Supplementary Information

Heterogeneous reactions control Cr(VI) release and sequestration in complex chemical mixtures of Cr, Fe, Cu, and organics

Noah Jemison,[1] Angelica Benavidez,[1, 2] Michael Spilde,[3] Angelica Saenz-Trevizo,[3] Adrian Brearley,[3] Juan Lezama Pacheco,[4] Drew Latta,[5] Kaelin Gagnon,[6] Stephen Emeanuwa,[2] Fernando Garzon,[1, 2] Stephen Cabaniss,[7] Peter Lichtner,[8] Abdul-Mehdi Ali,[3] José M. Cerrato[1, 6, 8]

[1] Center for Micro Engineered Materials, 1001 University Dr., Albuquerque, New Mexico 87106, USA
[2] Department of Chemical & Biological Engineering, University of New Mexico, Albuquerque, New Mexico 87131, USA
[3] Department of Earth and Planetary Sciences, MSC03 2040, University of New Mexico, Albuquerque, NM, 87131, USA
[4] Department of Environmental Earth System Science, Stanford University, California 94305, USA
[5] Department of Civil and Environmental Engineering, The University of Iowa, 4105 Seamans Center, Iowa City, Iowa 52242, USA
[6] Gerald May Department of Civil, Construction & Environmental Engineering, MSC01 1070, 1 University of New Mexico, Albuquerque, New Mexico 87131, USA
[7] Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, USA
[8] Center for Water and the Environment, University of New Mexico, Albuquerque, New Mexico, 87131, USA

Summary: 12 pages, 2 tables, 7 figures.

Contents

Table S1. Cr(VI) concentrations measured by UV-Vis of batch experiments. Percent Cr(VI) removed is calculated by comparing the remaining concentration to the initial 250 µM Cr(VI). ..3

Table S2. Linear combination fitting results from Cr K-edge XANES spectra. 5

Figure S1. A) Cr solutions used in the initial column experiment. No precipitation in the Cr solution, a yellow precipitate in the Cr and Cu solution, black precipitate in the Cr, Cu, and cysteine solution, and brown precipitate in the Cr, Cu, cysteine, and Fe solution. **B)** Precipitation of solids in the second column experiment. Yellow precipitate in the Cr and Cu solution, pink precipitate in the Cr, Cu, and ascorbic acid solution, and brown precipitate in the Cr, Cu, ascorbic acid, and Fe solution. 6

Figure S2. Concentrations of Br and Cl tracers in ascorbic acid column experiment **A)** versus time and **B)** versus number of pore volumes. 7

Figure S3. Concentrations of Cr, Cu, and Fe during the column experiment with ascorbic acid versus number of pore volumes. 8

Figure S4. Microprobe image of goethite collected from column experiment with ascorbic acid. Sampling locations are marked. 9

Figure S5. Microprobe images of goethite collected from column experiment with cysteine. Sampling locations are marked. 10

Figure S6. Additional TEM elemental maps of Fe and Cr of several goethite particles collected from the column experiment with ascorbic acid. 11

Figure S7. Additional TEM elemental maps of Fe and Cr of several goethite particles collected from the column experiment with cysteine. 12

Table S1. Cr(VI) concentrations measured by UV-Vis of batch experiments. Percent Cr(VI) removed is calculated by comparing the remaining concentration to the initial 250 μM Cr(VI).

Sample	Cr(VI) concentration	% Cr(VI) removed
goethite experiments		
Cr 1	202.50	19.00
Cr 2	223.38	10.65
Cr 3	228.29	8.68
Cr and cysteine 1	152.04	39.18
Cr and cysteine 2	147.87	40.85
Cr and cysteine 3	147.59	40.96
Cr and Cu 1	93.60	62.56
Cr and Cu 2	108.81	56.47
Cr and Cu 3	115.68	53.73
Cr and Fe 1	4.64	98.14
Cr and Fe 2	12.99	94.81
Cr and Fe 3	8.91	96.44
Cr and citrate 1	175.23	29.91
Cr and citrate 2	213.64	14.55
Cr and citrate 3	222.82	10.87
Cr and Cu and Fe 1	10.95	95.62
Cr and Cu and Fe 2	33.86	86.46
Cr and Cu and Fe 3	10.85	95.66
Cr and Cu and cysteine 1	83.02	66.79
Cr and Cu and cysteine 2	92.86	62.86
Cr and Cu and cysteine 3	98.05	60.78
Cr and ascorbate 1	7.55	96.98
Cr and ascorbate 2	10.92	95.63
Cr and ascorbate 3	11.02	95.59
Cr and ascorbate and Cu 1	10.61	95.76
Cr and ascorbate and Cu 2	5.31	97.88
Cr and ascorbate and Cu 3	5.31	97.88
ferrihydrite experiments		
Cr 1	169.11	32.36
Cr 2	175.77	29.69
Cr 3	188.32	24.67
Cr and Cu 1	170.37	31.85
Cr and Cu 2	167.66	32.93
Cr and Cu 3	166.80	33.28
Cr and Fe 1	1.83	99.27
Cr and Fe 2	0.58	99.77
Cr and Fe 3	0.39	99.85
Cr and cysteine 1	98.46	60.62
Cr and cysteine 2	123.65	50.54

Cr and cysteine 3	135.81	45.68
Cr and Cu and Fe 1	36.49	85.41
Cr and Cu and Fe 2	5.79	97.68
Cr and Cu and Fe 3	1.06	99.58
Cr and Cu and cysteine 1	97.39	61.04
Cr and Cu and cysteine 2	123.75	50.50
Cr and Cu and cysteine 3	121.53	51.39

Table S2. Linear combination fitting results from Cr K-edge X-ray absorption near edge structure (XANES) spectra.

Sample	% Average Content	
	$CrOH_3$	Cr(VI)
250 μM Cr	68%	32%
250 μM Cr and 1mM Fe(II)	100%	0%
250 μM Cr and 1mM Cu(II)	0%	100%

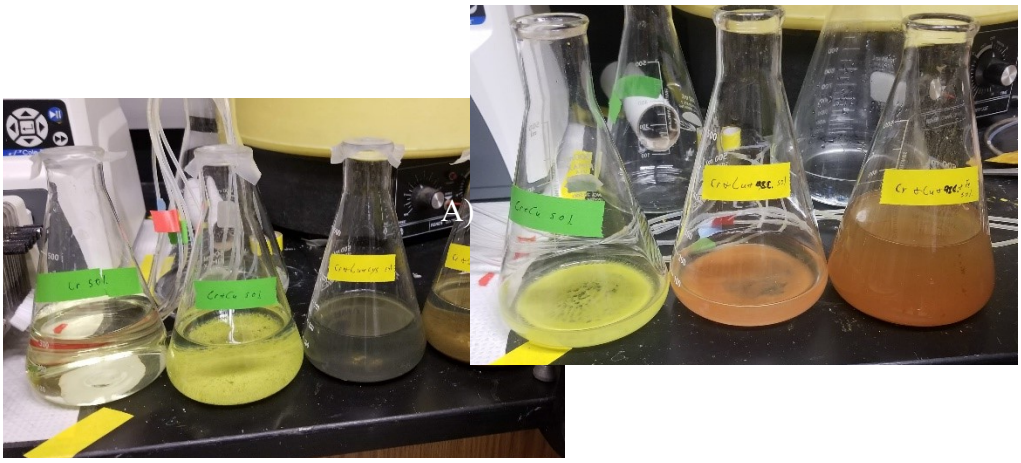

Figure S1. A) Cr solutions used in the initial column experiment. No precipitation in the 250 µM Cr solution, a yellow precipitate in the 250 µM Cr and 1mM Cu solution, black precipitate in the 250 µM Cr, 1mM Cu, and 1mM cysteine solution, and brown precipitate in the 250 µM Cr, 1mM Cu, 1mM cysteine, and 1mM Fe solution. **B)** Precipitation of solids in the second column experiment. Yellow precipitate in the 250 µM Cr and 1mM Cu solution, pink precipitate in the 250 µM Cr, 1mM Cu, and 1mM ascorbic acid solution, and brown precipitate in the 250 µM Cr, 1mM Cu, 1mM ascorbic acid, and 1mM Fe solution.

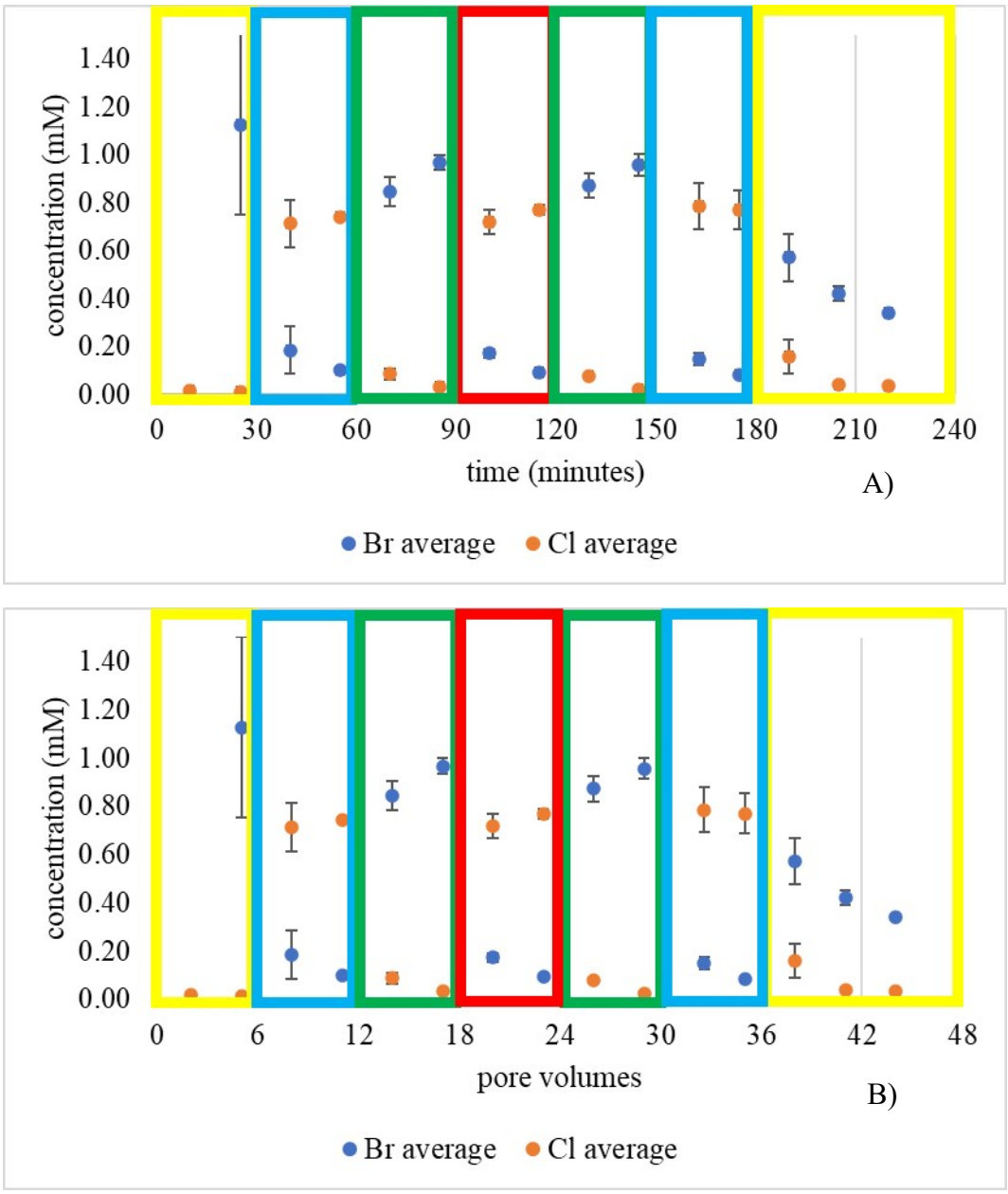

Figure S2. Concentrations of 1mM Br and 1mM Cl tracers in ascorbic acid column experiment **A)** versus time and **B)** versus number of pore volumes.

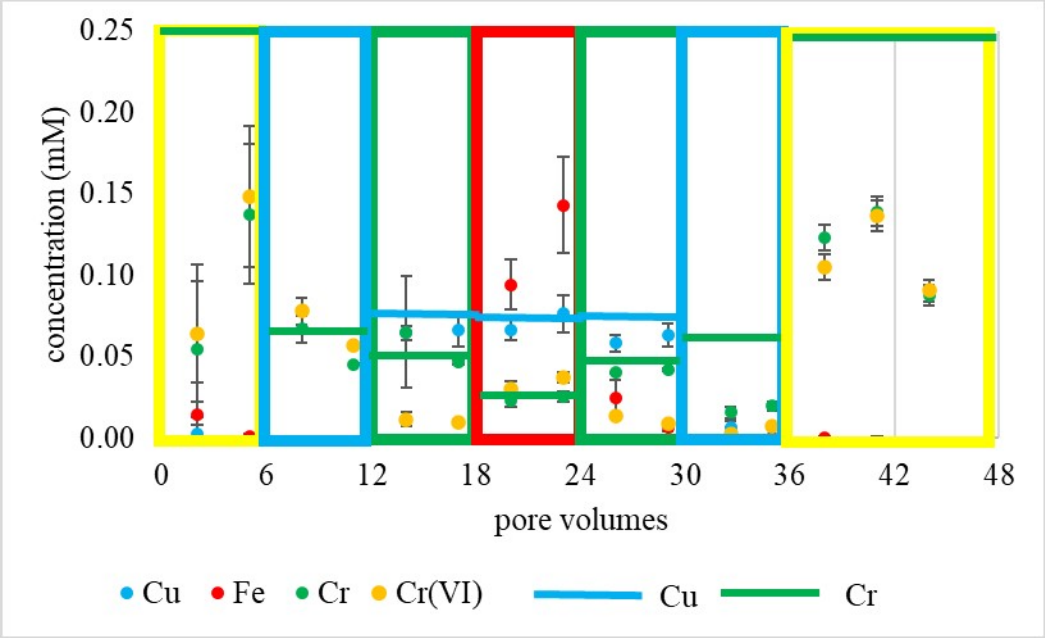

Figure S3. Concentrations of Cr, Cu, and Fe(II) during the column experiment with ascorbic acid versus number of pore volumes. Initial concentrations were 250 µM, 1mM, and 1mM for Cr, Cu, and Fe(II), respectively.

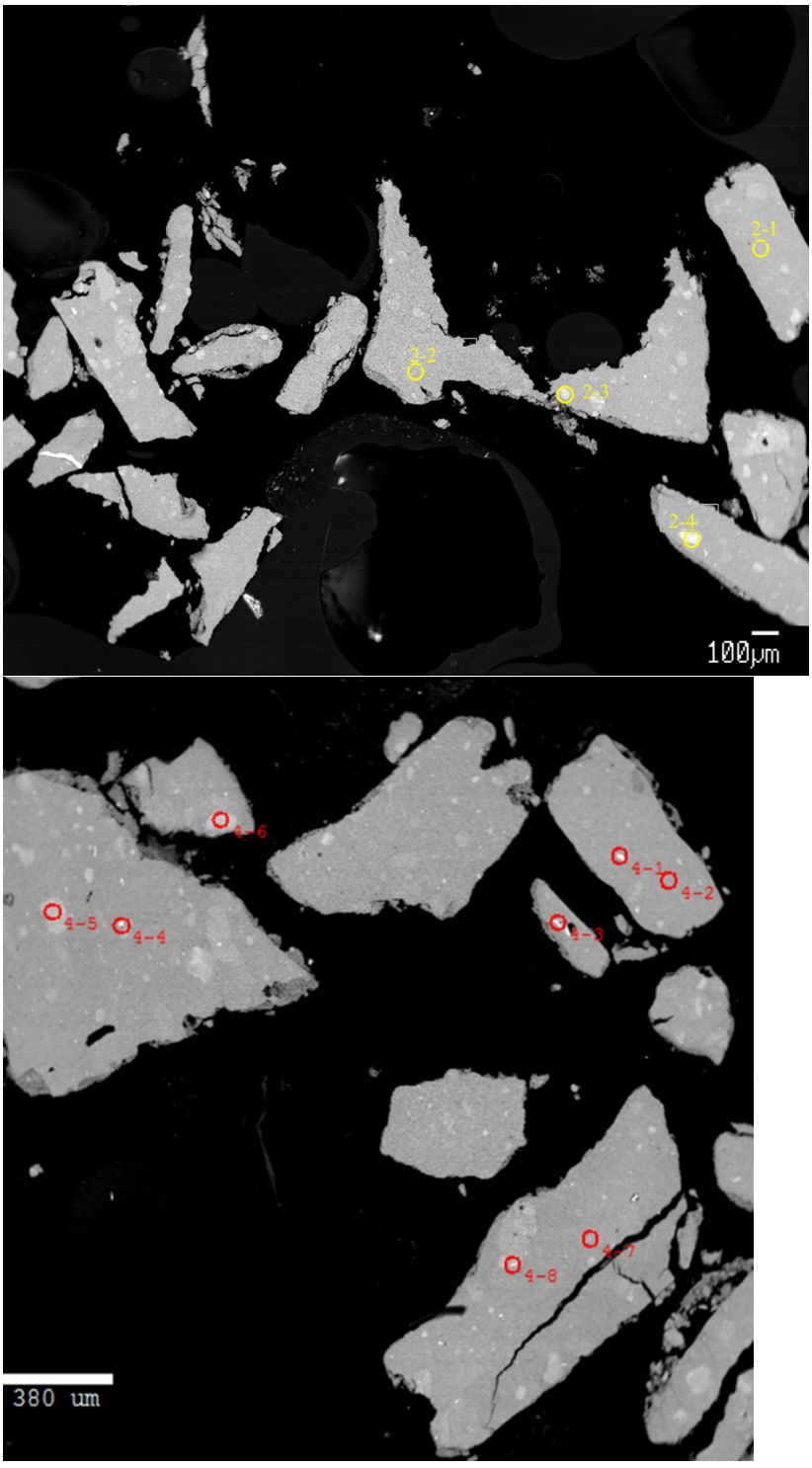

Figure S4. Backscattered electron (BSE) images for electron microprobe analyses (EMPA) of goethite collected from column experiment with ascorbic acid. Sampling locations are marked. Sampling locations 2-3 and 2-4 appear as bright spots on microprobe and have higher Cu and Cr concentrations, possibly due to Cr and Cu co-precipitation.

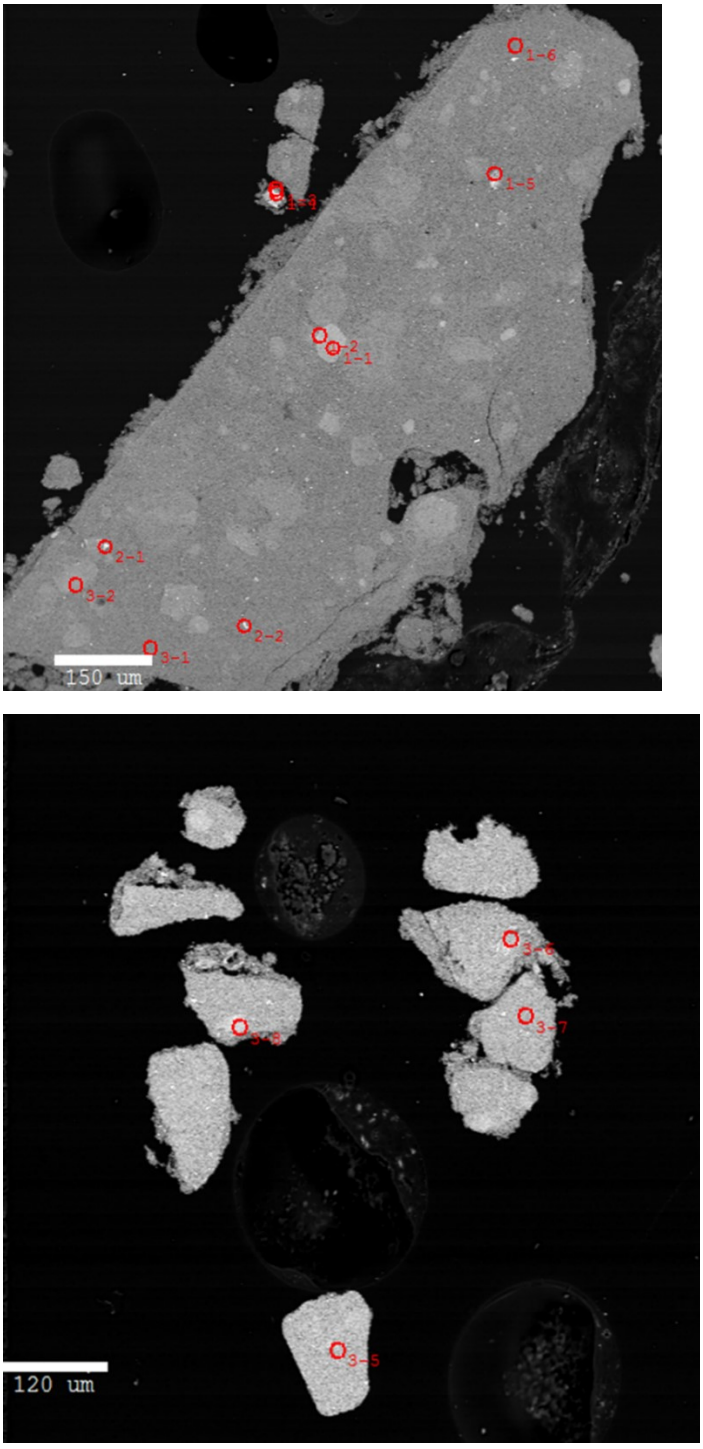

Figure S5. Backscattered electron (BSE) images for electron microprobe analyses (EMPA) of goethite collected from column experiment with cysteine. Sampling locations are marked.

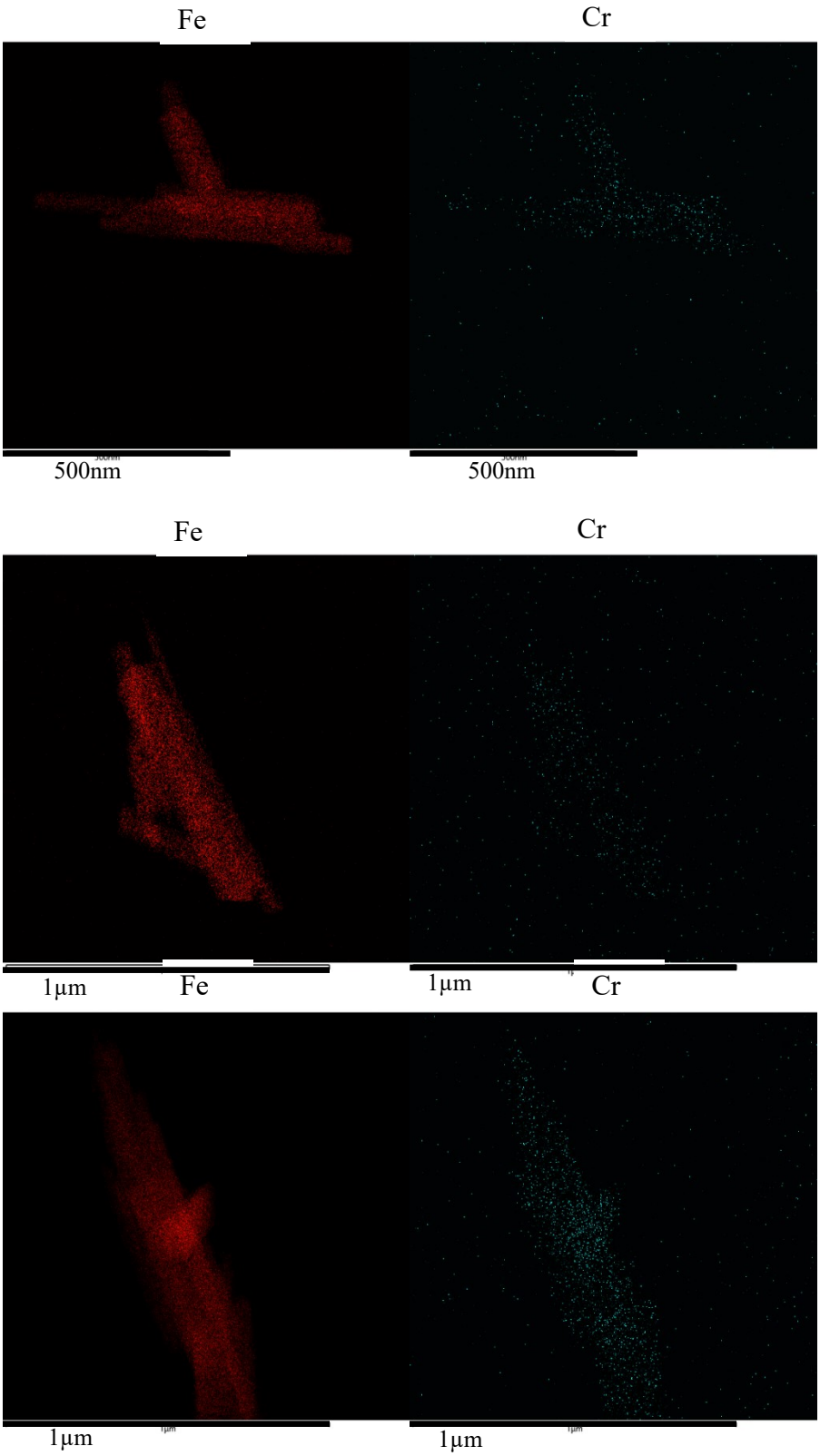

Figure S6. Transmission electron microscopy (TEM) elemental maps of Fe and Cr of several goethite particles collected from the column experiment with ascorbic acid.

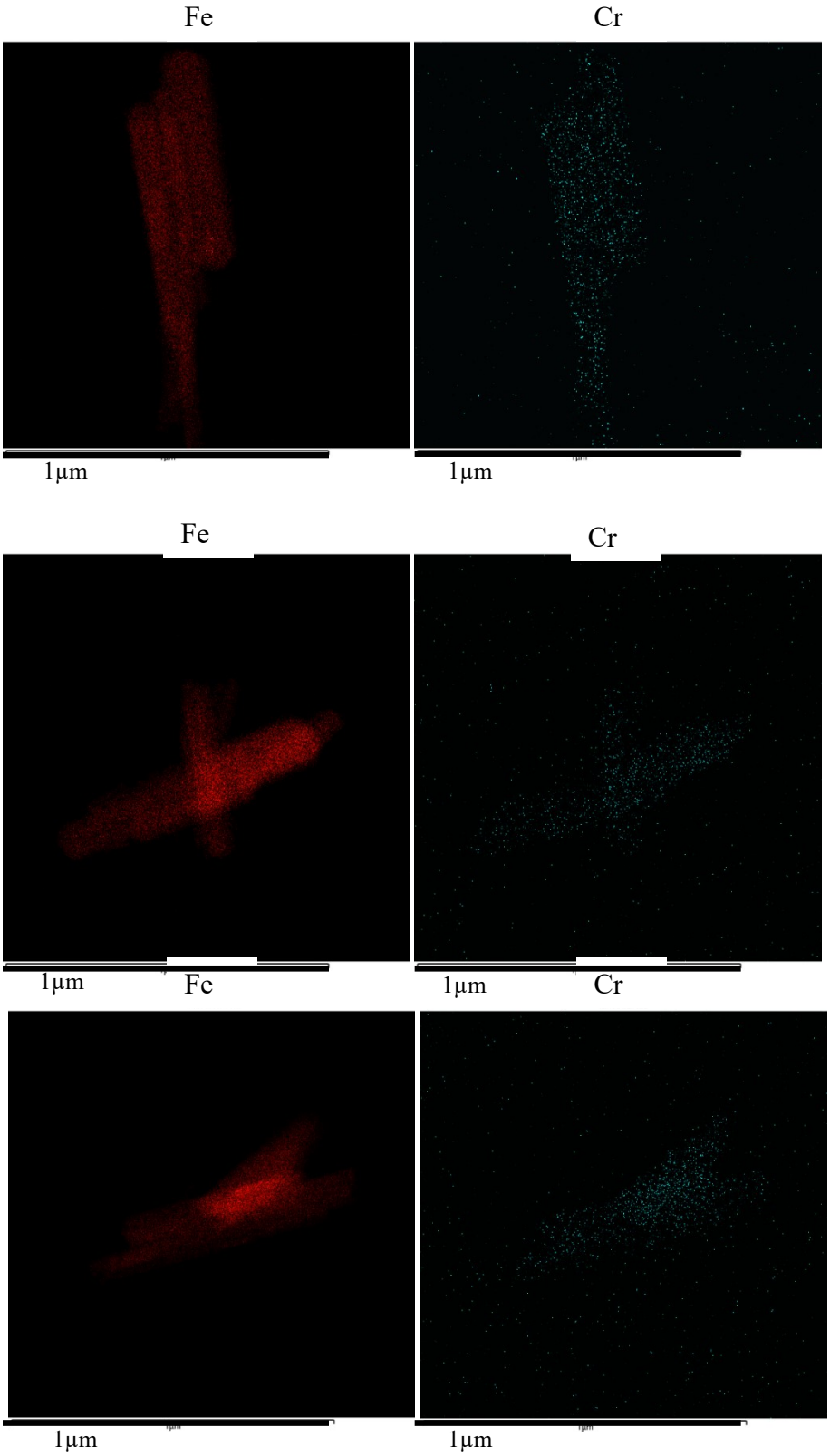

Figure S7. Transmission electron microscopy (TEM) elemental maps of Fe and Cr of several goethite particles collected from the column experiment with cysteine.