Electronic Supplementary Information

for

Incorporation of Pb(II) into hematite during ferrihydrite transformation

Yang Lu,^a Shiwen Hu,^a Zheng Liang,^b Mengqiang Zhu,^c Zimeng Wang,^d Xiaoming Wang,^e Yuzhen Liang,^a Zhi Dang,^a Zhenqing Shi^{*,a}

^a The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters,

Ministry of Education, School of Environment and Energy, South China University of

Technology, Guangzhou, Guangdong 510006, People's Republic of China

^b Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences,

Guangzhou, 510640, Guangdong, People's Republic of China

^c Department of Ecosystem Science and Management, University of Wyoming,

Laramie, WY, 82071, United States

^d Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, People's Republic of China

^e Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, People's Republic of China

*Corresponding author: Zhenqing Shi;

Email: zqshi@scut.edu.cn; Tel: 86-20-39380503.

Number of pages: 22

Number of figures: 15

Number of tables: 3

S1. Details of Experimental Procedures

(1) Iron oxide transformation experiments

Ferrihydrite and Pb coprecipitates were synthesized using the method described by Schwertmann and Cornell,¹ in which the 0.1 M Fe(NO₃)₃·9H₂O solution was titrated with 1 M NaOH with continuous stirring until the pH was stabilized at 7.5. Then the suspensions were shaken at a rotator of 200 rpm for 24 h at room temperature (25 °C). The mixed suspensions were titrated with 1 M NaOH with continuous stirring until the pH was stabilized at 10.0 and then the suspension was put in a water bath shaker at 70 °C. During the aging and transformation process, suspension pH was checked with a pH probe (Seven CompactTM S220, Mettler Toledo, Switzerland) and maintained to pH 10.0 using 0.1M NaOH/0.1M HNO₃. The bottles were tightly sealed. FeOOH was used to represent ferrihydrite for related calculations. Duplicated experiments were conducted, which showed good replicability. For the Pb adsorbed hematite particles, 3 mM Pb(II) was added with 8.9 g L⁻¹ hematite at pH 5.5 and reacted for 4h. Then suspensions were collected for TEM analysis.

(2) Powder X-ray Diffraction (XRD)

The XRD equipment was operated at 40 kV and 40 mA by step-scanning from 10° to 70° 2 θ at increments of 0.02° 2 θ with 0.6s acquisition time for all curves in Figure S1. Samples aged 168 h were used for XRD fine scan with a step size of 0.002° 2 θ and 0.2 s acquisition time from 10 – 80° 2 θ to quantify crystal structure changes. TOPAS 5.0 was used to perform the Rietveld refinements to quantify the proportions of goethite and hematite in the solids. TOPAS 5.0 uses the integrated intensity of the diffraction peaks and the crystal structure to calculate the relative mass of each phase identified in a sample.² Jade 6.0 was used to conduct ferrihydrite (Joint Committee on Powder Diffraction Standards, JCPDS Card No. 46-1315), goethite (JCPDS Card No. 29-0713), and hematite (JCPDS Card No. 33-0664) analysis of the mixed phases.^{3, 4} The gradually significant peaks at certain 2 θ angle in Figure S1 indicated the appearance of some crystal lattice planes of iron minerals, which were in accordance with the morphology observed in TEM during the

S2

transformation process.

In order to dismiss the influences of mineral growth on the changes on *d* spacings, XRD data from the Fh only treatment was also used as reference. There were no apparent changes of *d* spacings for the comparison between Fh only and hematite standard (JCPDS Card No. 33-0664) while significant *d* spacing changes were observed when Fh-Pb treatment was compared with hematite standard (JCPDS Card No. 33-0664) (Figure S14). This phenomenon indicated that the addition of Pb during the iron oxide transformation at high pH enlarged crystal *d* spacings of hematite and lead to the changes of hematite crystal structures.

(3) XAS data collection and analysis

Samples at different aging time were centrifuged and washed by DI water for three times and then freeze dried for EXAFS experiments. The instrument information were the same as in a previous study.⁵ Multiple EXAFS scans of each sample were aligned, merged, and processed using the Athena program. The spectra were baseline corrected using a linear pre-edge function between -150 and -45 eV and normalized using a linear or quadratic function between 150 and 550 eV, including a flattening function in the post-edge region. The EXAFS signal was isolated from the absorption edge background by using a fit to a cubic spline with nodes defined by the AUTOBKG function in IFEFFIT. A k³-weighting and a R_{bkg} parameter of 1.1 were used for all spectra. Fourier transforms of k³-weighted spectra were conducted across a k range of 2.5 to 10.5 Å⁻¹ using a Kaiser-Bessel window with a 1 Å⁻¹ sill width.

For the EXAFS shell fitting, FEFF6 was used to calculate phase shift and magnitude for Pb-O, Pb-Pb and Pb-Fe scattering paths based on the crystal structure of PbO with a portion of Pb replaced with Fe. All EXAFS spectra were fit using Artemis for interatomic distance (R), coordination number (CN), and Debye-Waller factors (σ^2) across the R range of 1.1-5.0 Å with a fixed amplitude reduction factor (S₀²) of 0.80. The fitting was performed on R space spectra and the parameters were first established with reasonable guess. The goodness of fit was determined using R-factor = $\Sigma(\chi_{data} - \chi_{fit})^2 / \Sigma(\chi_{data})^2$. Good fits were obtained if R-factor ≤ 0.05 .

S2. Additional Figures



Figure S1. XRD stack curves of different aging times. Character F, H and G represent the ferrihydrite, hematite and goethite, respectively.



Figure S2. Pb(II) concentrations of supernatant samples: (a) Pb(II) concentrations during the Fh-Pb co-precipitation process before pH reached 7.5; (b) Pb(II) concentrations during iron oxide transformation process. The initial Pb(II) concentration was 1 mM.



Figure S3. Concentrations of Fe (a) and Pb (b) during the acid dissolution experiments.



Figure S4. XRD peaks of different samples including Pb precipitates aged for 168 h at the same transformation conditions in the absence of Fe, co-precipitation samples aged for 168 h, pure hematite, and goethite samples.



Figure S5. Morphological changes of iron oxides during the aging process as shown with HAADF-STEM images (Gt, Goethite; Hm, Hematite).

(a) Fh-Pb



Figure S6. HAADF-STEM images and Fe, O, and Pb distribution on iron oxide samples (a) iron oxides at various aging times; (b) samples aged for 168 h after acid wash; (c) Pb adsorbed hematite nanoparticles. Blue, red, and green colors refer to Fe, O, Pb, respectively.

(a) Fh-Pb 168 h: Without acid wash



Figure S7. Elemental distribution on Fe oxide samples: (a) aged for 168 h without acid wash, (b) aged for 168 h after acid wash, and (c) Pb adsorbed hematite nanoparticles. EDS spectra and elemental contents at the bulk and the edge of the selected areas of the iron oxide nanoparticles are shown in each plot.



Figure S8. Statistical analysis of EDS quantitative results for hematite edge and bulk areas. Statistical di \Box erences among various elements were determined by Duncan's test (p < 0.05). Di \Box erent letters on the columns denote a significant di \Box erence at p < 0.05 using the DMRT (Duncan's new multiple range tests) method.

Noise filtering process of HR-HAADF images



Figure S9. Scheme of noise filtering process of atomic scale HAADF-STEM images with high resolution.



Figure S10. Additional HAADF - STEM images of iron oxide samples (aged 168 h and washed 2 times by pH 3.0 solution). The bright atoms pointed by the arrows are considered to be Pb atoms, and the darker atoms are considered to be iron atoms. (a)-(c) Denoted the different rotation angles for one specific area.



Figure S11. Pb distribution on Pb adsorbed hematite particles at the sub-nano resolution.



Figure S12. High resolution TEM images of iron oxide samples aged for 168 h. Crystal disordered areas and lattice defects at sub-nano scale were observed.



Figure S13. XRD fine scan curves of iron oxide samples aged for different times (120 h, 168 h, and 360 h) at a scan speed of 0.002° /step with an acquisition time of 0.2s. Hematite, Pb adsorbed hematite, and goethite were also scanned as reference samples. Panel a, b, c, and d denoted the scan range of $10^{\circ}-30^{\circ}$, $30^{\circ}-45^{\circ}$, $45^{\circ}-67^{\circ}$ and $67^{\circ}-80^{\circ}$ (2 θ), respectively. Data from different ranges of 2 θ degrees were acquired under the same instrumental conditions. Hematite was denoted as Hm, and goethite was denoted as Gt, respectively.



Figure S14. Average changes of *d* spacings for different hematite lattice planes. Hm STD denoted as hematite standard (JCPDS Card No. 33-0664). Fh only vs. Hm STD represents the comparison between Fh only treatment and Hm STD, Fh-Pb vs. Hm STD represents the comparison between Fh-Pb treatment and Hm STD, and Fh-Pb vs. Fh only represents the compassion between Fh-Pb treatment and Fh only treatment.



Figure S15. Possible Pb incorporation sites in hematite crystals during the iron oxide transformation process. The figure was drawn with DIAMOND software (Version 3.2i).⁶

S3. Supplementary Tables

Table S1. EDS quantitative analysis of bulk and edge areas of hematite after 168 h aging before and after acid wash. Average values in the table were expressed as mean \pm standard error of the replicates.

Hematite					
bulk	Fe (wt %)	O (wt %)	Pb (wt %)	PD/Fe molar ratio	
1	55.87	28.70	15.43	0.075	
2	54.47	28.52	17.01	0.084	
3	54.48	29.30	16.22	0.081	
4	55.80	28.20	16.00	0.078	
5	55.62	28.96	15.43	0.075	
6	54.78	28.85	16.98	0.084	
7	53.01	29.29	17.70	0.090	
8	54.14	30.25	15.61	0.078	
Average	54.77 ± 0.91	29.01 ± 0.58	16.30 ± 0.79	0.080 ± 0.10	
Hematite					
edge	Fe (wt %)	O (wt %)	Pb (wt %)	Pb/Fe molar ratio	
1	54.23	29.00	16.77	0.084	
2	52.10	30.41	17.49	0.091	
3	51.82	30.80	17.38	0.091	
4	54.71	29.99	15.29	0.076	
5	49.62	33.07	17.31	0.094	
6	51.22	31.89	16.89	0.089	
7	48.28	29.66	22.05	0.124	
8	53.70	28.87	17.42 0.088		
Average	51.96 ± 2.10	30.46 ± 1.35	17.58 ± 1.82	0.092 ± 0.010	
Fh-Pb 168 h: af	fter acid wash				
Bulk	Fe (wt %)	O (wt %)	Pb (wt %)	Pb/Fe molar ratio	
1	58.98	29.11	11.91	0.055	
2	59.70	27.44	12.86	0.058	
3	59.05	29.43	11.52	0.053	
4	58.35	27.93	13.72	0.064	
5	58.75	28.63	12.62	0.058	
6	59.69	27.99	12.33	0.056	
7	57.34	28.97	13.70 0.065		
8	57.84	27.61	14.55 0.068		
Average	58.71 ± 0.78	28.39 ± 0.70	12.90 ± 0.96	0.059 ± 0.01	
Edge	Fe (wt %)	O (wt %)	Pb (wt %)	Pb/Fe molar ratio	
1	56.86	33.45	9.70 0.046		
2	60.06	33.06	6.88	0.031	
3	37.66	53.62	8.72	0.063	
4	58.54	35.18	6.29	0.029	

Fh-Pb 168 h: before acid wash

5	56.74	33.00	10.26	0.049
6	59.12	30.34	10.54	0.048
7	57.39	30.73	11.88	0.056
8	59.02	31.37	9.61	0.044
Average	55.67 ± 6.90	35.09 ± 7.16	9.24 ± 1.75	0.045 ± 0.01

Bulk	O (wt %)	Fe (wt %)	Pb (wt %)	Pb/Fe molar
				ratio
1.00	33.92	64.47	1.60	0.007
2.00	33.41	65.77	0.82	0.003
3.00	33.50	65.05	1.45	0.006
4.00	32.78	66.28	0.94	0.004
5.00	31.69	66.44	1.87	0.008
6.00	31.29	67.30	1.40	0.006
7.00	31.69	67.31	1.00	0.004
8.00	33.69	64.23	2.08	0.009
9.00	33.28	66.12	1.60	0.007
Average	32.81 ± 0.94	65.89 ± 1.05	1.42 ± 0.40	0.005 ± 0.002
F 1	- / 0	_ /		Pb/Fe molar
Edge	0 (wt %)	Fe (wt %)	Pb (wt %)	ratio
1.00	34.81	52.64	12.55	0.064
2.00	33.47	44.93	21.60	0.130
3.00	31.92	50.87	17.21	0.092
4.00	33.30	52.93	13.76	0.070
5.00	36.10	50.06	13.84	0.075
6.00	33.84	50.81	15.35	0.082
7.00	35.07	45.09	19.84	0.119
8.00	33.69	50.60	15.70	0.084
9.00	31.65	49.41	19.21	0.105
10.00	35.67	52.98	10.45	0.053
11.00	42.80	41.57	15.63 0.102	
12.00	54.77	30.81	14.42	0.127
Average	36.42 ± 6.18	47.73 ± 6.15	15.80 ± 3.07	0.085 ± 0.023

Table S2. EDS quantitative analysis of bulk and edge areas of Pb adsorbed hematite particles. 3 mM Pb (II) was added to 8.9 g L⁻¹ hematite at pH 5.5. Average values in the table were expressed as mean \pm standard error of the replicates.

Table S3. Unit cell parameters for hematite from calculations using the Unitcell program;⁷ Δx represents the differences in the unit cell parameters between the hematite products in the the kinetic experiments (Fh-Pb and Fh only treatments), and the hematite standard (JCPDS Card No. 33-0664).

Samples	a Axis (Å)	⊿a (Å)	b Axis (Å)	⊿b (Å)	c Axis (Å)	⊿c (Å)
Hm STD (JCPDS Card	5.036	0.000	5.026	0.000	12 740	0.000
No. 33-0664)	5.050	0.000	5.050	0.000	13.749	
Alfa hematite (Hm)	5.036	0.000	5.036	0.000	13.752	0.003
Hematite Fh only 168h	5.039	0.003	5.039	0.003	13.767	0.018
Hematite Fh only 360h	5.036	0.000	5.036	0.000	13.767	0.018
Hematite Fh-Pb 120h	5.052	0.017	5.052	0.017	13.818	0.069
Hematite Fh-Pb 168h	5.052	0.016	5.052	0.016	13.828	0.079
Hematite Fh-Pb 360h	5.052	0.017	5.052	0.017	13.828	0.080

References

- 1 U. Schwertmann and R. M. Cornell, Iron oxides in the laboratory: preparation and characterization, Wiley-VCH, Weinheim, 2nd ed. edn., 2000.
- 2 A. Coelho, TOPAS V5, Bruker AXS, 2014.
- 3 H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.*, 1969, **2**, 65-71.
- 4 X. M. Wang, M. Q. Zhu, S. Lan, M. Ginder-Vogel, F. Liu and X. H. Feng, Formation and secondary mineralization of ferrihydrite in the presence of silicate and Mn(II), *Chem. Geol.*, 2015, **415**, 37-46.
- 5 S. Hu, Y. Lu, L. Peng, P. Wang, M. Zhu, A. C. Dohnalkova, H. Chen, Z. Lin, Z. Dang and Z. Shi, Coupled kinetics of ferrihydrite transformation and As(V) sequestration under the effect of humic acids: a mechanistic and quantitative study, *Environ. Sci. Technol.*, 2018, **52**, 11632-11641.
- 6 K. Brandenburg, Diamond (version 3.2 i), Crystal and Molecular Structure Visualization, Crystal Impact–H. Putz & K. Brandenburg GbR, Bonn (Germany) 2012.
- 7 T. Holland and S. Redfern, Unit cell refinement from powder diffraction data: the use of regression diagnostics, *Mineral. Mag.*, 1997, **61**, 65-77.