

10.1071/EN17221_AC

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Environmental Chemistry 2018, 15(5), 259-266

Supplementary Material

Abiotic reduction of insensitive munition compounds by sulfate green rust

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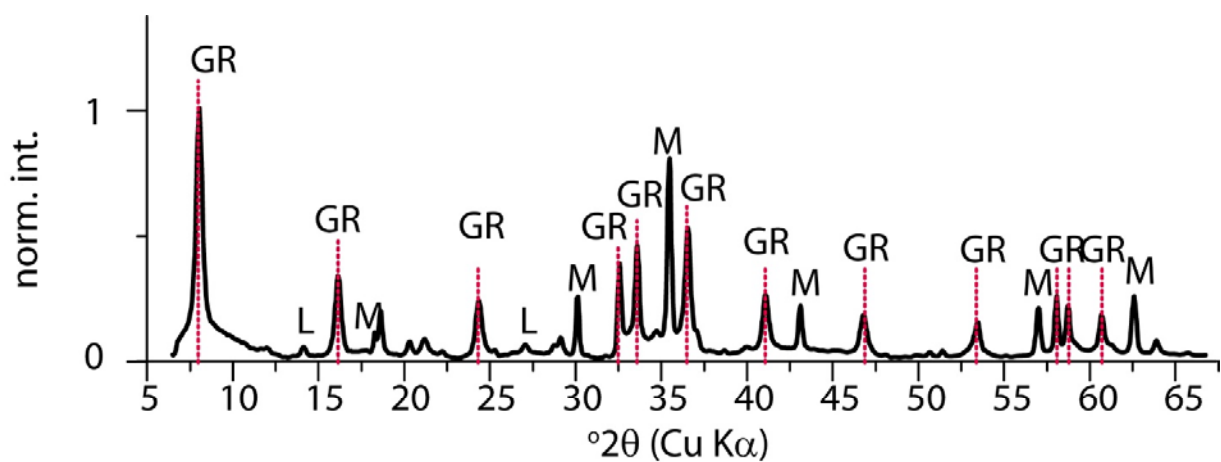
X-ray Absorption Spectroscopic (XAS) Methods

X-ray absorption near edge structure (XANES) is a spectroscopic technique sensitive to Fe redox state (Wilke et al., 2001; O'Day et al., 2004). *Bulk* iron speciation was interrogated with Fe K α XANES spectra collected on beam line 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL), a National Laboratory user facility operated by the DOE. The X-ray beam was operated at 3 GeV and 500 mA and a double-crystal monochromator (Si [220] crystal, $\phi=90$) was used to tune the incident energy on the sample, the beam was detuned 40% and slit down to 2 mm vertical and 4.5 mm horizontal, and energy was calibrated to an iron foil (Fe⁰) by defining the first inflection of the absorbance edge to 7112 eV. Fluorescence was measured with a 100 element Ge detector, and samples were held under LN₂ cryostat during analysis. Samples were ground and homogenized in an anaerobic chamber (Coy, MI), mounted in aluminum plates, sealed with Kapton tape, transferred to the beam line under anoxic conditions, and placed in the cryostat LN₂. XAS data were acquired between 6860 and 7810 eV ($k=13.5$) using 0.35 eV energy steps in the XANES region. Reference samples were collected in fluorescence and transmission mode using the same procedures as for the samples. Data collection and analysis of Fe reference compounds are described in detail in O'Day et al. (2004). *Real time* speciation was examined using a flow-through apparatus with Fe K α XANES at beam line 4-3, at SSRL with a Si [111] crystal, $\phi=90$ double crystal monochromator detuned 10%, energy resolution is $\Delta E/E = 10^{-4}$. The beamline was equipped with a passivated implanted planar silicon (PIPS) detector and SiNi coated collimating mirror for harmonic rejection; samples were collected at room temperature. The full beam was slit down to 2 x 2 mm and targeted at the base of the reaction cell window. The reaction cell was packed at a concentration of 1 g GR kg⁻¹ DDI water (solid to solution ration = 1:1000) under anaerobic conditions (97/3 N₂/H₂) in a glove bag (Coy, MI) at SSRL. The reservoir of IMC was

sparged with UHP He_(g) before and during the flow through experiment. Collection of Fe XANES every 7 minutes was continued for 200 minutes, the reaction was allowed to continue and was analyzed at 320 and 680 minutes to check for completion of reaction. The DNAN concentration was 0.25 mM and NTO was 0.5 mM. A control sample (no IMC) of green rust was loaded into a reaction cell and was measured at the onset of the experiment and periodically for 14.75 hours (**Fig. S3**) under the same flow conditions (with DDI only) to confirm that the GR was stable in the absence of IMC. *Spectral fitting* of Fe K α XANES were accomplished using SIXPACK software package (Webb, 2005) for dead-time correction and averaging replicate scans (min. of 3 for bulk, 1 scan for flow through). The averaged XANES spectra for both the standards and the samples were background subtracted, normalized and post edge flattened by regressing polynomials to the data regions before and after the edge step in the software package Athena (Ravel and Newville, 2005). The first derivative of the normalized and flattened spectra were used for linear combination analysis by fitting a binary mixture of reference spectra iteratively fit by trial-and-error with green rust and lepidocrocite, which were determined from a reference library of ~30 spectra (Hayes et al., 2014). Goodness-of-fit is reported as χ^2 , a statistical confidence limit indicator of the goodness of the calculated fit from the sum of squared error divided by the degrees of freedom in the fit and the R-factor, which is the mean square sum of the misfit at each data point. These parameters of confidence limit are measures of the precision of a varied parameter but not necessarily the accuracy of the fit, in that it does not account for appropriateness of reference spectra, data quality, or differences in data collection. All fit components were constrained to be positive and component sum was forced to unity.

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GR = green rust $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_5(\text{SO}_4)$
M = magnetite Fe_3O_4
L = Lepidocrocite $\gamma\text{-FeOOH}$

Figure S1. X-ray diffractogram of sulfate green rust. Small amounts of lepidocrocite were present, and confirmed with XANES collected under anaerobic conditions, possibly due to partial oxidation of GR. The presence of magnetite is attributed to exposure to oxygen during diffractogram collection, magnetite was not observed in Fe XANES.

Table S1 Linear combination fits of green rust reacted with IMC.

IMC	Green rust ^a	\pm^b	Lepidocrocite ^c	\pm^b	reduced χ^2 ^d	R-factor ^e
NTO ^f	0.060	(0.009)	0.940	(0.015)	0.000022	0.0056
DNAN ^g	0.387	(0.018)	0.613	(0.021)	0.000083	0.0226

^a Green rust II sulfate, collected in transmission mode at SSRL on BL 4-1 Si(220). ^b \pm is the estimated error (\pm) of the weighted fit. ^c Lepidocrocite (γ -FeOOH) collected in transmission mode at SSRL on BL 4-3 Si(220). ^d Reduced chi square $\chi^2 = \left(\frac{1}{\epsilon^2 N} \sum_i [y_i^{data} - y_i^{model}]^2\right) / (N_{ind} - N_{fit\ par})$, where ϵ is assumed to equal unity for LCF, N is the number of independent and fit variables, y_i are the experimental data and simulated model. ^e R-value = $\sum[(data - fit)^2 / (data)^2]$. ^f NTO = 3-nitro-1,2,4-triazole-5-one, ^g DNAN = 2,4-dinitroanisole.

Table S2 Linear combination XANES fits of green rust reacted with IMC NTO.

step	time	minutes	NTO LCF fits ^a				goodness of fit	
			Lepidocrocite γ FeOOH	+/- ^b	Green rust $Fe^{II}_2Fe^{III}(OH)_5(SO_4)$	+/- ^b	red χ^2 ^c	R ^d
0	12:22	0	0.197	0.027	0.803	0.033	0.000109	0.01880
1	12:29	7	0.247	0.024	0.753	0.030	0.000086	0.01460
2	12:36	14	0.297	0.023	0.703	0.028	0.000072	0.01340
3	12:44	22	0.281	0.019	0.719	0.024	0.000624	0.01140
4	12:51	29	0.338	0.017	0.662	0.020	0.000045	0.00828
5	12:58	36	0.344	0.016	0.656	0.020	0.000045	0.00838
6	13:06	44	0.410	0.018	0.590	0.023	0.000061	0.01014
7	13:14	52	0.443	0.015	0.557	0.019	0.000046	0.00750
8	13:21	59	0.433	0.017	0.567	0.021	0.000061	0.01033
9	13:28	66	0.458	0.020	0.542	0.025	0.000079	0.01377
10	13:35	73	0.500	0.019	0.500	0.025	0.000074	0.01268
11	13:43	81	0.533	0.018	0.467	0.022	0.000060	0.01023
12	13:50	88	0.562	0.025	0.438	0.032	0.000121	0.02070
13	13:57	95	0.593	0.021	0.407	0.027	0.000091	0.01563
14	14:04	102	0.650	0.020	0.350	0.026	0.000076	0.01337
15	14:12	110	0.612	0.016	0.388	0.022	0.000039	0.00620
16	14:19	117	0.818	0.056	0.182	0.071	0.000365	0.06100
18	14:33	131	0.751	0.031	0.249	0.039	0.000178	0.02580
19	14:41	139	0.849	0.048	0.151	0.058	0.000214	0.03650
20	14:48	146	0.808	0.019	0.192	0.025	0.000699	0.01180
42	15:43	201	0.918	0.043	0.082	0.052	0.000167	0.03120

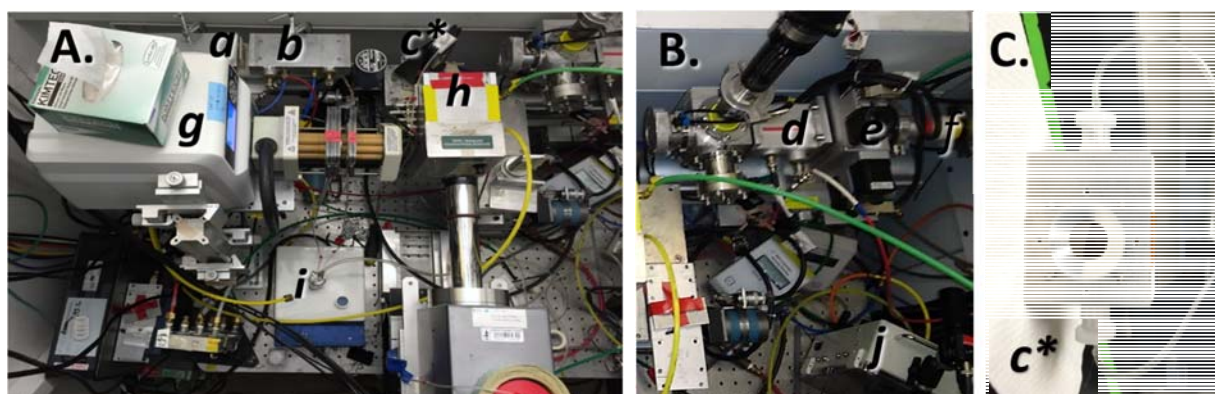
^a Linear combination fits (LCF) of iron K-edge XANES spectra to binary mixtures of green rust and lepidocrocite, ^b \pm error reported as the estimated standard deviation. ^c Reduced chi squared (χ^2) is a fit statistic indicators of goodness of fit, minimized in iterative fits, calculated from the sum of the error divided by the degrees of freedom in the fit to estimate how well the components fit the data; ^d R factor is the mean square sum of the misfit at each data point, and along with χ^2 , is another indicator of goodness of fit. Equations for χ^2 and R are given in Table S1.

Table S3 Linear combination XANES fits of green rust reacted with IMC DNAN.

step	time	minutes	DNAN LCF fits ^a				goodness of fit	
			Lepidocrocite γ FeOOH	+/- ^b	Grenrust $Fe^{II}_2Fe^{III}(OH)_5(SO_4)$	+/- ^b	red χ^2 ^c	R ^d
0	6:00	0	0.231	0.015	0.769	0.018	0.000045	0.00705
1	6:10	10	0.232	0.020	0.768	0.023	0.000080	0.01430
2	6:18	18	0.238	0.023	0.762	0.026	0.000600	0.01056
3	6:30	30	0.249	0.025	0.751	0.029	0.000119	0.02145
4	6:37	37	0.275	0.026	0.725	0.030	0.000120	0.02158
5	6:45	45	0.328	0.023	0.672	0.027	0.000098	0.01817
6	6:52	52	0.340	0.028	0.660	0.032	0.000139	0.02546
7	6:59	59	0.400	0.027	0.600	0.032	0.000126	0.02449
8	7:06	66	0.362	0.033	0.638	0.040	0.000175	0.03344
9	7:14	74	0.395	0.018	0.605	0.024	0.000725	0.01385
10	7:21	81	0.445	0.027	0.555	0.033	0.000126	0.02409
11	7:28	88	0.447	0.019	0.553	0.022	0.000091	0.01755
12	7:35	95	0.489	0.017	0.511	0.020	0.000057	0.01346
13	7:43	103	0.435	0.017	0.565	0.018	0.000074	0.01436
14	7:50	110	0.454	0.015	0.546	0.017	0.000049	0.01028
15	7:57	117	0.513	0.018	0.487	0.021	0.000074	0.01480
16	8:04	124	0.482	0.014	0.518	0.016	0.000042	0.00885
17	8:12	132	0.559	0.014	0.441	0.017	0.000032	0.00680
18	8:19	139	0.526	0.018	0.474	0.021	0.000051	0.01054
19	8:26	146	0.525	0.016	0.475	0.020	0.000048	0.01013
20	8:33	153	0.540	0.017	0.460	0.021	0.000053	0.01096
21	8:41	161	0.531	0.018	0.469	0.023	0.000059	0.01290
22	8:48	168	0.573	0.014	0.427	0.018	0.000036	0.00738
23	8:55	175	0.582	0.022	0.418	0.028	0.000085	0.01809
24	9:03	183	0.608	0.023	0.392	0.030	0.000095	0.01940
25	9:10	190	0.638	0.019	0.362	0.024	0.000064	0.01377
26	9:17	197	0.632	0.018	0.368	0.022	0.000060	0.01226
27	9:24	204	0.664	0.022	0.336	0.028	0.000089	0.01850
28	9:32	212	0.686	0.019	0.314	0.025	0.000069	0.01440
29	9:39	219	0.669	0.019	0.331	0.023	0.000058	0.01190
30	9:46	226	0.675	0.019	0.325	0.024	0.000063	0.01320
31	9:53	233	0.688	0.022	0.312	0.027	0.000076	0.01540
32	10:01	241	0.723	0.018	0.277	0.024	0.000068	0.01450
33	10:08	248	0.700	0.017	0.300	0.021	0.000048	0.00979
34	10:15	255	0.720	0.019	0.280	0.022	0.000066	0.01408
39	11:19	319	0.732	0.023	0.268	0.029	0.000091	0.01858
42	17:21	681	0.781	0.022	0.219	0.029	0.000093	0.01830

^aLinear combination fits (LCF) of iron K-edge XANES spectra to binary mixtures of green rust and lepidocrocite, ^b \pm error reported as the estimated standard deviation. ^c Reduced chi squared (χ^2) is a fit statistic indicators of goodness of fit, minimized in iterative fits, calculated from the sum of the error divided by the degrees of freedom in the fit to estimate how well the components fit the data; ^dR factor is the mean square sum of the misfit at each data point, and along with χ^2 , is another indicator of goodness of fit. Equations for χ^2 and R are given in Table S1.

2 **Figure S2.** Flow through X-ray absorption near edge structure set up.



10 A) Flow through setup for closed loop up-flow of IMC into green rust within experimental hutch at
11 beamline 4-3 (left side of hutch) with XANES collected every 7-7.5 minutes for 200 minutes. B)
12 incident X-ray into experimental hutch (right side of hutch). C) Flow cell made of teflon with Kapton
13 windows clamped between two aluminum plates. a) I₂, b) I₁, c*) sample in reaction cell, d) I₀, e) beam
14 slits, f) X-ray entrance, g) peristaltic pump, h) PIPS detector, i) He(g) sparged IMC (close up in right
15 panel), j) O₂ sensor.

16 **Figure S3.** Green rust control, reacted >14.5 hours in flow through without IMC.

