SUPPORTING INFORMATION

MANUSCRIPT TITLE:
Dual mechanism conceptual model for Cr isotope fractionation during reduction by zero-valent iron under saturated flow conditions

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Table S1. Reactive transport model reaction equations, rates and parameters.

Primary Reactions:			
	Parameter	Batch	Column
$Fe^0(s) + 2H^+ \rightarrow Fe^{2+} + H_2(aq)$	*log k*	-11.2	-11
$R_{Fe^0-H_2O} = k\mathrm{S}_0 \exp(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t))$	S_0	382	28900
	α_{ferri}	160	160
	φ_{0_ferri}	1.0 x 10^{-10}	1.0 x 10^{-10}
	α_{arag}	25	25
	φ_{0_arag}	1.0 x 10^{-10}	1.0 x 10^{-10}
$0.667\ {}^{52}CrO_4^{2-} + Fe^0 + 4H^+ \rightarrow Fe^{2+} + 0.667\,{}^{52}Cr(OH)_2^+ + H_2O$	*log k*	-1.2	-4.7
	S_0	382	28900
$R_{Fe^0-{}^{52}Cr(VI)} = k_{52}\mathrm{S}_0 \exp\left(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t)\right)\{{}^{52}CrO_4^{2-}\}\{\varphi_{Fe^0-Cr(VI)}(x,t)\}$	α_{ferri}	160	160
	φ_{0_ferri}	1.0 x 10^{-10}	1.0 x 10^{-10}
	α_{arag}	25	25
	φ_{0_arag}	1.0 x 10^{-10}	1.0 x 10^{-10}
	$\varphi_{0\_FeO\text{-}Cr(VI)}$	6.2 x 10^{-6}	6.7 x 10^{-4}
$0.667\ {}^{53}CrO_4^{2-} + Fe^0 + 4H^+ \rightarrow Fe^{2+} + 0.667\,{}^{53}Cr(OH)_2^+ + H_2O$	α_{53}	0.9998	0.9998
	ε	-0.2	-0.2
$R_{Fe^0-{}^{53}Cr(VI)} = k_{53}\mathrm{S}_0 \exp\left(\alpha_{ferri}\varphi_{ferri}(x,t)\alpha_{arag}\varphi_{arag}(x,t)\right)\{{}^{52}CrO_4^{2-}\}\{\varphi_{Fe^0-Cr(VI)}(x,t)\}$			
${}^{52}CrO_4^{2-} + 3Fe^{2+} + 6H^+ \rightarrow {}^{52}Cr(OH)_2^+ + 3Fe^{3+} + 2H_2O$	*log k*	2.18	2.18
	α_{53}	0.9991	0.9985
$R_{Fe^{2+}-{}^{52}Cr(VI)} = k_{52}\{{}^{52}CrO_4^{2-}\}\{Fe^{2+}\}$	ε	-0.9	-1.5
${}^{53}CrO_4^{2-} + 3Fe^{2+} + 6H^+ \rightarrow {}^{53}Cr(OH)_2^+ + 3Fe^{3+} + 2H_2O$			
$R_{Fe^{2+}-{}^{53}Cr(VI)} = k_{52}\{{}^{53}CrO_4^{2-}\}\{Fe^{2+}\}$			
Secondary Reactions: $R = k\left(1 - \frac{IAP}{K}\right)$			
${}^{52}Cr(OH)_{3(am)} + H^+ \rightarrow {}^{52}Cr(OH)_2^+ + H_2O$	*log k*	-11.9	-8.7
${}^{53}Cr(OH)_{3(am)} + H^+ \rightarrow {}^{53}Cr(OH)_2^+ + H_2O$	*log K*	-0.75	-0.75
	α_{53}	1.0	1.0
	ε	0.0	0.0
$Fe(OH)_{2(s)} + 2H^+ \rightarrow Fe^{2+} + 2H_2O$	*log k*	-7.9	-8.0
	log K	13.9045	13.9045

$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$	*log k*	-9.0	-7.2
	log K	-4.36	-4.36
$Fe_2(OH)_2CO_{3(s)} + 2H^+ \rightarrow 2Fe^{2+} + CO_3^{2-} + 2H_2O$	*log k*	-13.3	-14.3
	log K	-0.0753	-0.0753
$Fe(OH)_{3(am)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O$	*log k*	-9.7	-8.7
	log K	4.891	4.891

k – effective rate constant

S_0 - initial reactive surface area of the iron (m^2 iron L^{-1} bulk)

α_i - proportionality constant for mineral phase i

φ_0 - volume fraction of mineral phase i (m^3 mineral m^{-3} bulk).

α_{53} – isotope fractionation factor

ε – isotope fractionation value

K – equilibrium constant (mol L^{-1} H_2O)

Table S2. Summary of geochemical data and $\delta^{53}Cr$ values for the batch experiment.

Time (days)	pH	Eh (mV)	Alk (mg L^{-1})	Cr(VI) (mg L^{-1})	% removal	$\delta^{53}Cr$ (‰)
0.00	8.77	370	128	46.57	0.0	0.00
0.04	9.42	380	110	26.26	43.6	0.45
0.07	9.45	125	118	23.46	49.6	0.49
0.10	n/a	n/a	n/a	26.87	42.3	0.44
0.14	n/a	n/a	n/a	25.05	46.2	0.45
0.28	n/a	n/a	n/a	18.03	61.3	0.67
0.46	9.67	215	78	14.83	68.2	0.76
0.94	n/a	n/a	n/a	8.31	82.2	1.01
1.16	9.74	-135	63	7.02	84.9	1.10
1.46	n/a	n/a	n/a	3.04	93.5	1.25
1.96	9.91	-170	56	1.60	96.6	*
2.32	n/a	n/a	n/a	1.00	97.9	*
3.03	n/a	n/a	n/a	0.55	98.8	*
4.15	9.96	110	58	0.07	99.8	*

Alk: total alkalinity as mg L^{-1} $CaCO_3$
n/d: not detected
n/a: not analysed
* concentration too low for Cr isotope analysis

Table S3. Summary of geochemical data and $\delta^{53}Cr$ values for the column effluent.

Time (days)	pH	Eh (mV)	Alk (mg L^{-1})	Cr(VI) (mg L^{-1})	% removal	$\delta^{53}Cr$ (‰)
0	8.86	-260	50	n/d	100	*
1	8.85	-460	68	n/d	100	*
3	9.33	-485	55	n/d	100	*
5	9.31	-425	52	n/d	100	*
12	10.00	-465	47	n/d	100	*
16	10.28	-455	47	n/d	100	*
20	9.13	-410	48	n/d	100	*
23	10.17	-415	49	n/d	100	*
27	10.50	-470	48	n/d	100	*
33	10.34	-540	48	n/d	100	*
41	10.50	-240	53	n/d	100	*
44	n/a	n/a	n/a	n/d	100	*
48	10.64	-135	55	n/d	100	*
51	10.52	-170	54.5	n/d	100	*
55	10.43	-150	57	0.004	100	*
62	10.64	40	54	2.03	95.5	*
65	10.61	15	50	6.46	85.6	1.55
69	10.54	5	49	10.11	77.4	1.38
72	10.59	-30	48	12.52	72.0	1.33
76	10.47	-95	52	15.64	65.0	1.11
79	10.21	-5	52	17.31	61.3	1.06
83	10.08	60	49	19.09	57.3	1.06
86	9.77	60	52	19.96	55.4	n/a
90	10.01	-35	46	21.70	51.5	0.94
93	9.96	-10	44	24.42	45.4	0.91
97	9.62	75	50	26.23	41.3	0.86
100	9.68	75	44	28.23	36.9	0.83
104	9.50	80	42	25.60	42.7	0.92
107	9.39	250	53	26.93	39.8	0.93
126	n/a	n/a	n/a	33.97	24.0	0.71

Alk: total alkalinity as mg L^{-1} $CaCO_3$
n/d: not detected
n/a: not analysed
* concentration too low for Cr isotope analysis

Table S4. Summary of geochemical data and $\delta^{53}Cr$ values for the column profiles.

Time (days)	Distance (m)	pH	Eh (mV)	Alk (mg L^{-1})	Cr(VI) (mg L^{-1})	% removal	$\delta^{53}Cr$ (‰)
33	0.000	8.02	480	113	44.71	0.0	0.00
	0.035	8.08	295	107.5	46.05	0.0	0.07
	0.065	8.90	-20	85	31.89	28.7	0.45
	0.095	8.95	-120	65	29.32	34.4	0.81
	0.125	10.06	-160	52	9.64	78.4	1.32
	0.155	10.55	-555	60	n/d	100	*
	0.185	10.47	-545	55	n/d	100	*
	0.220	10.34	-540	48	n/d	100	*
41	0.000	7.99	300	111	44.71	0.0	0.00
	0.035	8.12	300	107.5	46.24	0.0	0.01
	0.065	8.73	-5	82.5	36.40	18.6	0.34
	0.095	8.78	-275	80	30.67	31.4	0.58
	0.125	9.75	-300	50	18.15	59.4	1.01
	0.155	10.72	-515	52.5	2.85	93.6	*
	0.185	10.61	-535	57.5	n/d	100	*
	0.220	10.50	-240	53	n/d	100	*
55	0.000	8.09	335	107	44.71	0.0	0.00
	0.035	8.08	280	110	46.28	0.0	-0.02
	0.065	8.40	25	110	40.46	9.5	0.25
	0.095	8.36	-45	100	37.5	16.1	0.40
	0.125	9.39	-165	50	23.92	46.5	0.67
	0.155	10.10	-255	65	18.84	57.9	1.09
	0.185	10.72	-310	80	0.003	100	*
	0.220	10.43	-150	57	0.004	100	*
76	0.000	8.17	365	98	44.71	0.0	0.00
	0.035	8.15	265	97.5	46.18	0.0	0.00
	0.065	8.36	65	100	41.98	6.1	0.24
	0.095	8.70	-10	110	37.91	15.2	0.36
	0.125	9.46	-180	75	26.85	39.9	0.55
	0.155	9.66	-80	65	26.01	41.8	0.77
	0.185	10.36	-130	60	19.3	56.8	1.14
	0.220	10.47	-95	52	15.64	65.0	1.11

Alk: total alkalinity as mg L^{-1} $CaCO_3$

n/d: not detected; n/a: not analysed; * concentration too low for Cr isotope analysis

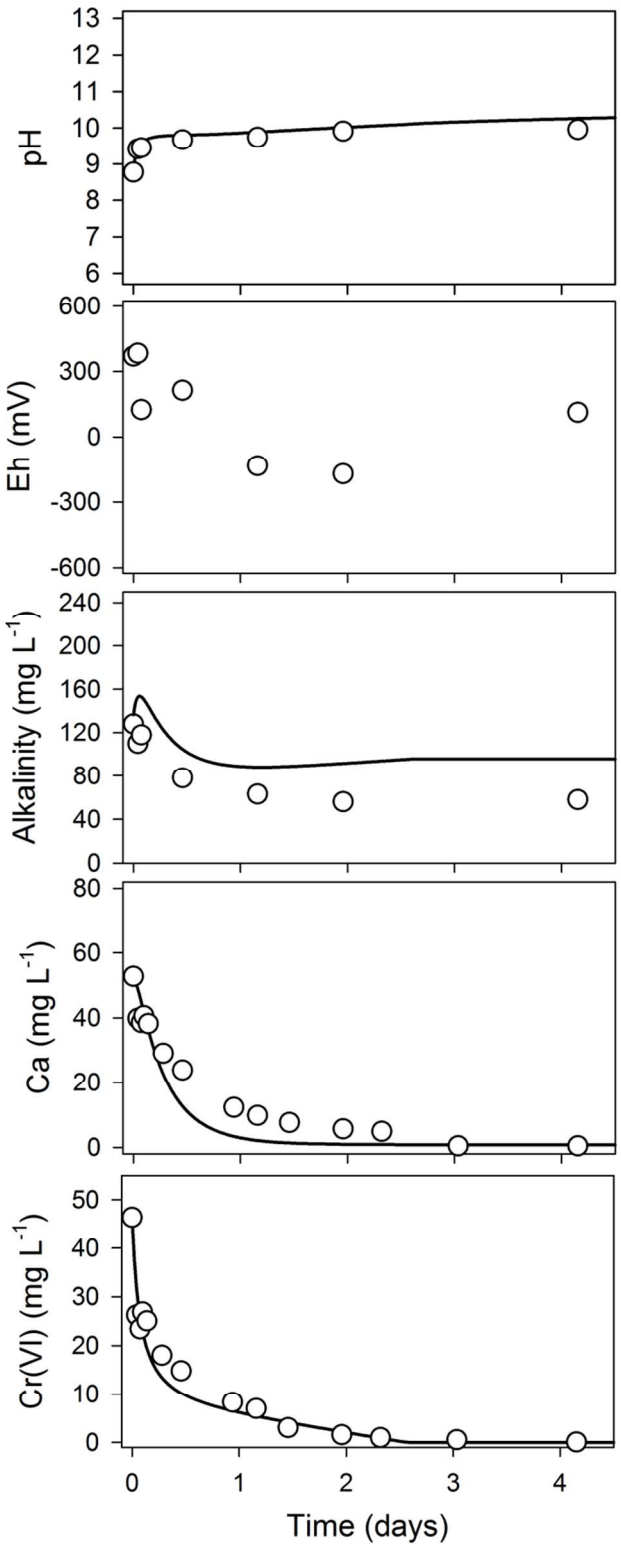

Figure S1. Geochemical evolution of the batch experiment, where the symbols represent the experimental data and the solid line represents the simulation results. Alkalinity is reported in mg L^{-1} as $CaCO_3$.

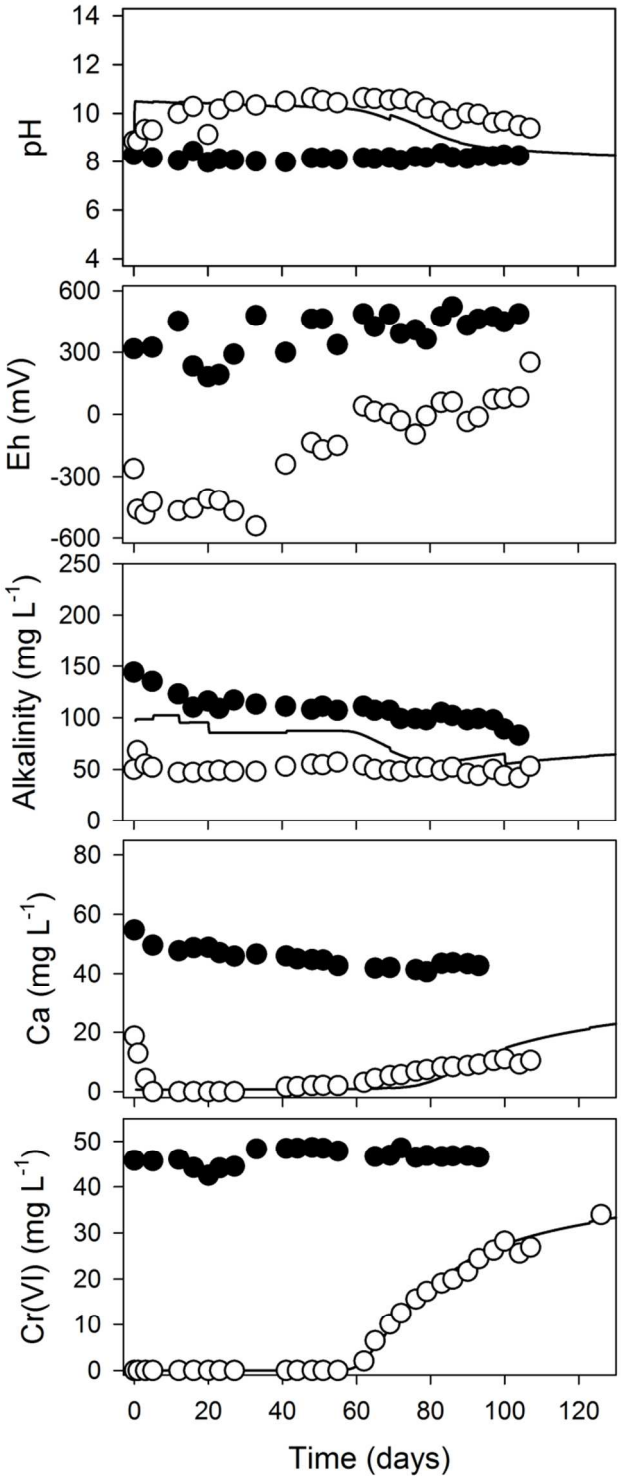

Figure S2. Geochemical evolution of the column experiment, where (●) represents the input data and (○) represents the effluent data, and the solid line represents the simulation results. Alkalinity is reported in mg L^{-1} as $CaCO_3$.

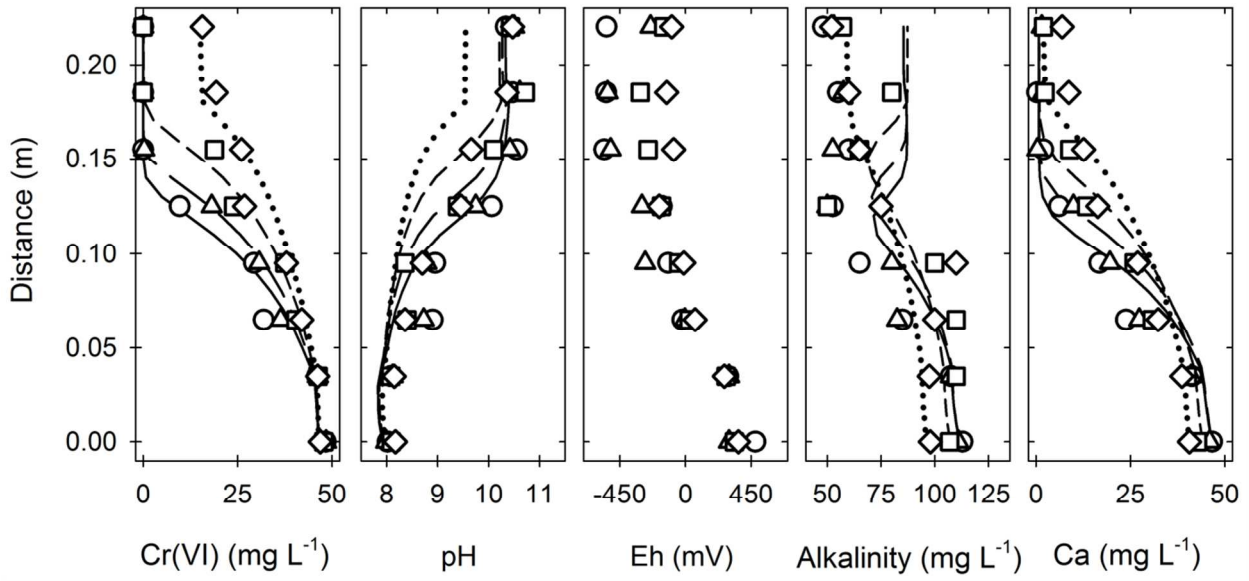

Figure S3. Geochemical evolution of the profile samples from the column experiment (symbols) with simulation results (lines). Sample collection times include 33 days (○; solid), 41 days (△; long dash), 55 days (□; short dash), and 76 days (◇; dotted). Alkalinity is reported in mg L^{-1} as $CaCO_3$.

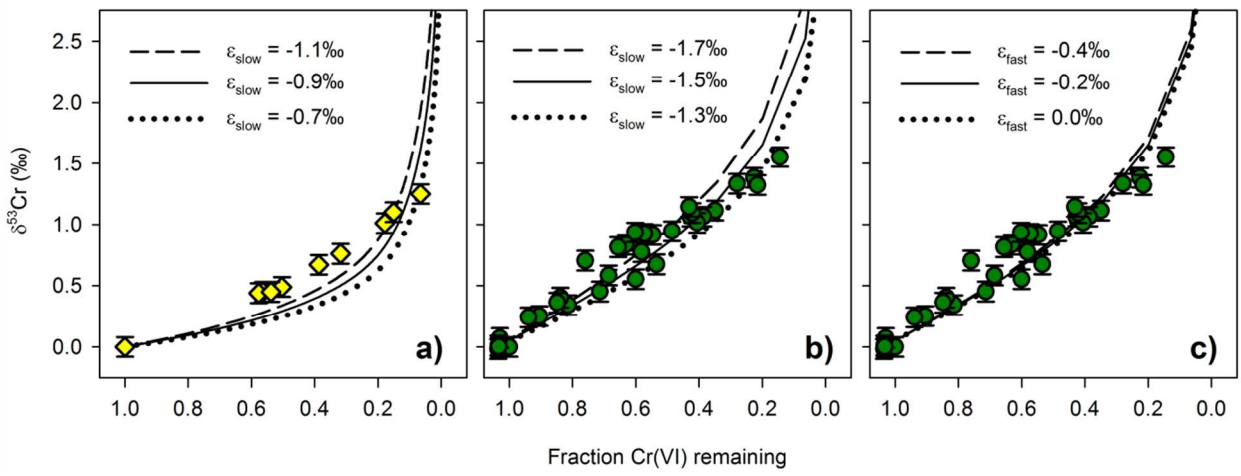

Figure S4. Sensitivity analysis of ε values for the reactive transport simulations, where ε for one mechanism is held constant while the other is varied: a) batch, ε_{fast} = −0.2‰; b) column, ε_{fast} = −0.2‰; and c) column, ε_{slow} = −1.5‰.