

Supporting Information

Natural reduction of hexavalent chromium revealed by Cr stable isotopes in an oxic, basalt-hosted aquifer

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Quantifying Isotopic Fractionation

The magnitude of isotope fractionation is rigorously described using an instantaneous fractionation factor, α , defined by $\alpha = R_{\text{react}}/R_{\text{prod}}$, where R_{prod} and R_{react} are the $^{53}\text{Cr}/^{52}\text{Cr}$ ratios for the reaction product flux and the reactant, respectively, at one instant in time. This fractionation factor is often conveniently expressed as $\varepsilon = (\alpha - 1)$, which is a very close approximation to the difference in $\delta^{53}\text{Cr}$ between the reactant and the reaction product flux: $\varepsilon \approx \delta^{53}\text{Cr}_{\text{reactant}} - \delta^{53}\text{Cr}_{\text{product}}$.

We have chosen to define α as reactant isotope ratio divided by product ratio (not vice versa) because this leads to positive ε values for normal kinetic isotope effects. Negative values can lead to cumbersome language (e.g., a stronger isotopic fractionation gives a lesser, or more negative, ε value). Our convention here follows that used for most carbon and sulfur isotope work over several decades.

Experimental Methods

Sample collection. Sampling methods and descriptions of the multi-level monitoring wells are given in a recent U.S. Geological Survey report (1). Groundwater samples were filtered upon collection using 0.45 μm filters. No preservatives were added. Samples were packed in ice for shipping to Urbana, IL, then stored at 4°C for up to three months prior to analysis.

Isotope analysis. Isotope analyses were completed using a double isotope spike technique used in previous Cr isotope studies (2-3). The double spike solution contains ^{50}Cr and ^{54}Cr with a calibrated $^{50}\text{Cr}/^{54}\text{Cr}$ ratio. This solution is mixed with samples and allows for correction of isotopic fractionation that might occur during sample purification, and mass bias effects during mass spectrometry. A measured amount of double spike solution was added to an aliquot of each sample containing 500-1000 ng of Cr(VI). Each sample was then acidified with HCl to attain a pH between 3 and 5, then passed through a 2 mL bed of BioRad AG1-X8 anion exchange resin. The Cr(VI) adsorbed onto the resin, and cations and weak acid anions were eluted with 15 mL 0.2M HCl followed by 4 mL 2M HCl. The Cr(VI) was then reduced to Cr(III) on the resin by adding a mixture of 1 mL of 2M HNO_3 and several

drops 30% H₂O₂. The Cr(III) was eluted with 6 mL of 2M HNO₃, evaporated to dryness, and treated with several drops concentrated HNO₃ to decompose organic residues. The sample was then dissolved in 2% HNO₃ for mass spectrometry. Quartz distilled acids were used for all steps. The average measured mass of Cr in blank preparations was 1 ng, with a maximum of 4 ng.

Mass spectrometry was conducted on a Nu Instruments Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the University of Illinois at Urbana-Champaign following methods described by Schoenberg *et al.* (3). Analyses were completed using pseudo-high resolution mode to measure Cr isotope intensities without interference from resolvable polyatomic ions such as ArN, ArC, and ArO. Interferences caused by Fe, V, and Ti isotopes were measured and corrected for. A purified standard solution of known isotopic composition, NIST SRM 979, was measured after approximately every 10 samples. Results were normalized to the mean value of SRM 979 for each analysis day. External precision was $\pm 0.14\%$, defined as twice the root mean square difference for the 17 samples prepared and analyzed in duplicate (Table S1).

Concentrations. Preliminary Cr(VI) concentrations were measured colorimetrically using EPA method 7196A. HCl was added to an aliquot of each sample to achieve a pH of approximately 2. Absorbance was measured at 540 nm using a Thermo Genesis spectrophotometer and diphenyl carbazide indicator. Reproducibility was ± 4 $\mu\text{g/L}$. These concentrations were used only to achieve optimal proportions of double spike and sample.

More precise and sensitive concentration determinations were obtained via isotope dilution, as part of the isotope ratio measurements. When the double spike was added to each sample, volumes of double spike and sample solutions were measured. Mass spectrometry yielded precise, mass bias-corrected $^{54}\text{Cr}/^{52}\text{Cr}$ measurements that were used to determine concentrations via routine isotope dilution calculations (*e.g.*, 4).

Mixing equation. $\delta^{53}\text{Cr}$ values of mixtures of water containing background Cr with contaminated water were calculated using

$$\delta_M = \frac{\delta_A C_A f_A + \delta_B C_B (1 - f_A)}{C_A f_A + C_B (1 - f_A)}$$

where δ_M is the $\delta^{53}\text{Cr}$ value of the mixture, δ_A and δ_B are the $\delta^{53}\text{Cr}$ values of waters A and B, C_A and C_B are their concentrations, and f_A is the volume fraction of A in the mixture (4).

Table S1. Measured Cr(VI) concentrations and $\delta^{53}\text{Cr}$ values.

Sample Location	Date Sampled	Cr(VI)		$\delta^{53}\text{Cr}$ (‰)	Sampling Depth (m)	Dissolved O ₂ (mg/L)
		Concentration (μg/L)				
		Historical Maximum	This Study			
<i>Upgradient Wells</i>						
TRA-1	4/22/08	2 ³	3.21	1.23‰	183	--
TRA-4	4/22/08	2 ³	3.89	1.13‰	294	--
" (duplicate)			3.67	1.11‰		
USGS 006	11/27/07	<1 ⁵	48.5 ¹	0.94‰	189	--
" (duplicate)			48.2 ¹	1.04‰		
USGS 006 Resampled	10/30/08		38.5 ¹	1.13‰	189	--
USGS 015	11/27/07	8 ³	7.72	1.24‰	186	--
" (duplicate)			7.71	1.24‰		
USGS 133, zone 1	9/2/08	--	5.10	0.82‰	227	13.8 ⁴
USGS 133, zone 2	9/2/08	--	5.92	0.86‰	209	11.4 ⁴
USGS 133, zone 3	9/2/08	--	5.79	0.84‰	173	11.1 ⁴
USGS 133, zone 4	9/2/08	--	1.99	2.51‰	143	7.46 ⁴
" (duplicate)			1.93	2.40‰		
USGS 134, zone 1	9/3/08	--	4.17	1.37‰	261	10.3 ⁴
" (duplicate)			4.39	1.41‰		
USGS 134, zone 2	9/3/08	--	6.76	0.77‰	246	10.4 ⁴
USGS 134, zone 3	9/3/08	--	6.86	0.83‰	215	10.5 ⁴
USGS 134, zone 4	9/4/08	--	4.54	1.21‰	196	8.90 ⁴
" (duplicate)			4.47	1.27‰		
USGS 134, zone 5	9/4/08	--	6.99	1.03‰	176	10.0 ⁴
<i>Downgradient Wells</i>						
EBR 1	4/24/08	3 ³	7.05	0.73‰	328	6.6 ⁵
M1SA (RWMC)	11/27/07	--	30.0	1.41‰	194	--
" (duplicate)			29.4	1.39‰		
Middle 2050a, zone 2	8/26/08	--	3.66	1.06‰	304	9.80 ⁴
" (duplicate)			3.63	1.04‰		
Middle 2050a, zone 3	8/26/08	--	8.60	0.95‰	241	7.79 ⁴
Middle 2050a, zone 4	8/26/08	--	2.98	0.93‰	196	7.42 ⁴
Middle 2050a, zone 5	8/26/08	--	8.80	0.63‰	157	7.60 ⁴
Middle 2051, zone 1	8/21/08	--	7.06	0.71‰	348	10.7 ⁴
Middle 2051, zone 2	8/21/08	--	7.49	0.66‰	333	9.31 ⁴
Middle 2051, zone 3	8/21/08	--	8.68	0.67‰	252	10.3 ⁴
Middle 2051, zone 4	8/21/08	--	7.90	0.58‰	229	9.80 ⁴
Middle 2051, zone 5	8/25/08	--	1.10	0.59‰	184	7.55 ⁴
Middle 2051 zone 6	8/25/08	--	1.99	2.65‰	178	--
" (duplicate)			1.81	2.58‰		
USGS 034	4/17/08	28 ⁵	33.7	0.31‰	213	--
USGS 036	4/17/08	16 ⁵	27.7	0.47‰	173	--
USGS 038	4/17/08	10 ⁵	19.6	0.78‰	187	--
USGS 058	4/29/08	29 ⁵	9.69	0.53‰	153	--
USGS 065	4/15/08	500 ⁵	92.4	0.25‰	152	8.6 ⁵

" (duplicate)			98.4	0.34‰		
" (duplicate)			100.86	0.32‰		
USGS 076	4/28/08	16 ⁵	12.4	0.65‰	219	8.8 ⁵
" (duplicate)			11.43	0.51‰		
USGS 079	4/24/08	11 ⁵	5.05	1.14‰	214	10.0 ⁵
USGS 082	4/18/08	1 ⁵	3.80	1.92‰	211	9.5 ⁵
" (duplicate)			3.63	1.87‰		
USGS 103, zone 1	8/19/08	--	6.30	0.87‰	387	9.96 ⁴
USGS 103, zone 2	8/18/08	--	6.46	0.90‰	372	10.2 ⁴
USGS 103, zone 3	8/18/08	--	6.50	0.86‰	334	9.21 ⁴
USGS 103, zone 4	8/18/08	--	6.79	0.81‰	305	8.90 ⁴
USGS 103, zone 5	8/19/08	--	6.26	0.93‰	278	10.8 ⁴
USGS 103, zone 6	8/19/08	--	5.70	1.08‰	245	12.4 ⁴
" (duplicate)			5.54	1.18‰		
USGS 103, zone 7	8/20/08	--	0.60	1.84‰	208	5.47 ⁴
USGS 109	4/28/08	4 ⁵	5.15	1.61‰	244	7.8 ⁵
" (duplicate)			5.05	1.61‰		
USGS 111	4/9/08	3 ⁵	29.6	1.14‰	171	10.3 ⁵
" (duplicate)			29.6	1.15‰		
USGS 113	4/23/08	5 ⁵	10.0	0.67‰	172	9.5 ⁵
USGS 116	4/8/08	8 ⁵	6.54	1.44‰	174	9.5 ⁵
USGS 121	4/24/08	7 ⁵	4.61	0.79‰	145	--
USGS 127	4/7/08	--	11.3	1.30‰	182	11.9 ⁵
USGS 131	4/21/08	--	12.3	0.65‰	243	--
USGS 132, zone 1	8/12/08	--	8.20	0.59‰	357	9.49 ⁴
USGS 132, zone 2	8/12/08	--	7.61	0.52‰	308	8.89 ⁴
USGS 132, zone 3	8/13/08	--	8.56	0.53‰	280	10.2 ⁴
USGS 132, zone 4	8/13/08	--	8.70	0.52‰	252	9.28 ⁴
USGS 132, zone 5	8/13/08	--	8.64	0.66‰	233	8.38 ⁴
USGS 132, zone 6	8/14/08	--	17.4	1.79‰	194	6.94 ⁴
<i>Perched Water Zone</i>						
PW 8	4/14/08	30 ⁵	3.34	2.87‰	52	--
" (duplicate)			3.01	2.95‰		
PW 9	10/6/08	260 ⁵	12.4	1.26‰	61	4.5 ⁵
USGS 053 (archived) ²	1967	630 ⁶	510	0.18‰	27	--
USGS 054	10/4/07	727 ⁵	6.11	0.76‰	28	--
USGS 054 (archived) ²	1967		530	0.38‰		
USGS 055	4/15/08	230 ⁵	17.0	0.51‰	25	--
" (duplicate)			16.0	0.60‰		
USGS 055 (archived) ²	1967		270	1.13‰		
USGS 072	4/22/08	2 ³	0.48	1.44‰	61	--
USGS 073	10/7/08	237 ⁵	37.8	0.69‰	39	8.4 ⁵

--" data unavailable; ¹Outlier (see text); ²Archived samples from 1967; ³Data from Liszewski and Mann (5); ⁴Data from Bartholomay and Twining (1); ⁵Data from NWIS database (6); ⁶Data from Bartholomay (7)

References for Supporting Information

- (1) Bartholomay, R. C.; Twining, B. V. *Chemical constituents in groundwater from multiple zones in the snake river plain aquifer at the Idaho national laboratory, Idaho, 2005–08*, Scientific Investigations Report 2010–5116, U. S. Geological Survey: Reston, VA, 2010.
- (2) Ellis, A.S.; Johnson, T.M.; Bullen, T.D. Chromium isotopes and the fate of hexavalent chromium in the environment. *Science* **2002**, 295, 2060-2062.
- (3) Schoenberg, R.; Zink, S.; Staubwasser, M.; von Blanckenburg, F. The stable Cr isotope inventory of solid Earth reservoirs determined by double spike MC-ICP-MS. *Chem. Geol.* **2008**, 249, 294-306.
- (4) Faure, G.; Mensing, T.M. *Isotopes: Principles and Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, 2005.
- (5) Liszewski, M.J.; Mann, L.J. *Concentration of 23 trace elements in ground water and surface water at and near the Idaho National Engineering Laboratory, Idaho, 1988-91*. Open-File Report 93-126, U. S. Geological Survey: Reston, VA, 1993.
- (6) U.S. Geological Survey National Water Information System: Web Interface. Available at <http://nwis.waterdata.usgs.gov/usa/nwis/qwdata>.
- (7) Bartholomay, R.C. *Distribution of selected radiochemical and chemical constituents in perched ground water, Idaho National Engineering Laboratory, Idaho, 1992-95*. Water-Resources Investigations report 98-4026, U. S. Geological Survey, Reston, VA, 1998.