Supporting information

Accurate determination of As(V) coordination environment at the surface of ferrihydrite using synchrotron extended X-ray absorption fine structure spectroscopy and *ab initio* Debye-Waller factors

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This material includes 2 tables and 1 figure.

Table S1 Computed DW factors (σ^2) at 300 K for each path of DFT optimized scorodite and different As-ferrihydrite models.

Path	CN	scorodite	$HAsO_4$-BB	$HAsO_4$-MM	AsO_4-BB	AsO_4-MM
		σ^2 (10^{-3} Å^2)	σ^2 (10^{-3} Å^2)	σ^2 (10^{-3} Å^2)	σ^2 (10^{-3} Å^2)	σ^2 (10^{-3} Å^2)
As-O shell						
As-O1	1	1.84	1.64	1.60	1.925	1.717
As-O2	1	1.91	1.87	1.94	2.200	2.198
As-O3	1	1.83	1.85	1.74	2.176	1.927
As-O4	1	1.85	2.06	2.25	1.480	1.844
As-O1-O2	2	3.45	3.65	3.54	3.830	3.683
As-O1-O3	2	3.63	3.56	3.33	3.826	3.496
As-O1-O4	2	3.64	4.18	3.94	3.489	3.415
As-O2-O3	2	3.81	3.64	3.62	4.093	3.870
As-O2-O4	2	3.63	5.37	3.90	3.719	3.699
As-O3-O4	2	3.27	6.81	3.97	3.713	3.487
As-O1-As-O1	1	7.12	7.30	6.27	18.892	6.822
As-O2-As-O2	1	7.76	7.13	7.75	8.915	8.665
As-O3-As-O3	1	7.33	6.98	10.61	8.766	25.989
As-O4-As-O4	1	7.57	16.12	8.44	5.468	7.463
As-Fe shell						
As-Fe1	1	4.52				
As-Fe2	1	4.56	5.29	5.40	4.644	5.392
As-Fe3	1	4.78	5.86		4.706	
As-Fe4	1	4.49				
As-O1-Fe1	2	3.64				
As-O2-Fe2	2	3.54	3.76	3.26	3.453	3.172
As-O3-Fe3	2	3.89	4.67		3.590	
As-O4-Fe4	2	4.20				

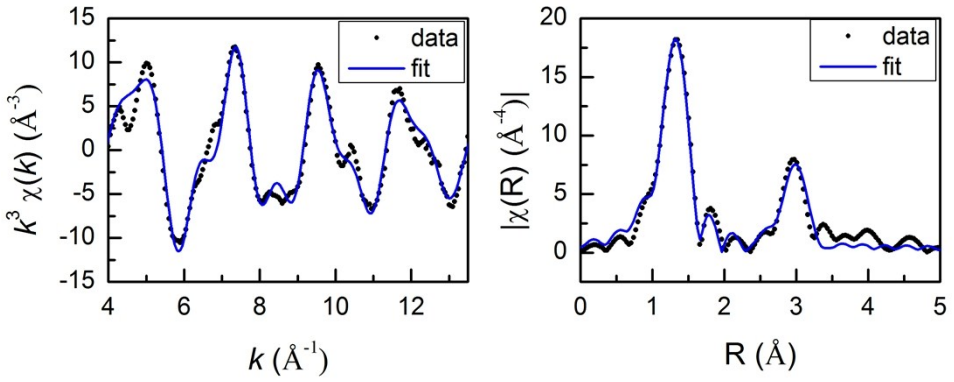

Fig. S1 Arsenic *K*-edge EXAFS spectra and magnitude of Fourier-transformed EXAFS spectra of scorodite. The black dots and blue lines represent experimental and fitted data, respectively. The shell-fit parameters are listed in the Table S4.

Table S2. Shell-fit parameters determined from *R*-space fit (*k*-weight = 3) of the As *K*-edge EXAFS spectra of scorodite using *ab initio* DW factors. Bold values were fixed and fit uncertainties are given for the last significant figure. The *k* range and *R* range were 4 – 13.5 Å^{-1} and 0.9 – 3.3 Å, respectively.

Sample	Path	**σ^2 (10^{-3} Å^2)**	CN	*d* (Å)	S_0^2	ΔE (eV)	*R*-factor	Red χ^2
Scorodite	As-O	**1.86**	**4**	1.69(0)	0.96(4)	6.9(9)	0.007	193
	As-O-O	**3.57**	**12**	3.09(5)				
	As-O1-As-O1[a]	**7.45**	**4**	3.38				
	As-Fe	**4.59**	3.5(4)	3.37(1)				
	As-O-Fe	**3.82**	6.9(8)	3.45(40)				

Note: CN: number of neighboring scatters; *d* (Å): interatomic distance; σ^2 (Å^2): Debye Waller factor, ΔE (eV): difference between the user-defined threshold energy and the experimentally determined threshold energy; *R*-factor = $\Sigma_i(\text{data}_i - \text{fit}_i)^2/\Sigma_i\text{data}_i^2$; red χ^2 = $(N_{idp}/N_{pts}\,\Sigma_i(\text{data}_i - \text{fit}_i)/\varepsilon_i)^2/(N_{idp}/N_{var})$, where N_{idp}, N_{pts}, and N_{var} are the numbers of independent points, data points, and variables, respectively, and ε_i is the uncertainty at each data point *i*. Fit uncertainties in parentheses are given for the last significant figure.

[a] The Δ*d* of As-O-As-O multiple scattering paths is defined as $\Delta d_{\text{As-O-As-O}}=\Delta d_{\text{As-O}}\times 2$.

[b] The Δ*d* of As-O-Fe multiple scattering paths is defined as $\Delta d_{\text{As-O-Fe}}=(\Delta d_{\text{As-O}}+\Delta d_{\text{As-Fe}})/2$.