Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information

Persistent arsenate – iron(III) oxyhydroxide – organic matter nanoaggregates observed in coals

Yinfeng Zhang[a,b], Shehong Li[b], Jing Sun[b], Benjamin C. Bostick[c], Yan Zheng[d,e*]

[a] Yunnan Key Laboratory of Plateau Wetland Conservation, Restoration and Ecological Services, College of Wetlands, Southwest Forestry University, Kunming, China 650224

[b] State Key Lab of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China 550081

[c] Lamont-Doherty Earth Observatory, Columbia University, 61 Route 9W, Palisades, NY, United States 10964

[d] State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, China 518055

[e] Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, China 518055

* Corresponding author: Yan Zheng

Email: yan.zheng@sustech.edu.cn ORCID: 0000-0001-5256-9395

3 Sections

15 Pages

6 Tables

3 Figures

SUPPLEMENTAL METHODS

SM1. Coal storage methods

Coals are formed in a coalification process under high temperature and pressure and has lost its water from its precursor, peat, which is formed from water-saturated anoxic sediments. Investigators have stored coals in atmosphere at room temperature, because they are considered as geological specimen. Prior studies of As speciation in coals did not use anaerobic storage such as glove box with nitrogen or noble gas to protect samples against atmospheric oxygen (Table S1). This was likely due to the fact that oxidation of pyrite by atmospheric oxygen is slow, and is accelerated only when water is involved[1, 2] . A recent paper identified organic-associated As in coals from a mine ~500 m underground from Slovenia with the coal samples stored by wrapping them in plastic foil[3]. In other words, weathering of coal beds by atmospheric oxygen alone is a process occurring over geologic time scales, which is very different if/when water is involved.

SM2. Synthesis of 2-line ferrihydrite and goethite

1) 2-line Ferrihydrite: 40 g of $Fe(NO_3)_3$ was dissolved in 500 ml of ultrapure water, into which about 330 ml of 1mol/L KOH was added drop by drop with constant stirring until the final pH of suspension reaching 7-8. Subsequently, the dark brown suspension was centrifuged at 3000 rpm for 10 minutes. The precipitates were then rapidly dialyzed and freeze dried for use;

2) Goethite: 100 mL of 1 mol/L $Fe(NO_3)_3$ solution was added into a 2 L beaker, immediately, another 180 mL of 5 mol/L KOH solution was poured in with constant stirring. Subsequently, the solution was diluted to total volume of 2 L with ultrapure water. The beaker was then sealed and placed in an oven at 70 ℃ for 60 hours. During this process, the suspensions turned from dark red-brown to yellow precipitates, which was subsequently washed and freeze dried for use.

SM3. Preparation of As-HA, As-FA, As-Fe-HA and As-Fe-FA complexes

1) Humic Acid (HA)/Fulvic Acid (FA) Stock Solution (200 mg HA/mL) preparation: 5.0000 g of Humic Acid (or Fulvic Acid) was dissolved in 25 mL of deionized water, during which the pH is maintained around 10 with 10 M NaOH. This solution was then shaken for 4 hours using an Orbital Shaker at 200 rpm and centrifuged for 15 minutes at 7000 rpm, and the supernatant is poured into a vial;

2) Preparing As-HA/FA Working Standard (0.05mg As/mL and 4 mg HA or FA/mL), 1 mL of HA or FA solution obtained in first step was poured into a vial to which 2.5 mL of 1000 ppm standard As solution was added. The 1000 ppm of As standard solution is prepared by dissolving desired amounts of sodium meta-arsenate (98%, Aldrich) in deionized water. This solution was diluted to 50 mL with ultrapure water and left for shaking overnight at 200 rpm on the Orbital Shaker. During this process, the pH was monitored and maintained around 7 using 0.5 M HNO_3;

3) Preparing Fe-HA/FA Stock Solution (2 mg Fe/mL and 40 mg HA/mL): 10 mL of the supernatant (HA/FA solution) obtained in first step was poured into a vial. The $FeCl_3 \cdot 6H_2O$ solution was slowly (drop by drop) added into the vial containing the 10 mL of HA solution. During this process, the pH was monitored after the addition of each drop of $FeCl_3 \cdot 6H_2O$ and, if necessary, the pH was adjusted to 9-10 by adding KOH of 0.1mol/L. After each step, supernatant was collected and tested for concentrations of As, Fe and C. The vial was left shaking overnight. The following day the sample was centrifuged for 15 min at 7000 rpm and the supernatant was poured into a vial to which water was added to bring the volume to 42.5 mL;

4) Preparing As-Fe-HA/FA Working Standard (0.05mg As/mL, 0.2 mg Fe/mL and 4 mg HA or FA/mL), 5 mL of Fe-HA/FA solution was poured into a vial to which 2.5 mL of 1000 ppm standard As solution is added. The following day the solution was centrifuged for 15 min at 7000 rpm, and the supernatant was decanted for analysis of As-Fe-HA and As-Fe-FA complexes.

SUPPLEMENTAL TABLES

Table S1 Coal storage methods used in prior As speciation XAS studies

Location of Coal	Numbers of coal	Speciation	Storage Method	Reference
Kentucky, USA	6	8%-75% As(V), 25%-92% pyritic-As	room temperature in atmosphere	[4]
Guizhou, China	18	As(V), As(III), As- bearing pyrite and possibly Fe-oxides	room temperature in in atmosphere	[5]
Guizhou, China	33	75% As(V), 20% As(III), possibly organo-As	room temperature in atmosphere	[6]
China and America	--	0.7%-28.7% As(V), 9%-52% As(III)	pre-cleaned glass bottles at room temperature in atmosphere	[7]
Velenje basin, Slovenia	45	Organo-As (34.8%)	wrapped in plastic foil at room temperature in atmosphere.	[3]
China	--	acid soluble and water soluble	room temperature in atmosphere	[8]

Table S2 Standard reference materials (SRM) used in linear combination fits

Type of LCF	Type of SRMs	SRMs	Beamline and collection time	Combinations of SRM [a]			
				①	②	③	④
(1) LCF for As speciations in XANES(Fig 1 and Table 1)	**As(V)**	**$FeAsO_4·2H_2O$**	**Beijing, 2014**	✓		✓	✅
	As(III)	**Na_2AsO_3**	**Beijing, 2012**	✓		✓	✅
	As(0)	**FeAsS**	**Beijing, 2012**		✓	✓	
	As-Sulfide	**AsS**	**Beijing, 2012**		✓		✅
		As_2S_3	**Beijing, 2012**		✓		✅
	R-factor			0.017	0.150	0.011	0.004
(2) LCF for As structure in EXAFS (Fig S3 and Table S6)	As-Inorganic adsorbents [b]	**As-Hematite**	**Beijing, 2013**	✓			
		As-Goethite	**Beijing, 2013**	✓			
		As-Montmorillonite	**Beijing, 2013**	✓			
		As-Kaoline	**Beijing, 2013**	✓			
		$As-MnO_2$	**Beijing, 2013**	✓			
		As-AlOOH	**Beijing, 2013**	✓			
	As-Organic compunds	**As-Fe-HA**	**Beijing, 2014**			✅	
		As-HA	**Beijing, 2014**			✅	
	As-S	**FeAsS**	**Beijing, 2012**		✓		
		AsS	**Beijing, 2012**		✓		
		As_2S_3	**Beijing, 2012**		✓		
	R-factor			0.18	1.02	0.04	

[a] The green ones represent the best fits. Fitting results for best fits were given in Table 1 and Table S6;

[b] These As-inorganic adsorbents were synthesized and analysed by XAS in our previous study[9].

Table S3. Chemical composition of a larger group of Guizhoi coals used to select the 5 representative samples (Table 1) in this study. Many from Xingren are very high in As and exhibit low or variable Fe content.

	Place of origin	As (mg/kg)	Fe (%)	Ash (%)	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	K_2O (%)	Na_2O (%)	MgO (%)	P_2O_5 (%)	SiO_2 (%)	TiO_2 (%)	SO_3 (%)	I (%)
		HG-AFS	XRF	XRD	XRD	XRD	XRD	XRD	XRD	XRD	XRD	XRD	XRD	XRD	XRD
JL18	Anlong	*	*	24.5	4.6	0.03	2.38	0.41	0.06	0.1	0.03	18.8	0.3	6.03	28.3
JL20	Anlong	43.2	40600	43.1	2	0.04	5.8	0.36	0.02	0.04	0.01	37.5	0.1	14.98	1.92
JL25	Anlong	105.2	7460	56.7	2.2	0.02	1.07	0.49	0.03	0.06	0.01	54.4	0.4	6.23	7.83
YL-1A	Anlong	141.8	104850	67.4	11.3	2.29	14.99	2.1	0.06	0.67	0.16	32.1	1.7	27.73	1.03
YL-2	Anlong	*	*	37.4	14	0.07	0.45	0.15	0.16	0.14	0.04	20.6	0.9	0.68	26.79
ML-1 (C1)	Anlong	5676	10928	*	3.6	0.19	1.15	0.21	0.07	0.15	0.01	21.5	0.5	10.09	5.81
JL-92 (C2)	Anlong	175	7859	*	5.4	0.07	1.09	0.56	0.06	0.03	0.01	42.7	0.7	7.24	1.07
LC-1 (C3)	Anlong	698	15480	*	2.6	0.03	2.03	1.04	0.03	0.06	0.05	30.6	1.1	21.55	3.34
Hz-Au-97 (C5)	Anlong	111	6885	*	9.7	0.24	0.98	0.33	0.10	0.27	0.03	19.1	0.6	16.39	1.85
HLG2#	Xingren	57.8	28330	28.1	5.8	1.88	4.05	0.44	0.04	0.19	0.12	13.3	0.4	8.23	1.39
GCQ-5 (C4)	Xingren	45	21733	*	4.6	0.04	3.47	1.18	0.15	0.13	0.05	12	0.5	7.09	1.51
HZ-2	Xingren	*	*	26.9	7.5	0.05	3.68	0.95	0.37	0.19	0.06	13	0.8	7.68	1.95
HZ-9-2	Xingren	16121.0	7380	30.6	4.7	0.03	1.05	1.67	0.11	0.15	0.02	23	0.6	*	*

HZ-9-3	Xingren	20214.0	15300	21.9	4.2	0.02	2.19	1.33	0.11	0.18	0.02	12	0.5	*	*
HZ-9-4	Xingren	9070.4	9270	56.7	4.8	0.08	1.32	0.96	0.1	0.09	0.01	50.6	0.2	*	*
HZ-9-5	Xingren	29435.7	3600	6.1	1.4	0.04	0.51	0.6	0.12	0.04	0.01	3.3	0.2	*	*
HZ-9-6	Xingren	12417.0	3600	10	2.3	0.02	1.14	0.32	0.11	0.06	0.01	5.2	0.3	*	*
HZ-9-7	Xingren	8555.7	4130	6.9	1.7	0.02	0.59	0.2	0.09	0.04	0.01	3.5	0.2	*	*
HZ-9-8	Xingren	4720.1	9850	15.6	2.7	0.03	1.41	0.39	0.11	0.06	0.02	11.5	0.4	*	*
HZ-9	Xingren	15205	8440	21.11	3.12	0.03	1.21	0.85	0.1	0.09	0.01	15.59	0.33	9.7	1.81
HZ-14-5	Xingren	*	*	21.2	5.3	0.03	1.01	0.36	0.06	0.08	0.01	12.3	0.5	2	5.93
ZJ-1	Zhijin	849.5	8450	20.6	5.6	0.08	1.21	0.73	0.22	0.12	0.02	13.3	0.5	3.08	4.54
ZJ-4	Zhijin	*	*	37.4	3.1	11.3	1.55	0.6	0.06	0.25	0.02	10.1	0.2	5.05	0.77
ZJ-8	Zhijin	5237.4	81520	53.7	7.7	0.86	11.66	0.75	0.11	0.26	0.07	29.3	0.5	1.45	2.7

Note: Data (except C1, C2, C3, C4, C5 form this study) are from the PhD thesis of Ding[10].

Table S4. Mineralogical data fom selected high-As coals used to select the 5 representative samples (Table 1) in this study. Mineral proportions are based on quantitative XRD using pattern matching and relative peak area ratios for quantification (%).

	Place	Qtz	Fld	Cal	Sid	Ank	Ill	Kao	Chl	Gib	Bhm	Py	Spl	Bas	Anl	Hem	Apa	Ana	Gyp
JL-20	Anlong	68					9	5				13	1		2	3			
JL-25	Anlong	84	1				10	1				1						3	
ML-1 (C1)	Anlong	45	3	3			28	12				4				2			
JL-92 (C2)	Anlong	36	1	2			24	26				7				2			
LC-1 (C3)	Anlong	56	2				17	23				2							
HzAu97(C5)	Anlong	43	4	2			23	22				2				1			
HZ-9-8	Xingren	36	3			1	24	26				7				1	1	4	
HZ-9-7	Xingren	14					36	39	6	2		2				1			
HZ-9-6	Xingren	16	3			1	36	31	3	2		4			2		2		
HZ-9-5	Xingren	15	2			2	19	27		14	2	1				3	17		3
HZ-9-4	Xingren	66			1		7	23	2								1		
HLG2	Xingren	31		5			24	23		1		12		3					
GCQ-5 (C4)	Xingren	51	3	5			18	15				3				4			

Note: Qtz- quartz, Fld-feldspar, Cal-calcite, Sid-siderite, Ank-ankerite, Ill-illite, Kao-kaolinite, Chl-chlorite, Gib-gibbsite, Bhm-boehmite, Py-pyrite, Spl-sphalerite, Bas-bassanite, Anl-analcite, Hem-hematite, Apa-apatite, Ana-anatase, Rut-rutile, Gyp-gypsum

Table S5 Arsenic and iron local structures from published studies for selected model compounds used in this study

Sample	path	CN[a]	R[b]	σ^{2} [c]	path	CN[a]	R[b]	σ^{2} [c]
As K-edge								
As-Fe-HA[11]	As-O	4.0	1.70	0.003	As-Fe	0.5	3.30	0.003
As-Fe-FA[11]	As-O	4.0	1.70	0.003	As-Fe	0.7	3.29	0.007
$FeAsO_4 \cdot 2H_2O$[12]	As-O	4.0	1.68	0.003	As-Fe	4.0	3.36	0.004
Iron K-edge								
Ferrihydrite[13]	Fe-O	3.1	1.94	0.008	Fe-Fe	1.5	3.03	0.005
Goethite[14]	Fe-O	3.0	1.95	0.004	Fe-Fe	2.0	3.03	--
As-Fe-HA[11]	Fe-O	5.8	1.99	0.006	Fe-Fe	2.0	3.48	0.015
As-Fe-FA[11]	Fe-O	5.8	1.99	0.007	Fe-Fe	2.0	3.47	0.015

[a] coordination number; [b] path length (Å); [c] Debye-Waller parameter;

Table S6. Normalized Linear combination fits (LCF) results for As speciation in various coal samples using various combinations of standard reference materials (SRM) (plotted in Fig. S3).

Adsorbed As on Various minerals

	As-Hematite	As-Goethite	As-Montmorillonite	As-Kaoline	As-MnO_2	As-AlOOH	R-factor
C1	0	5	55			40	0.18
C2	14		53			33	0.18
C3	0	7	37	15		41	0.22
C4		4	48		8	40	0.21
C5		8	59		4	29	0.19

As-Org

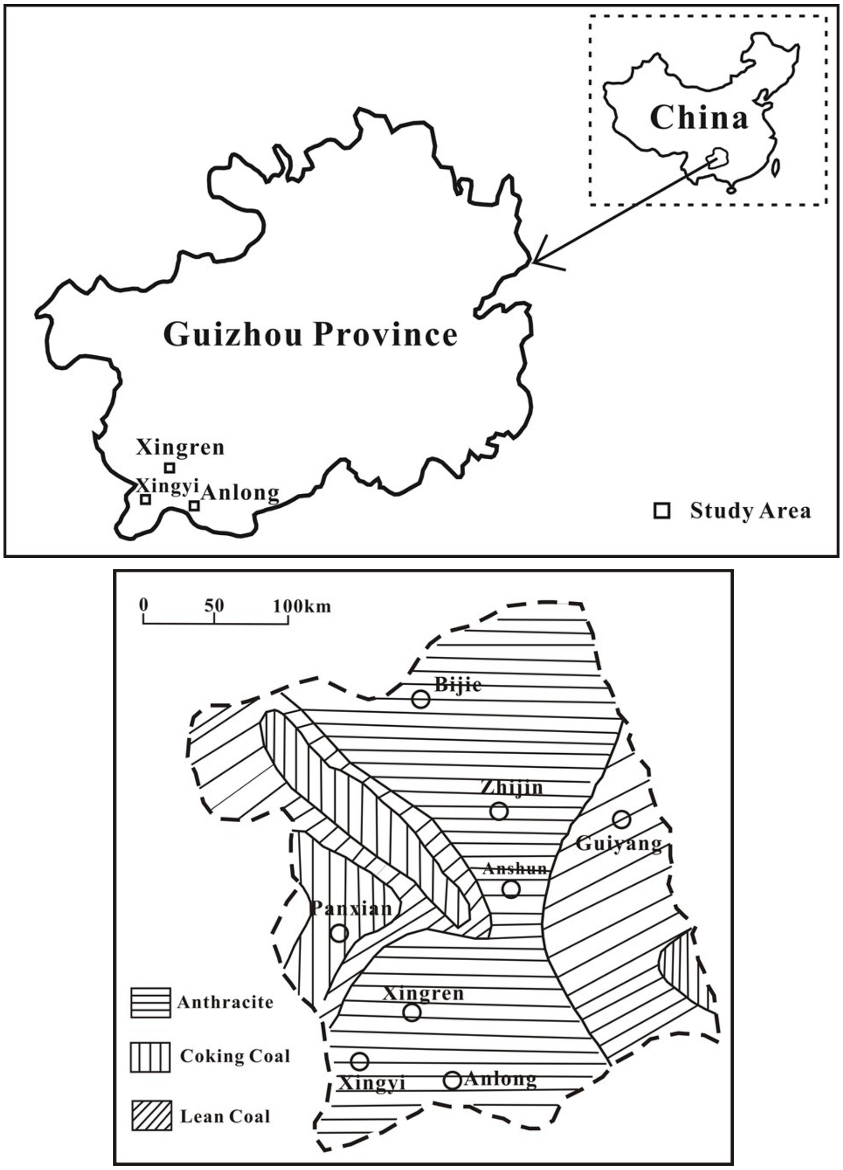
	As-Fe-HA (%)	As-HA (%)	R-factor[a]
C1	39±6	61±11	0.04
C2	42±6	58±10	0.05
C3	49±7	51±11	0.05
C4	56±6	44±6	0.08
C5	59±13	41±8	0.05

As-Sulfur

	FeAsS (%)	AsS (%)	As_2S_3 (%)	R-factor[a]
C1	49±7	24±5	27±9	1.06
C2	49±9	11±4	40±7	1.02
C3	52±7	15±5	33±3	1.05
C4	54±5	29±6	17±4	1.06
C5	47±10	18±6	35±7	1.08

SUPPLEMENTARY FIGURES.

Fig S1. Map of Guizhou province in China (top). Squares indicate locations of Xingren, Xingyi, Anlong County where there are high-As Permian coal deposits. In this study, Guizhou coal samples are collected from Anlong County (C1, C2, C3 and C5) and Xingren County (C4) where the three types of coal deposits of study area are also shown (bottom).



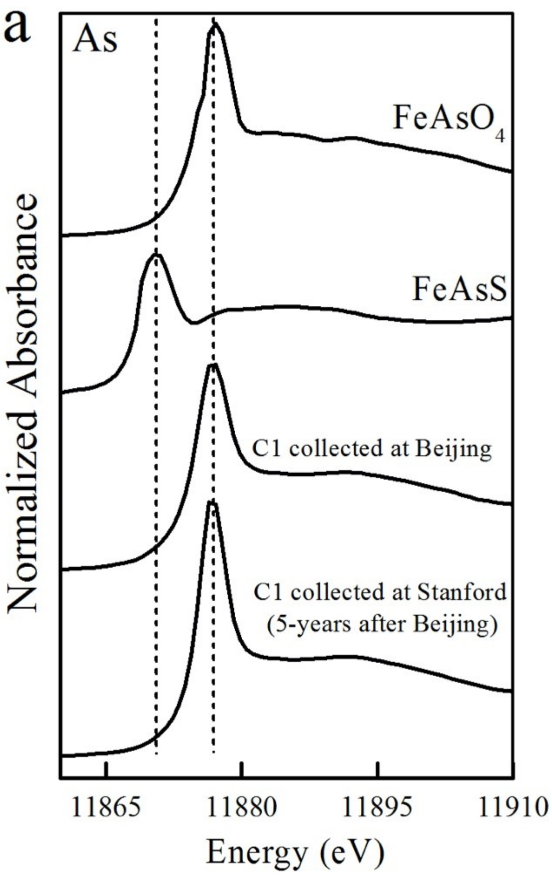
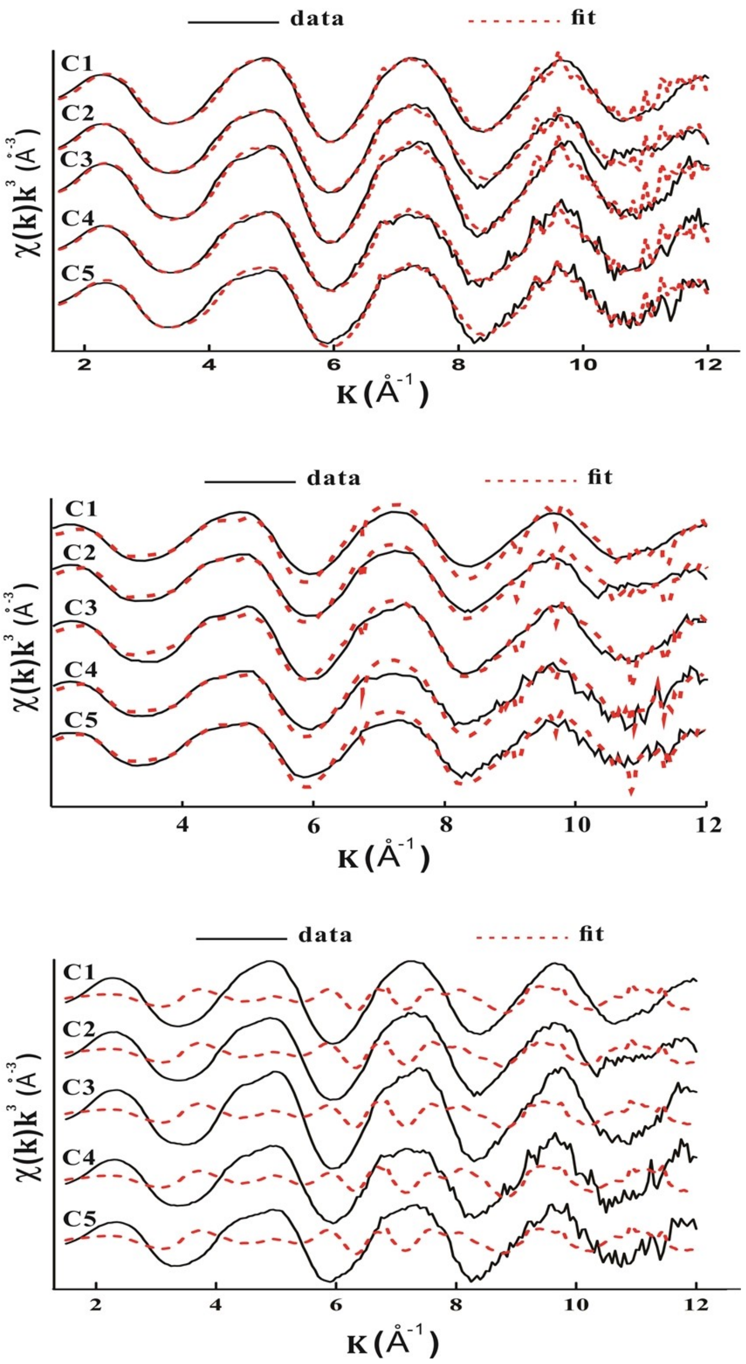


Fig. S2. Absorption edge of As of C1 collected at Beijing in July 2014 and at Stanford in 2019; b. Absorption edge of Fe of C3 collected at Beijing in July 2014 and at Stanford in 2019.

Fig S3. As K-edge spectra and their linear combination fits (LCF) using different sets of reference standards: (top) *only* As-Fe-HA and As-HA; (middle) *only* As adsorbed on inorganic minerals, and (bottom) using *only* As-Sulfur minerals as standards. Solid lines represent data and dash lines represent fit. Quantitative fits using each of these approaches are presented in Table S3. In general, fits with synthetic Fe-As-HA/FA reference materials produced superior fits for these samples.



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