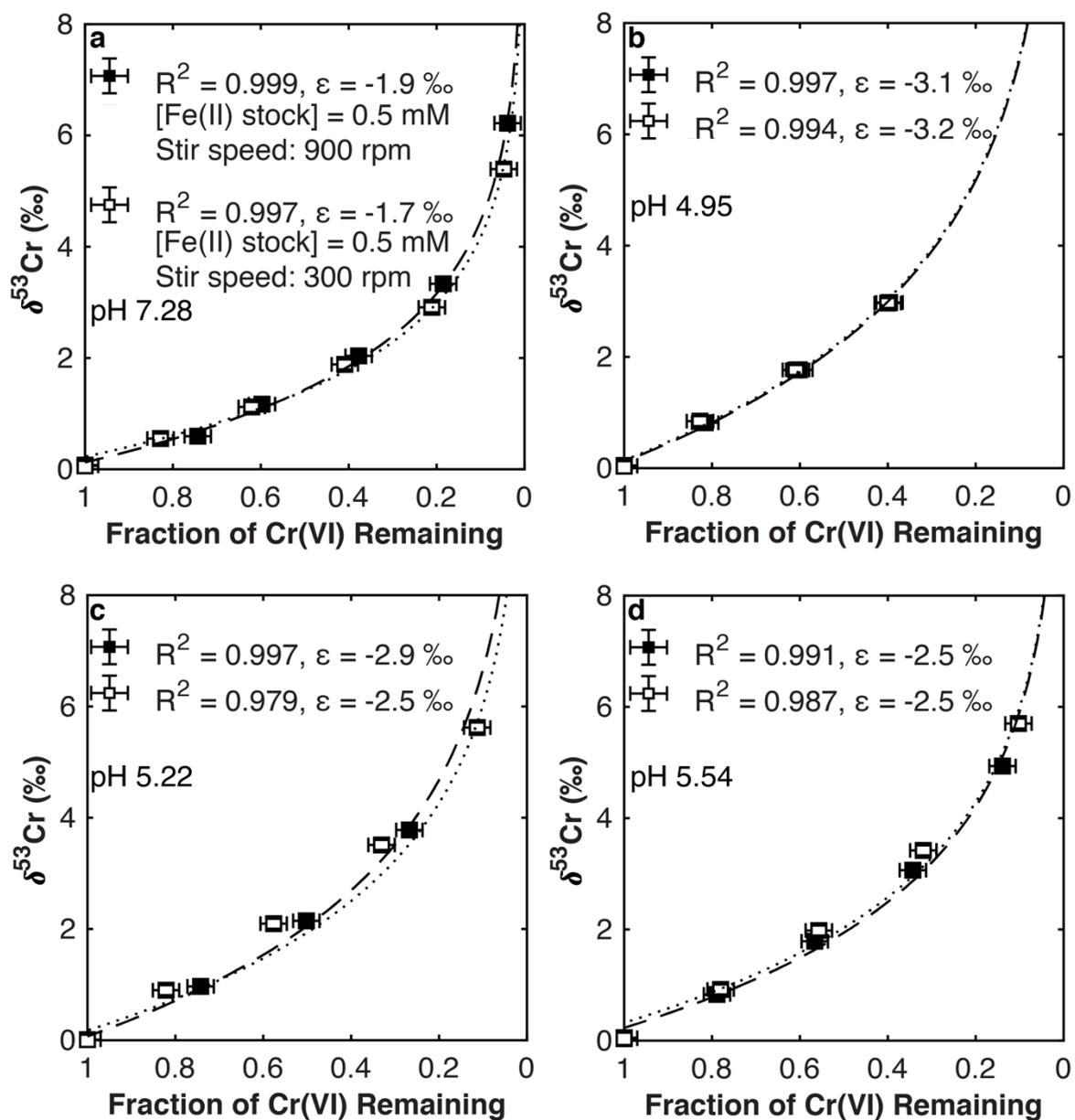


Figure S-1 Rayleigh plots of isotope fractionation during Cr(VI) reduction by aqueous Fe(II) at (a) different experimental conditions and (b-d) pH values. Filled and open symbols in each plot show duplicate reactors. Rayleigh curves based on linear best fits are plotted as dashed lines (filled symbols) and dotted lines (open symbols). Vertical error bars (2 S.D.) are smaller than the symbols.

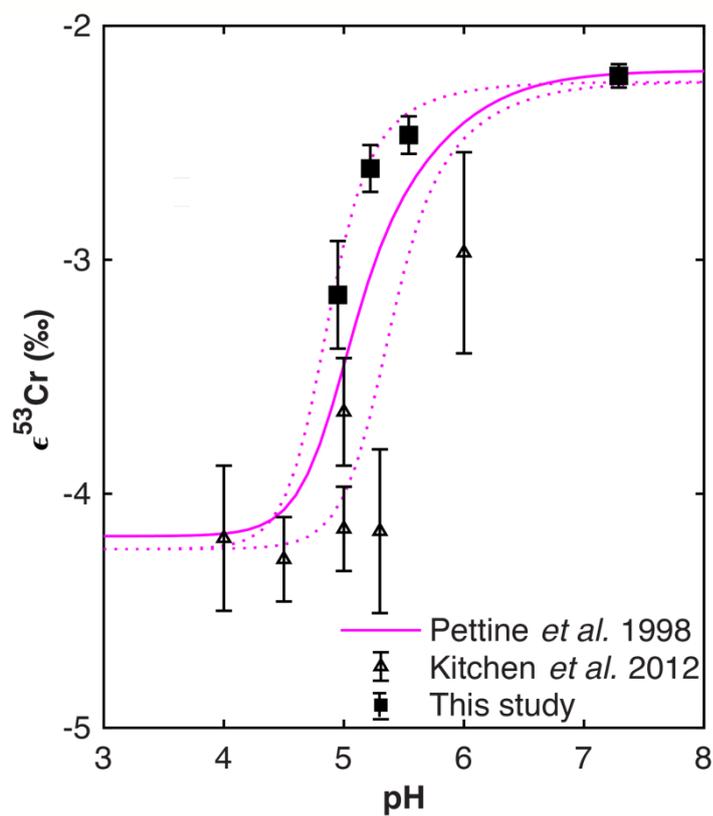


Figure S-2 Uncertainties on the modelled pH dependence of isotope fractionation of Cr(VI) reduction by aqueous Fe(II). The solid line is based on the species-specific rate constants of Pettine *et al.* (1998), and the dashed lines show variations in the model when the species-specific rate constants are varied by 25.D. as reported by Pettine *et al.* (1998).

Supplementary Information References

- Basu, A., Johnson, T.M. (2012) Determination of Hexavalent Chromium Reduction Using Cr Stable Isotopes: Isotopic Fractionation Factors for Permeable Reactive Barrier Materials. *Environmental Science & Technology* 46, 5353–5360.
- Beard, B.L., Johnson, C.M., Skulan, J.L., Nealon, K.H., Cox, L., Sun, H. (2003) Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology* 195, 87–117.
- Buerge, I.J., Hug, S.J. (1997) Kinetics and pH Dependence of Chromium(VI) Reduction by Iron(II). *Environmental Science & Technology* 31, 1426–1432.
- Buerge, I.J., Hug, S.J. (1998) Influence of Organic Ligands on Chromium(VI) Reduction by Iron(II). *Environmental Science & Technology* 32, 2092–2099.
- Ellis, A.S., Johnson, T.M., Bullen, T.D. (2002) Chromium Isotopes and the Fate of Hexavalent Chromium in the Environment. *Science* 295, 2060–2062.
- Environmental Protection Agency (1992) EPA Method 7196A. Environmental Protection Agency.
- Fujii, T., Moynier, F., Blichert-Toft, J., Albarède, F. (2014) Density functional theory estimation of isotope fractionation of Fe, Ni, Cu, and Zn among species relevant to geochemical and biological environments. *Geochimica et Cosmochimica Acta* 140, 553–576.
- Gustafsson, J.P. (2013) *Visual MINTEQ*. KTH, Stockholm, Sweden.
- Joe-Wong, C., Brown, G.E., Maher, K. (2017) Kinetics and Products of Chromium(VI) Reduction by Iron(II/III)-Bearing Clay Minerals. *Environmental Science & Technology* 51, 9817–9825.
- Jouvin, D., Louvat, P., Juillot, F., Maréchal, C.N., Benedetti, M.F. (2009) Zinc Isotopic Fractionation: Why Organic Matters. *Environmental Science & Technology* 43, 5747–5754.
- Kitchen, J.W., Johnson, T.M., Bullen, T.D., Zhu, J., Raddatz, A. (2012) Chromium isotope fractionation factors for reduction of Cr(VI) by aqueous Fe(II) and organic molecules. *Geochimica et Cosmochimica Acta* 89, 190–201.
- Morgan, J.L.L., Wasylenki, L.E., Nueter, J., Anbar, A.D. (2010) Fe Isotope Fractionation during Equilibration of Fe–Organic Complexes. *Environmental Science & Technology* 44, 6095–6101.
- Pan, C., Liu, H., Catalano, J.G., Wang, Z., Qian, A., Giammar, D.E. (2019) Understanding the Roles of Dissolution and Diffusion in Cr(OH)₃ Oxidation by δ-MnO₂. *ACS Earth and Space Chemistry* 3, 357–365.
- Pettine, M., D'Ottone, L., Campanella, L., Millero, F.J., Passino, R. (1998) The reduction of chromium (VI) by iron (II) in aqueous solutions. *Geochimica et Cosmochimica Acta* 62, 1509–1519.
- Pettine, M., Millero, F.J., Passino, R. (1994) Reduction of chromium (VI) with hydrogen sulfide in NaCl media. *Marine Chemistry* 46, 335–344.
- Qin, L., Wang, X. (2017) Chromium Isotope Geochemistry. *Reviews in Mineralogy and Geochemistry* 82, 379–414.
- Rudge, J.F., Reynolds, B.C., Bourdon, B. (2009) The double spike toolbox. *Chemical Geology* 265, 420–431.
- Schauble, E., Rossman, G.R., Taylor Jr., H.P. (2004) Theoretical estimates of equilibrium chromium-isotope fractionations. *Chemical Geology* 205, 99–114.
- Wang, X., Johnson, T.M., Ellis, A.S. (2015) Equilibrium isotopic fractionation and isotopic exchange kinetics between Cr(III) and Cr(VI). *Geochimica et Cosmochimica Acta* 153, 72–90.
- York, D., Evensen, N.M., Martínez, M.L., De Basabe Delgado, J. (2004) Unified equations for the slope, intercept, and standard errors of the best straight line. *American Journal of Physics* 72, 367–375.

