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The supplementary material for

Magnetic and structural characteristics associated with the transformation of As(V)-coprecipitated ferrihydrite to hematite: implications for magnetic enhancement in soils and sediments

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Section S1: Syntheses of hematite and maghemite.

Hematite and maghemite were prepared using an established method.[1] Briefly, 27 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 500 mL of deionized water, and precipitated with 300 mL of 1 M NaOH. Subsequently, 50 mL of 1 M $NaHCO_3$ was added to the brown voluminous precipitate, and the obtained suspension (pH = 8−8.5) was then held in a closed polyethylene flask at 90 °C for 48 h. Note that all the above-mentioned solutions were preheated to 90 °C before reaction. Maghemite was obtained by heating synthetic magnetite, precipitated using a mixed solution with an Fe(II)/Fe(III) ratio of 0.5, in a furnace at 250 °C for 2 h,[1] Unfortunately, our maghemite reference contains minor hematite as evidenced by the observation of weak characteristic hematite Raman bands (i.e., ~289 and 222 cm^{-1})..

Section S2: Phase identification and semi-quantitative Rietveld refinement

Phase identification and semi-quantitative Rietveld refinement for phase analysis was conducted with X'pert HighScore Plus software using the PAN-Inorganic and Mineral Crystal Structure Database version 2.0.23 (Table S1). In all cases, the iron oxyhydroxides used for analysis (with JCPDS #) were: 2-line ferrihydrite (98–011–1017),[2] hematite (98-006-0263),[3] and maghematite (98-005-0985).[4] The semi-quantitative Rietveld phase conducted with the X'pert HighScore Plus software was tested for validity by analyzing a reagent grade goethite standard and refining the XRD data with unlikely multiple phases with diffraction peaks in all regions. Rietveld analysis (accuracy of ≤5%) confirmed the major phase in the test samples.

Section S3: As *K*-edge X-ray absorption spectra experimental and analytical

methods.

The As *K*-edge X-ray absorption spectra (XAS) were collected at the biological X-ray absorption spectroscopy beamline (BioXAS) beamline, Canadian Light Source. A Si(220) monochromator crystal with the wiggler field of 1.9 T was used during data collection. The energy of the monochromator was calibrated using an Au foil. All samples were measured in the fluorescence mode with multiple scans to increase the signal-to-noise ratio. Energy calibration, pre-edge background subtraction, post-edge normalization, and linear combination fitting (LCF) were performed using the Athena program (Demeter package, version 0.9.25). Extended X-ray absorption fine structure (EXAFS) data analysis was performed by fitting the Fourier transformed experimental data with the theoretical amplitude and phase function calculated by the FEFF code. The crystallographic structure of scorodite[5] was used as the FEFF input structure for the EXAFS fittings. The least-squares fitting was performed in the *k* range of 4 – 12.5 $Å^{-1}$ with the Artemis software in the Demeter package by using a Kaiser−Bessel window function. On the basis of the fitting results of scorodite, the amplitude reduction factor (S_0^2) was set to 1.0 for all data.

Section S4: Raman spectra analysis

The Raman spectra of the synthetic hematite and the aged products were obtained using a Raman microscope (Thermo Scientific DXR xi) equipped with a solid-state laser diode operating at 785 nm. A 50 × objective lens and a 2.0 mW laser were used. In each case, approximately 50 mg of freeze-dried ground sample was mounted on a glass slide. All samples were measured from 60 to 3,300 cm^{-1} in the line focus confocal mode with a detector exposure time of 8 s and a resolution of 4 cm^{-1} with the accumulation of 30 spectra. All scans were performed at 10% of the laser output at the microscope exit to avoid radiation damage.

The Raman spectrum of hematite belongs to the D_{3d}^{6} crystal space group and seven phonon lines are expected, namely two A_{1g} modes (225 and 498 cm^{-1}) and five E_g modes (247, 293, 299, 412 and 613 cm^{-1}).[6] Synthetic hematite spectrum shows strong bands at ~222, ~289, and ~403 cm^{-1}, with the band at ~289 cm^{-1} being the strongest (Fig. 5 a). The hematite spectrum also includes three other weak bands at ~493, ~606 cm^{-1}, and 242 cm^{-1} as a shoulder (Fig 5a), in good agreement with previously published values.[6-9] The maghemite bands are not well defined and their resolution is highly dependent on the sample preparation procedures because it is directly related to the degree of crystallinity of the material. Nevertheless, synthetic maghemite spectrum can be characterized by three broad bands at approximately 350, 500, and 700 cm^{-1} with minor bands at 222 and 290 cm^{-1}.[6]

Section S5: FTIR analysis

All infrared spectra were collected using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific). Prior to the measurement, approximately 0.050 mg of each sample was mixed with 2 mg of high-purity KBr and then pressed into a disk. The spectra were recorded in the range of 400–4,000 cm^{-1} with a spectral resolution of 4 cm^{-1} and 200 co-added scans in the transmission mode.

FTIR was used to obtain the symmetry and structural information of reactive groups, such as OH, H_2O, and vibrational spectral information of arsenate complexes formed in the aged As(V)-ferrihydrite products at 90 °C for 720 h. Detailed displays of the investigated range (400–4,000 cm^{-1}) including the As–O stretching vibration region (650–950 cm^{-1}), as well as the Fe-O and Fe-OH stretching vibration region (425–700 cm^{-1}), are shown in the Fig. S3. Typically, the FTIR band at 3,444 cm^{-1} is attributed to the stretching vibration of the surface H_2O molecules or an envelope of hydrogen-bonded surface OH groups. A red shift from 3,444 to 3,396 cm^{-1} for the As(V)-ferrihydrite aged samples compared to pure hematite is observed in Fig. S2a. The band at 2,975 cm^{-1} appears in the As(V)-ferrihydrite aged samples is the OH stretching vibration in the structure.[10] The red shift in the stretching vibration of the H_2O and OH groups, as well as the presence of the OH stretching vibration in the structure, suggest that the presence of As(V) alters the local environment of OH in the aged products. The FTIR band at 1,632 cm^{-1} is matching closely to the position of the H_2O bending vibration. The bands between 1,000 and 1,500 cm^{-1} are assigned to the presence of carbonate groups, because of the addition of $NaHCO_3$ to maintain the suspension pH. With the decrease of Fe/As(V) molar ratios, the normalized absorbance of the carbonate groups bands increases, suggesting more carbonates in the aged products at high As(V) loading. The FTIR spectra of the aged As(V)-ferrihydrite samples show four distinctive bands in the As–O stretching region (i.e., 881, 850, 828, and 798 cm^{-1}), which are absent in the spectrum of pure hematite (Fig. S3b). The bands at 881 and 798 cm^{-1} are attributed to the symmetric and asymmetric stretching modes of As−O bond, which is close to the adsorbed species of As(V) on the surfaces of hematite[11] and ferrihydrite[12] at mildly alkaline pH. It is worth noting that the band at 828 cm^{-1}, assigned to the stretching vibration of As−O−Fe, is present in the sample of Fe/As(V)40, whereas the band at 850 cm^{-1} in the samples of Fe/As(V)10 and Fe/As(V)20 is attributed to "non-surface-complexed" As−O bonds of the adsorbed arsenate species. These observations are interpreted as the evidence for the occluded AsO_4 units relative to AsO_4 ions, which are present in more than one environment in the As(V)-ferrihydrite aged products including the surface adsorption.

The characteristic hematite band positions in the FTIR spectra have been reported to be highly dependent on its morphology.[13] For example, hematite spheres have the FTIR bands at 575, 485, 385, and 360 cm^{-1}, whereas hematite laths display the FTIR bands at 650, 525, and 440 cm^{-1}. The FTIR spectrum of synthetic hematite in this study exhibits strong bands at ~624, ~556, and ~478 cm^{-1} (Fig. S3c), which are close to the reported FTIR bands for hematite laths.[13] However, the FTIR spectra of the solids for the Fe/As(V) 100 to 40 system show ~581, ~548, and ~486 cm^{-1} (Fig. S3c), which are close to the FTIR bands of hematite spheres. The shift of the hematite FTIR bands suggests that there is some deformation in the hematite structure in the aged As(V)-ferrihydrite.

Table S1: Results of phase identification and semi-quantitative Rietveld refinement for phase analysis of the transformation products aged at 90 °C for 720 h as a function of the Fe/As (V) molar ratio.

Sample	Hematite %	Maghemite %	Ferrihydrite%	Rexp	Rwp
As free	99.2	0.3	0.3	4.8	16.05
Fe/As(V)100	99.1	0.5	0.2	4.63	13.76
Fe/As(V)80	98.9	0.5	0.6	4.31	18.6
Fe/As(V)60	98.7	0.5	0.9	4.4	18.56
Fe/As(V)40	97.6	0.6	0.7	4.51	16.26
Fe/As(V)20	9	83.9	7.2	4.52	11.38
Fe/As(V)10	3.8	73.5	22.7	4.45	14.01

Table S2. Mössbauer parameters of sample Fe/As(V)40-720h at 295 K and 12 K

Sample	Signal	IS (mm/s)	QS (mm/s)	BHF	Relative area (%)
Fe/As(V)40-720h -295K	Doublet	0.48	2.52		2.91
	Sextet A	0.39	-0.08	51.06	80.21
	Sextet B	0.33	-0.48	50.81	16.88
Fe/As(V)40-720h -12k	Sextet A	0.6	-0.12	45.03	67.52
	Sextet B	0.11	-0.22	45.3	32.48

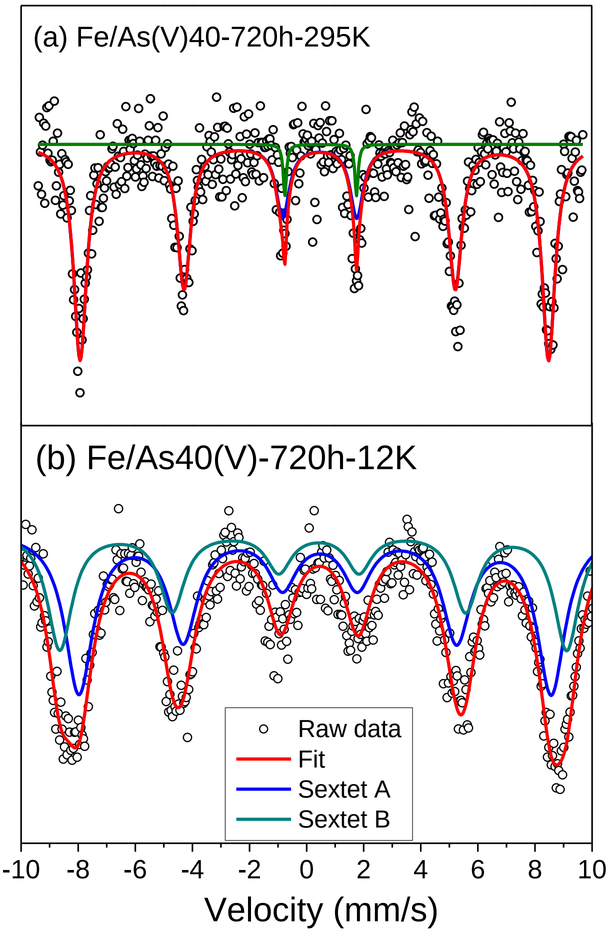

Figure S1. Mössbauer spectra of sample Fe/As(V)40-720h recorded at 295K and 12 K.

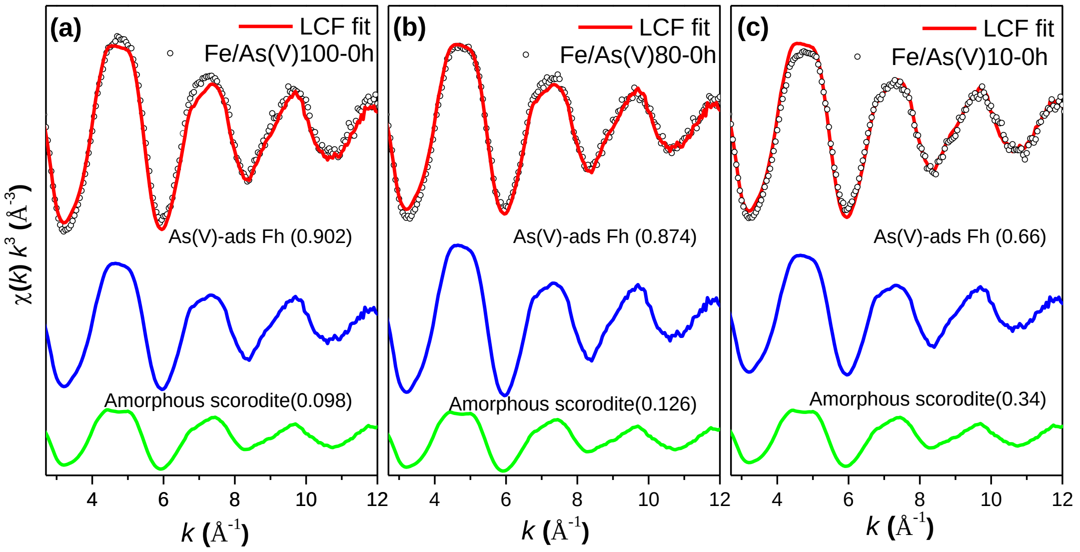

Fig. S2. Experimental and linear combination fits for *k* space spectra of fresh As(V)-ferrihydrite for the Fe/As(V)100-0h (a), Fe/As(V)80-0h (b), Fe/As10(V)-0h (c) samples and reference compounds (As(V) ads Fh and amorphous scorodite), along with spectra denoting the fractional contributions of the components used to generate the fitted spectra.

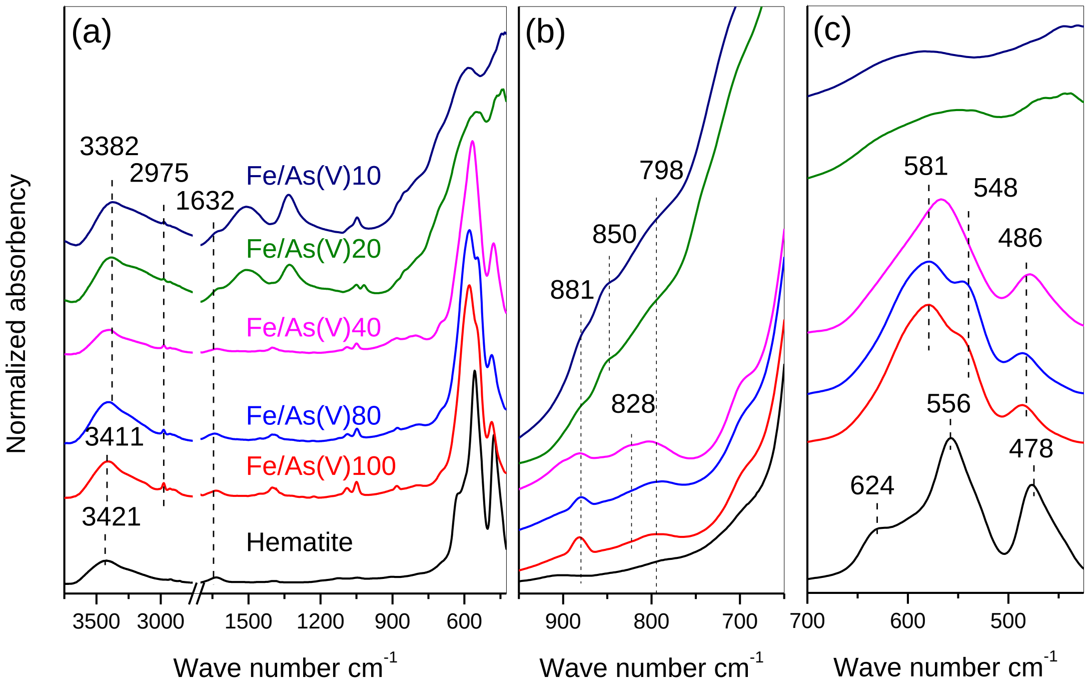

Figure S3. FTIR spectra of transformation products aged at 90 °C for 720 h as a function of the Fe/As(V) molar ratio (a), and their enlarged spectra in the range of 950–650 cm^{-1} (b) and 700–425cm^{-1} (c).

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