

# Supporting Information

## **An x-ray absorption and x-ray photoelectron spectroscopic study of arsenic mobilization during mackinawite (FeS) oxidation**

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## **XAS analysis.**

All XAS spectra were analyzed using SixPACK (1). Individual spectra were averaged, and the background x-ray absorbance was removed by a linear fit through the pre-edge region. The x-ray absorption near-edge structure (XANES) region of the spectrum (11,860–11,890 eV) was obtained by normalizing the fluorescence signal to the edge-jump height. The absorption edges (i.e., inflection energies) in the XANES spectra were determined to compare the oxidation state of arsenic between samples and reference compounds. Extended x-ray absorption fine structure (EXAFS) spectra were isolated by fitting a quadratic spline function above the edge. The EXAFS spectra were normalized using a Victoreen polynomial function and transformed from energy to momentum space ( $k$ -space) using an  $E_0$  of 11,885 eV. The resultant EXAFS functions ( $\chi(k)$ ) were weighted by  $k^3$  to amplify the upper  $k$ -range, and Fourier-transformed to produce radial structural functions (RSF) in  $R$  space over a  $k$  range of 3.5–11.5 Å<sup>-1</sup>. Structural parameters were determined by fitting the weighted EXAFS functions ( $k^3\chi(k)$ ) using phase and amplitude functions derived from FEFF 8 (2). The amplitude-reduction factor ( $S_0^2 = 0.92$ ) was optimized from the fitting of the reference spectra and constrained for all data analysis. Note that the Debye-Waller factors ( $\sigma^2$ ) were fixed based on either the similarity of the sample spectra to known reference compounds or the optimization among the sample spectra in order to reduce the degree of freedom in the data fitting. Other parameters such as coordination number ( $N$ ), interatomic distance ( $R$ ), and energy shift ( $\Delta E_0$ ) were allowed to vary. The data fitting was optimized by minimizing the goodness of fit parameter ( $R_f$ ). Errors estimates of the fitted parameters are typically  $R \pm 0.02$  Å and  $N \pm 20\%$  (3-5).

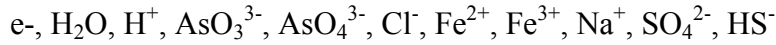
**XPS analysis.**

Raw spectra, after being smoothed, were fitted into a Shirley baseline and a Gaussian-Lorentzian peak shape. Arsenic-3*d* spectra were fitted with the doublets of As 3*d*<sub>5/2</sub> and 3*d*<sub>3/2</sub> peaks with a spin-orbit splitting of 0.70 eV. The As 3*d*<sub>3/2</sub> peak was constrained to be 2/3 the area of the As 3*d*<sub>5/2</sub> peak. The full width at half maximum (FWHM) of all peak components were constrained in the fit. The resultant peak positions (i.e., binding energies) of As 3*d*<sub>5/2</sub> lines for reference compounds are summarized in Table S1. Using the binding energies observed for five reference compounds, the As speciation of unoxidized samples was further determined. For quantitative analysis, the standard error of each component's contribution to the overall XPS spectrum was determined using Monte-Carlo analysis (CasaXPS, Casa Software Ltd., UK). This program applies artificial noise to a spectrum and calculates an error matrix to give the variance of each fit based on the fitting constraints used.

**Thermodynamic calculations for the equilibrium speciation of discrete As-bearing minerals under anoxic conditions using MINEQL+ 4.5 (ref 6).**

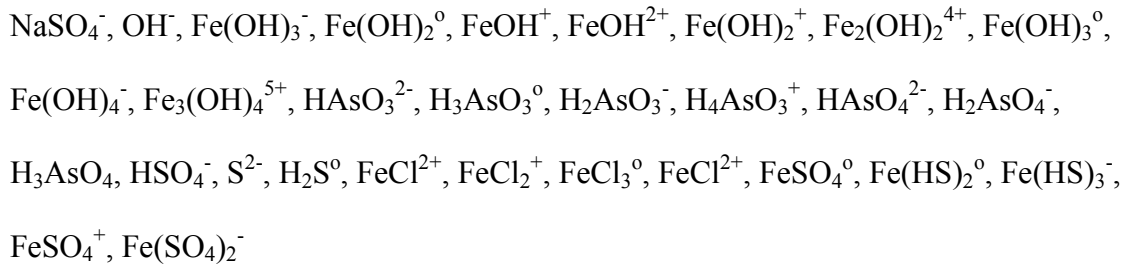
Calculations were made as a function of redox potential (Eh) at 25°C under the conditions of [mackinawite]<sub>0</sub> = 1 g/L, As<sub>0</sub> = 2×10<sup>-4</sup> M, [NaCl]<sub>0</sub> = 0.05 M, and ionic strength of 0.1 M. In the calculations, the database of MINEQL+ 4.5 was revised to reflect As-bearing minerals and dissolved thioarsenite species as follows:

*Type I species (components)*

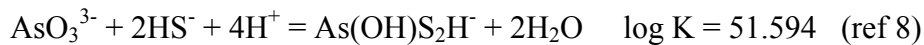
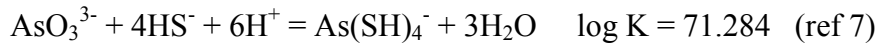
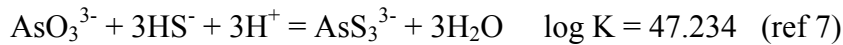
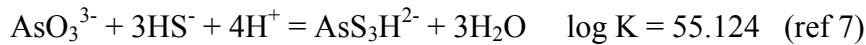
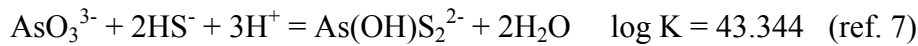
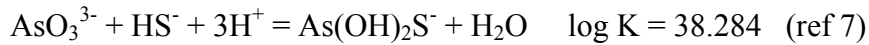


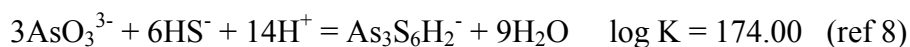
*Type II species (aqueous complexes)*

default K in MINEQL+4.5 (ref 6)



modified or added K



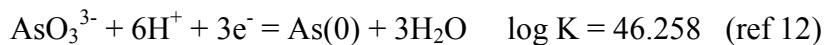
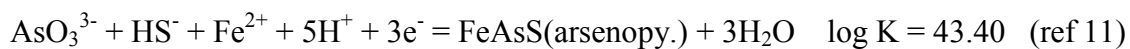
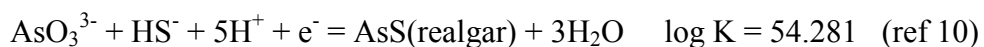


*Type V species (dissolved solids)*

default K in MINEQL+4.5 (ref 6)

scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), arsenolite ( $\text{As}_4\text{O}_6$ ),  $\text{As}_2\text{O}_5$ ,  $\text{Fe}(\text{OH})_2$ , greigite ( $\text{Fe}_3\text{S}_4$ ),  
mackinawite ( $\text{FeS}$ ), goethite ( $\alpha\text{-FeOOH}$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), halite ( $\text{NaCl}$ ),  
sulfur ( $\text{S}^0$ )

modified or added K



Note: Since no thermodynamic data are available for disordered AsS, its stability region may be smaller than that estimated based on the formation constant for crystalline realgar.

**Table S1. Characterization of reference compounds. Absorption edge positions and binding energies were obtained from XANES and XPS analyses, respectively.**

References	Absorption edge positions	Binding energies (As 3d <sub>5/2</sub> )
As(0)	11,867.0 eV	41.6 eV
FeAsS	11,867.0 eV	
AsS	11,868.1 eV	42.84 eV
As <sub>2</sub> S <sub>3</sub>	11,869.0 eV	43.2 eV
As(III) <sub>aq</sub>	11,870.9 eV	
NaAsO <sub>2</sub>		43.6 eV
As(V) <sub>aq</sub>	11,874.4 eV	
Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O		44.47 eV

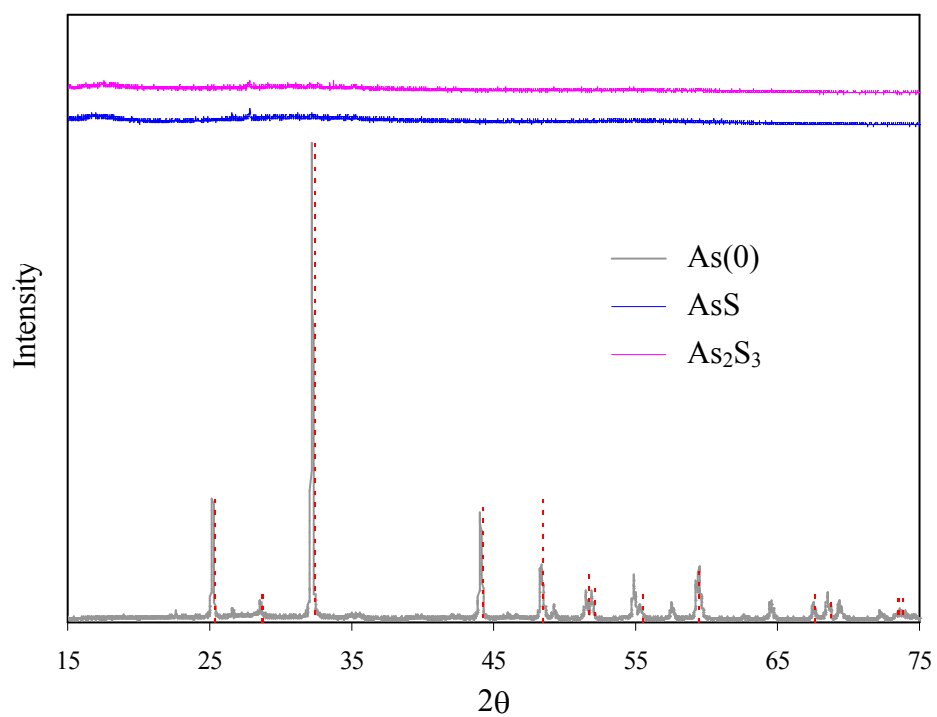
**Table S2. EXAFS fit results and crystallographic data for reference compounds.**

EXAFS fit*					Crystallographic data				
	Pair	<i>N</i>	<i>R</i> (Å)	$\sigma^2(\text{\AA}^2)$	<i>N</i>	<i>R</i> (Å)	Reference		
As(0)	As-As	3.0	2.52	0.008 <sup>†</sup>	3	2.50	ref 13		
	As-As	1.5	3.12	0.0098 <sup>†</sup>	3	3.13			
	As- As	4.1	3.75	0.014 <sup>†</sup>	6	3.75			
	As- As	4.6	4.15	0.014 <sup>†</sup>	6	4.12			
$\Delta E_0 = -11.85$ eV, $R_f = 0.028$									
FeAsS	As-S	1.3	2.34	0.035 <sup>†</sup>	1	2.34	ref 14		
	As-Fe	3.1	2.37	0.011 <sup>†</sup>	3	2.36			
	As-As	3.0	3.06	0.013 <sup>†</sup>	3	3.06-3.18			
	As-S				3	3.30			
	As-As	2.0	3.31	0.0092 <sup>†</sup>	2	3.32			
	As-Fe	4.0	3.78	0.0091 <sup>†</sup>	4	3.75			
	As-As	2.0	4.29	0.0065 <sup>†</sup>	2	4.12			
	$\Delta E_0 = -8.88$ eV, $R_f = 0.038$								
AsS	As-S	2.0	2.26	0.003 <sup>†</sup>	2	2.24	ref 15		
	As-As				1	2.57			
	As-As	0.41	3.50	0.006 <sup>†</sup>	2.5	3.44-3.51			
	As-S				1	3.41-3.52			
	$\Delta E_0 = -9.80$ eV, $R_f = 0.061$								
	As <sub>2</sub> S <sub>3</sub>	As-S	3.0	2.28	0.0045 <sup>†</sup>	3		2.24-2.31	ref 15
As-As		0.37	3.54	0.006 <sup>†</sup>	1	3.19			
As-S					3	3.22-3.57			
As-As					2.5	3.52-3.64			
$\Delta E_0 = -7.75$ eV, $R_f = 0.047$									
As(III) <sub>aq</sub>	As(III)-O	3.0	1.76	0.0045 <sup>†</sup>					
$\Delta E_0 = -7.90$ eV, $R_f = 0.069$									
As(V) <sub>aq</sub>	As(V)-O	4.0	1.69	0.0025 <sup>†</sup>					
$\Delta E_0 = -5.01$ eV, $R_f = 0.024$									

\*The amplitude-reduction factor ( $S_0^2$ ) was set at 0.92.

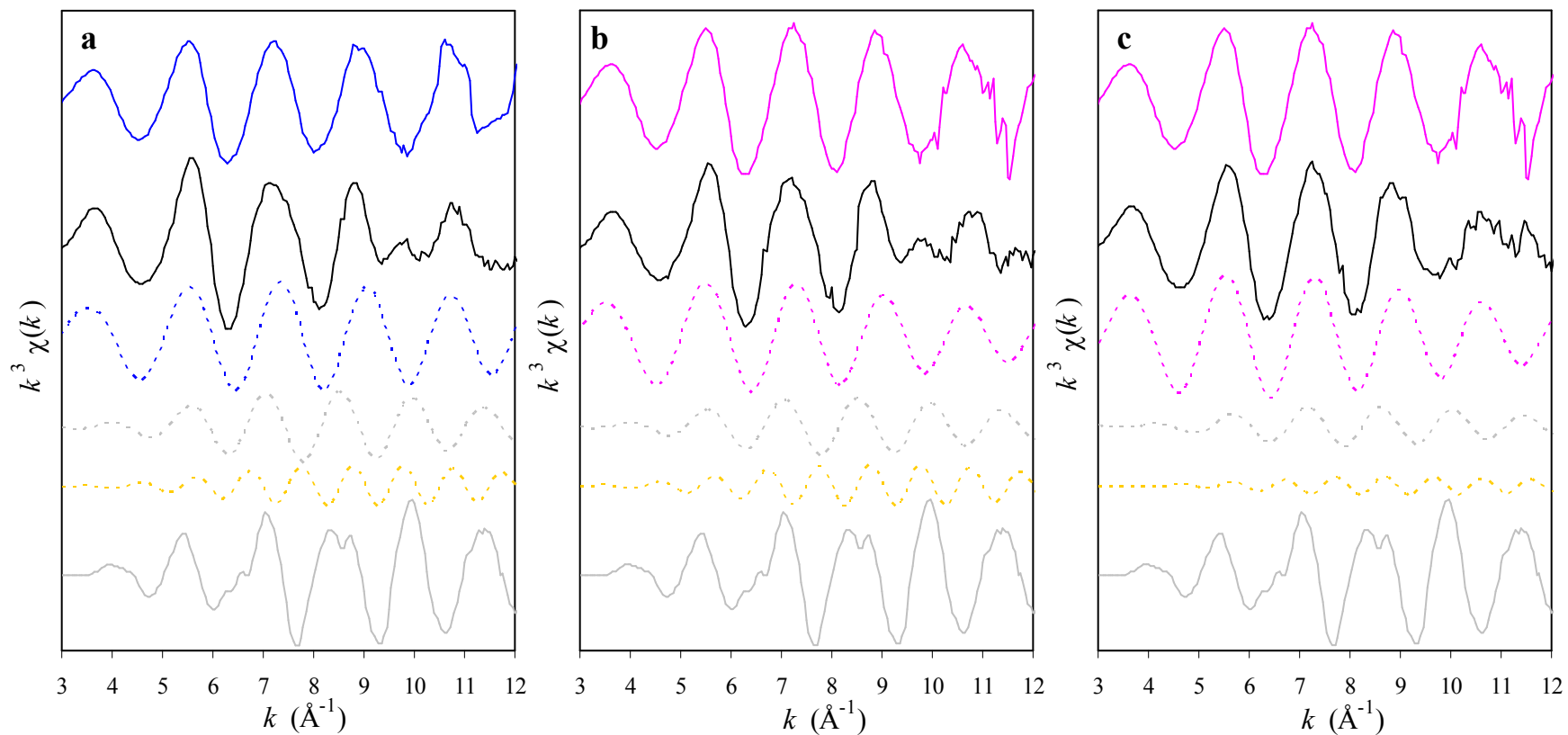
<sup>†</sup>The Debye-Waller factors ( $\sigma^2$ ) were fixed during the numerical fit.

$\Delta E_0$  and  $R_f$  indicate energy shift and goodness of the fit, respectively.

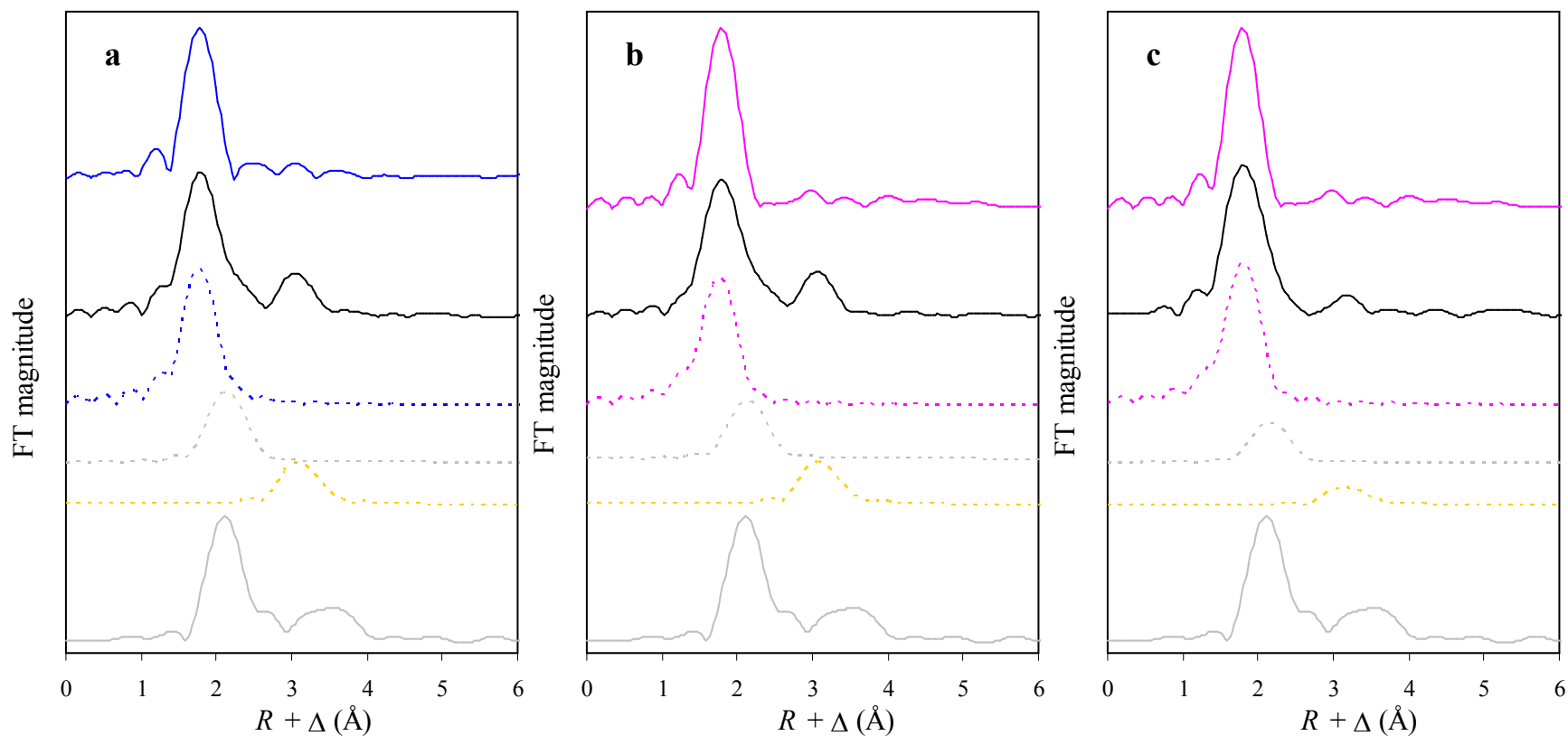


**Figure S1.** X-ray diffraction patterns for reference compounds with Cu-K $\alpha$  radiation (40 kV and 100 mV). The diffraction pattern of As(0) matches that of PDF No. 00-005-0632, which is indicated by red dashed lines.

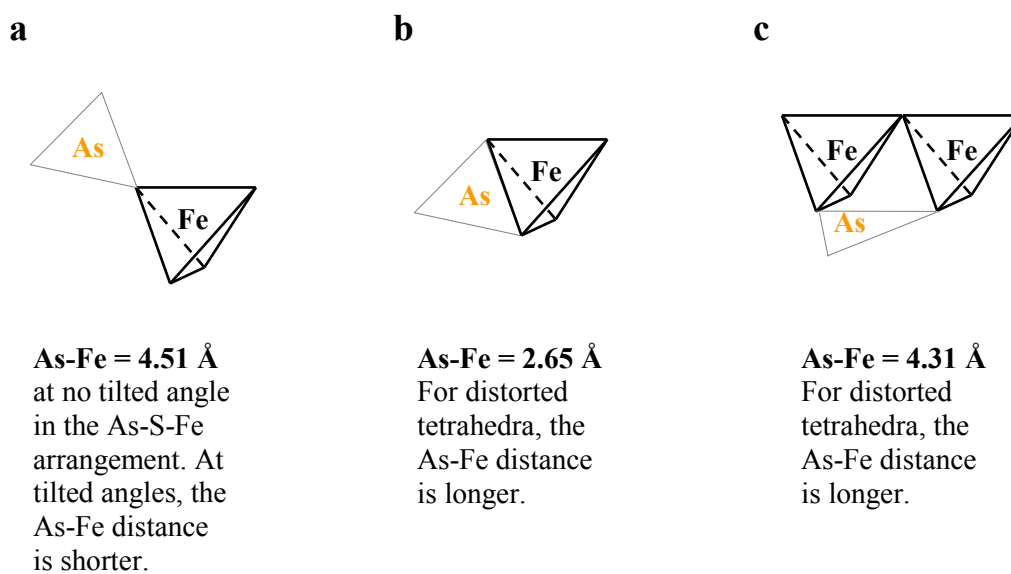




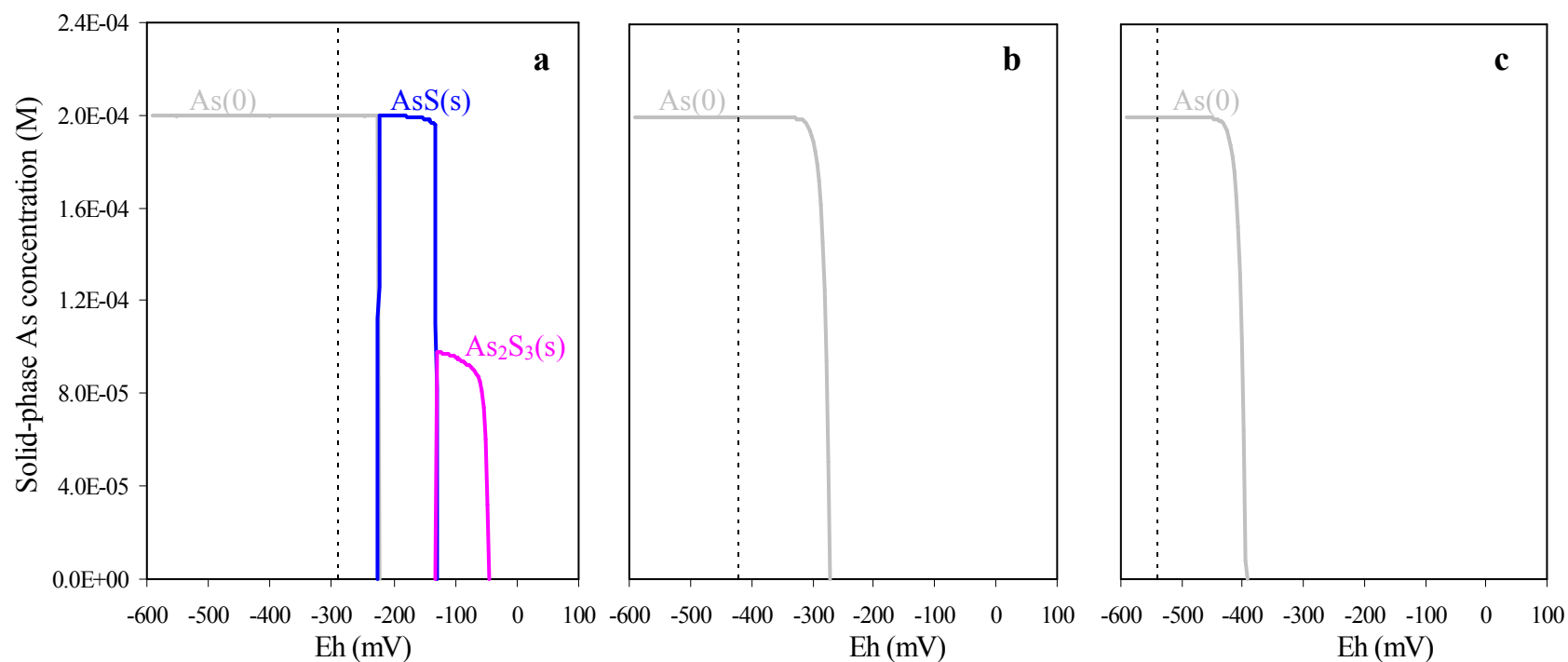
**Figure S2.** EXAFS component analysis of unoxidized samples at pH 4.9 (a), 7.1 (b), and 9.1 (c): the original sample spectra (black solid lines), As-S components (blue or pink dashed lines), As-As components at  $\sim 2.52$  Å (grey dashed lines), and As-As components at  $\sim 3.5$  Å (yellow dashed lines). The EXAFS spectra of As(0) (grey solid lines), disordered AsS (blue solid lines), and disordered As<sub>2</sub>S<sub>3</sub> (pink solid lines) are included for comparison.



**Figure S3.** Fourier transform (FT) component analysis of unoxidized samples at pH 4.9 (**a**), 7.1 (**b**), and 9.1 (**c**): the original sample spectra (black solid lines), As-S components (blue or pink dashed lines), As-As components at  $\sim 2.52$  Å (grey dashed lines), and As-As components at  $\sim 3.5$  Å (yellow dashed lines). The FT spectra of As(0) (grey solid lines), disordered AsS (blue solid lines), and disordered As<sub>2</sub>S<sub>3</sub> (pink solid lines) are included for comparison. Peak positions are uncorrected for phase shift.



**Figure S4.** Geometries of thioarsenite surface complexes. Monodentate (single-corner sharing) **(a)**, bidentate-mononuclear (edge sharing) **(b)**, and bidentate-binuclear (double-corner sharing) **(c)** complexes with undistorted  $\text{FeS}_4$  tetrahedra in mackinawite ( $\text{FeS}$ ). In this figure,  $\text{As-S} = 2.27 \text{ Å}$  (from the EXAFS analysis in this study),  $\text{Fe-S}$  in mackinawite  $= 2.24 \text{ Å}$  (16),  $\text{Fe-Fe}$  in mackinawite  $= 2.60 \text{ Å}$  (16), and  $\text{S-S}$  in mackinawite  $= 3.66 \text{ Å}$  (16) were used to calculate the As-Fe bonding distances. The As-Fe distance observed in our EXAFS study ( $3.57\text{--}3.67 \text{ Å}$ ) is unlikely due to formation of the surface complexes of thioarsenites unless significant distortion of the mackinawite surface occurs.



**Figure S5.** Equilibrium speciation of arsenic solids in unoxidized samples at pH 4.9 (**a**), 7.1 (**b**), and 9.1 (**c**) calculated by MINEQL+ 4.5. Black dashed lines indicate the lower stability limit of H<sub>2</sub>O (i.e.,  $H^+ + e^- = 1/2H_2(g)$ ). Input parameters and thermodynamic constants used are provided on pages S4-S5.

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