Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Electronic Supplementary Information

Interdependency of Green Rust Transformation and the Partitioning and Binding Mode of Arsenic

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1. Analysis of aqueous arsenic and iron

Aqueous arsenic was measured by flow injection, hydride generation atomic absorption spectrometry (FI-HG-AAS) using a Perkin Elmer AAnalyst 800 equipped with a hollow cathode lamp. The measurements were performed by first pre-reducing all arsenic in the sample to As(III) by mixing the filtered samples with concentrated HCl and a solution containing 5% (w/v) NaI and 5% (w/v) ascorbic acid and reacting the mixture for at least 1 h at room temperature. After pre-reduction, As(III) was converted to arsine gas (AsH_3) by mixing the sample with a strongly reducing solution consisting of 0.5% (w/v) $NaHB_4$ and 0.05% (w/v) NaOH using a peristaltic pump and a carrier solution of 10% (v/v) HCl. The limit of detection of total As was determined to be 0.1 μg/L.

Dissolved Fe was measured by flame atomic absorption spectrometry using a Perkin Elmer AAnalyst 800. For these measurements, the fresh green rust (GR) suspensions were filtered and the solution passing through the filter was acidified immediately using 70% HNO_3.

2. X-ray Diffraction

Powder diffraction patterns were collected using a Bruker D8 Advance diffractometer with Cu K-alpha radiation, a rotating sample stage and an energy dispersive detector to suppress fluorescence. Data were collected for 5 to 75° 2θ with 0.02° step size and total data collection time of ~4 h per sample. Samples for powder X-ray diffraction (XRD) were obtained by filtering the fresh GR suspension within an anaerobic chamber using 0.22 μm filters. The filtered solids were dried in the anaerobic chamber and ground into a powder using an agate mortar and pestle. Because of the potential for oxidation of the green rust solids during XRD data collection in air, glycerol was added to the solids.

3. X-ray absorption spectroscopy

3.1 Sample preparation

Solids for X-ray absorption spectroscopy (XAS) measurements were collected outside of the anoxic chamber for the oxic aging series and within the anoxic chamber for the anoxic series and the initial (i.e. t = 0) samples. For each sample, up to 10 mg of solids were collected as a wet paste on 0.22 or 0.45 µm filters. The volume of suspension passed through the filter was calculated to ensure that the amounts of filtered solids were optimized for Fe K-edge XAS data collection in transmission mode, i.e. the absorption of Fe was near 1.0 absorption lengths and the total absorption of the entire sample was <2.5 absorption lengths. Following our previous approach,[1] a small amount of glycerol (< 1 mL) was added to the filtered solids of both anoxic and oxic samples to prevent unwanted oxidation during transport to the beamline. The filters were then cut and affixed to custom sample holders with Kapton tape. All samples were transferred to secondary air tight containers in the anoxic chamber and shipped to the beamline in a unit cooled with ice packs and kept frozen at the beamline until analysis.

3.2. Shell by shell fits of Fe-bearing References

The EXAFS spectra of the reference GR, magnetite and lepidocrocite were analyzed using shell-by-shell fits. Theoretical curve fits were performed in $R+\Delta R$-space (Å) using SixPack software, which is built on algorithms derived from the IFEFFIT library.[2] Scattering paths used in the fits were derived from the structure of goethite.[3] Fits were typically performed by varying the coordination number (CN), change in threshold energy (ΔE_0), interatomic distance (R) and the mean squared displacement parameter (σ^2) for each path in the fit. For magnetite, the σ^2 for the first and second shell Fe-Fe paths were constrained to be equal during the fit. The passive electron reduction factor (S_0^2) was set to 0.8. The goodness of fit was determined using the R-factor, similar to the As K-edge EXAFS fits.

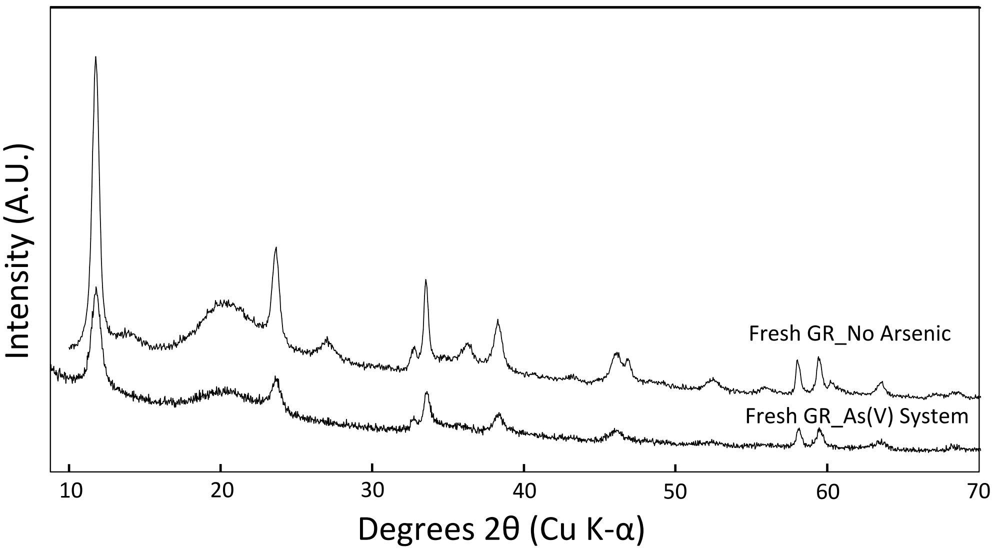

Figure ESI 1: X-ray diffraction patterns of fresh green rust suspensions generated in the presence and absence of As(V). The low intensity peak near 21° 2θ arises from glycerol added to prevent GR oxidation during the measurement. The Bragg diffraction peak near 12° 2θ is consistent with carbonate green rust (GR-CO_3).

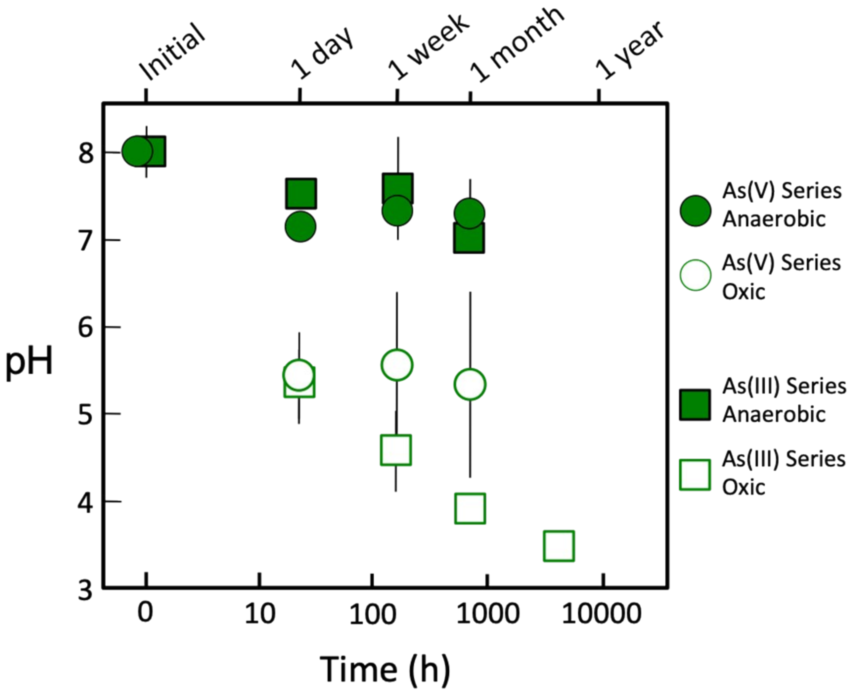

Figure ESI 2: Behavior of solution pH during aging of the As(V)-laden and As(III)-laden GR suspensions.

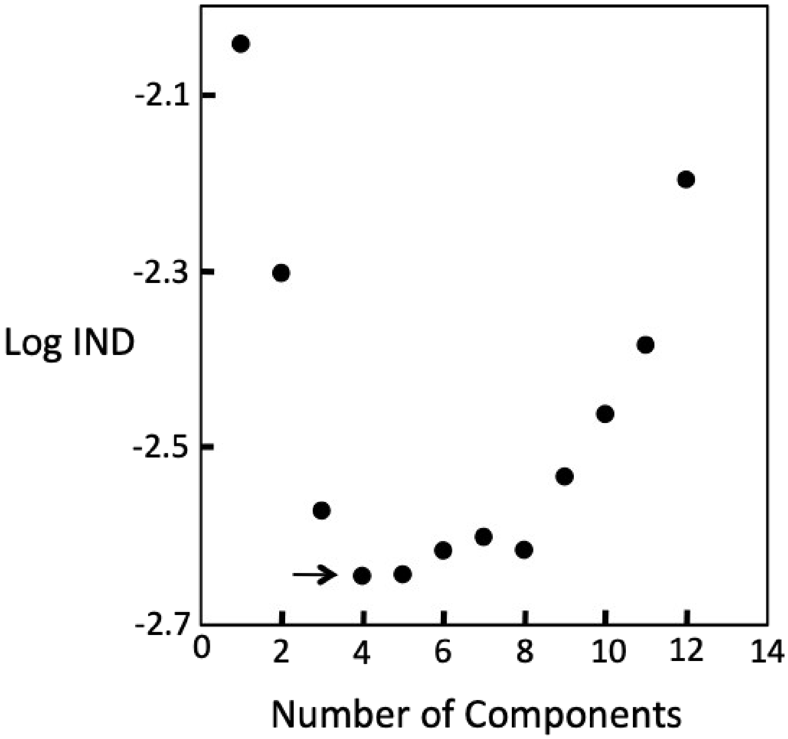

Figure ESI 3: Results of the principal component analysis of the Fe K-edge EXAFS spectra. The indicator function (IND) reaches a minimum with 4 components.

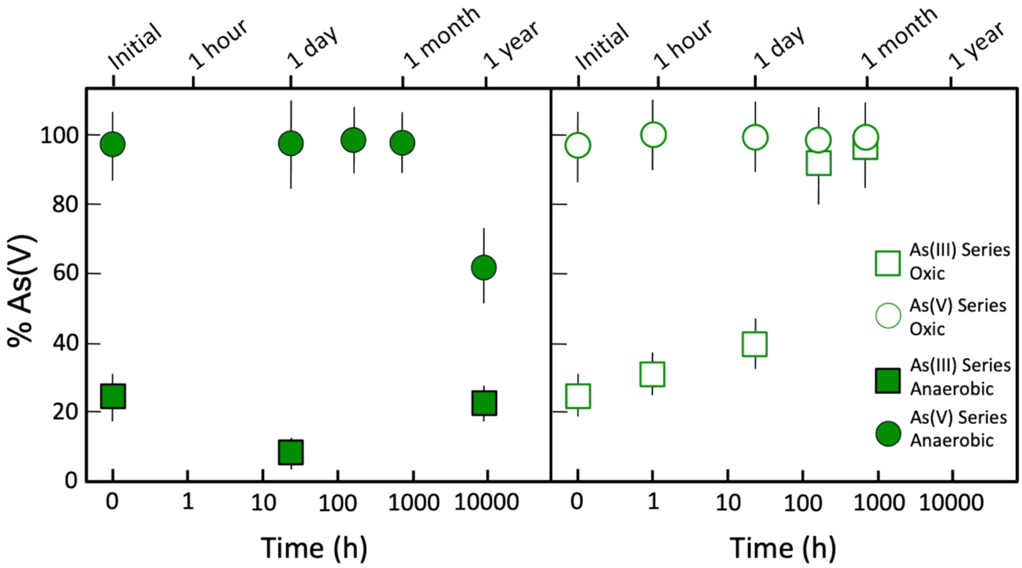

Figure ESI 4: Percentage of As(V) derived by XANES LCFs for aging samples.

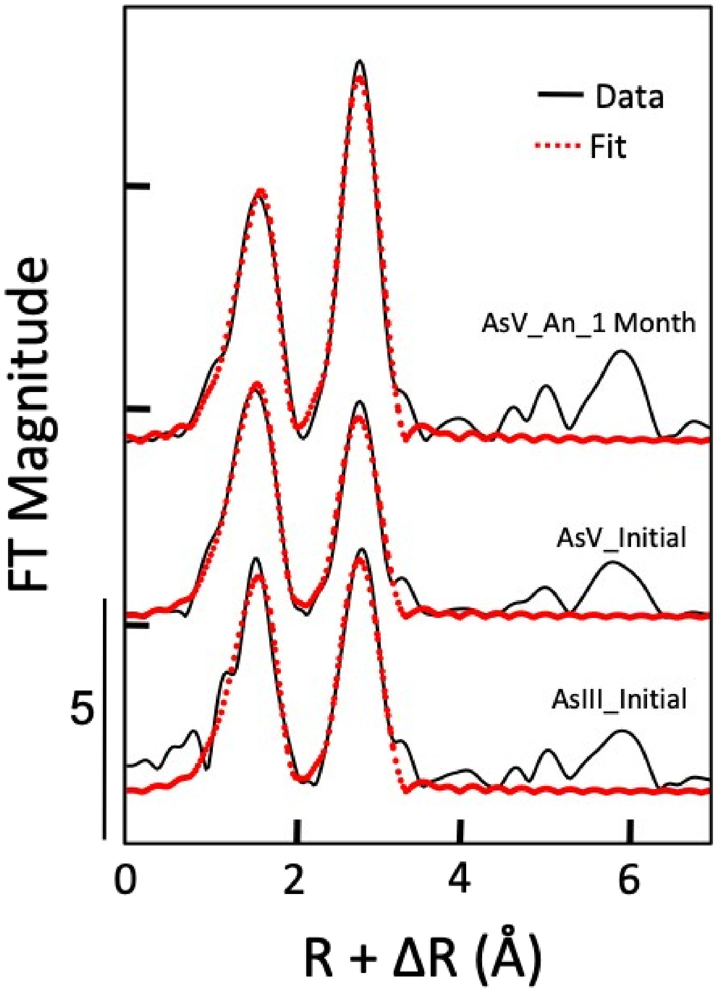

Figure ESI 5: Comparison of the Fourier-transformed Fe K-edge EXAFS spectra of the initial samples in the As(V) and As(III) aging series and the As(V)-laden GR sample aged one month. The output of the shell-by-shell fits (dotted red lines) is overlain to the data (solid black lines).

Table ESI 1A: Summary of Fe Shell-by-shell Fits for the Fe Reference Minerals

Sample	Atomic Pairs	CN	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)	R-factor
Green Rust	Fe-O	6.8 (1.0)	2.08 (0.01)	0.011 (0.002)	-2.7 (0.9)	0.018
	Fe-Fe1	7.5 (0.9)	3.18 (0.01)	0.007 (0.001)		
Magnetite	Fe-O	5.2 (1.4)	1.97 (0.02)	0.014 (0.004)	-4.5 (1.4)	0.032
	Fe-Fe1	2.8 (0.5)	2.98 (0.01)	0.007 (0.001)		
	Fe-Fe2	7.4 (1.3)	3.47 (0.01)	σ^2 Fe-Fe1		
Lepidocrocite	Fe-O	6.2 (0.7)	2.00 (0.01)	0.007 (0.001)	-2.9 (0.9)	0.018
	Fe-Fe1	5.9 (0.8)	3.07 (0.01)	0.006 (0.001)		

Table ESI 1B: Summary of Fe Shell-by-shell Fits for Select Aging GR Samples

Sample	Atomic Pairs	CN	R (Å)	σ^2 (Å^2)	ΔE_0 (eV)	R-Factor
Reference Green Rust	Fe-O	6.8 (1.0)	2.08 (0.01)	0.011 (0.002)	-2.7 (0.9)	0.018
	Fe-Fe1	7.5 (0.9)	3.18 (0.01)	0.007 (0.001)		
As(V)_An_1 Month	Fe-O	6.2 (0.8)	2.08 (0.01)	0.011 (0.002)	0 (0.9)	0.017
	Fe-Fe	6.4 (0.8)	3.18 (0.01)	0.007 (0.001)		
As(V)_Initial	Fe-O	6.4 (0.7)	2.05 (0.01)	0.013 (0.002)	0.1 (1.0)	0.019
	Fe-Fe	3.8 (0.6)	3.17 (0.01)	0.008 (0.001)		
As(III)_Initial	Fe-O	5.7 (1.0)	2.06 (0.02)	0.013 (0.003)	0.4 (1.4)	0.039
	Fe-Fe	4.2 (0.9)	3.18 (0.01)	0.007 (0.002)		

CN represents the coordination number, R the interatomic distance, σ^2 the mean squared atomic displacement and ΔE_0 represents the change in threshold energy. The passive electron reduction factor, S_0^2, was fixed at 0.8. Fitting parameters allowed to float are accompanied by fit-determined standard errors in parenthesis, while constrained parameters appear without a parenthesis. All fits were carried out from 1 to 4 Å in R+ΔR-space.

References

1. van Genuchten, C.; Behrends, T.; Kraal, P.; Stipp, S.; Dideriksen, K., Controls on the formation of Fe(II,III) (hydr)oxides by Fe(0) electrolysis. *Electrochimica Acta* **2018,** *286*, 324-338.
2. Newville, M., IFEFFIT: interactive XAFS analysis and FEFF fitting. *Journal of Synchrotron Radiation* **2001**, 322-324.
3. Gualtieri, A.; Venturelli, P., In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction. *American Mineralogist* **1999**, 895-904.