Supporting Information

Preferential Phosphate Sorption and Al Substitution on Goethite

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Experimental Details

Chemical analysis (total Al and Fe concentration)

Acid digestion for AlG samples was performed prior to the determination of Al and Fe concentrations. Briefly, 0.5 g of each AlG sample was dissolved into 10 mL of concentrated HCl. The suspensions were heated at 80 °C for 6 h. Concentrations of Al and Fe in acid digestates were determined using the flame atomic absorption spectrometry and used to calculate the molar ratios of Al/(Al+Fe) in AlG samples.[1]

X-ray diffraction (XRD)

The structure of precipitates was identified using the X-ray diffraction (XRD) (PANalytical XPert Pro MRD). The XRD patterns were collected from 10° to 45° (2θ) at a scanning rate of 1°(2θ) per min using the Cu-Kα radiation.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra for the AlG samples were determined using a ULVAC-PHI, PHI 5000 VersaProbe/Scanning ESCA Microprobe. During XPS, core electrons are excited by X-ray irradiation, and the kinetic energy of ejected electrons are measured to determine the binding energy of the electrons. The binding energies of Al and Fe were collected.[2]

Iron K-edge XAS

The local structure of Fe in AlG samples was characterized using Fe *K*-edge XAS including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy.

Samples were sealed with 8 μm Kapton film and Kapton tape. Spectra were acquired at Taiwan Light Source (TLS) beamline 17C1 and Taiwan Photon Source (TPS) beamline 44A at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. Samples were analyzed in transmission mode using ion chamber detectors. The monochromator energy calibration to 7112 eV was monitored during data collection using a Fe foil placed between the transmission (It) and reference (Ir) ion chamber detectors. Spectra were acquired at photon energies from -200 eV to a wavenumber (k) of 14 $Å^{-1}$ relative to 7112 eV, using a step size of 0.5 eV in the near edge region (-30 to +50 eV) and a step size of $k = 0.05$ $Å^{-1}$ at higher energies.

Multiple XAS scans for each sample were aligned, merged, baseline corrected, and normalized using the IFEFFIT interface including the Athena and Artemis programs.[3] For EXAFS fitting, the FEFF6[4] was used to generate the theoretical paths of Fe-O, Fe-Fe, and Fe-Al. Our fitting model consists of the single scattering (SS) Fe-O, Fe-Fe, and Fe-Al paths out to a maximum radial distance of 3.56 Å. Paths in our model designated as Fe-Fe1 and Fe-Fe2 represent the interatomic distances of edge-sharing (ES) FeO_6 linkages in the goethite structure, and the Fe-Fe3 path represents the corner-sharing (CS) FeO_6 linkages. A model of the goethite structure from the American Mineralogist Crystal

Structure database was used as a template to determine correlations in degeneracies between higher-shell Fe-O paths and ES/CS FeO_6 linkages. All EXAFS spectra were fit for coordination number (CN), distance (ΔR), and mean-square displacement of interatomic distance (σ^2) with a fixed amplitude reduction factor (S_0^2) of 0.68 derived from first-shell fitting of goethite (0-AlG).

Phosphate sorption isotherms

Sorption isotherms for AlG samples were conducted at pH 6.0 in 250 mL polycarbonate centrifuge bottles following the basic procedure described by Khare, et al. [5]

All samples had a suspended solids concentration of 1.50 g kg^{-1}, constant ionic strength of 0.01 mol L^{-1} KCl, and 30 g total mass in 50 mL polycarbonate centrifuge tubes. An appropriate aliquot of 0.01 mol L^{-1} KH_2PO_4 was slowly added to each vigorously stirred sample using a micropipetter. The pH was adjusted to pH 6.0 using 0.01 mol L^{-1} HCl or 0.01 mol L^{-1} KOH. Samples were shaken for 42 h on a reciprocating water bath shaker at a rate of 0.5 s^{-1} and 25°C for 42 h. After equilibration, samples were centrifuged at approximately 6000 *g* for 15 min, and the supernatant solutions were decanted. The pH was measured in a portion of the supernatant solution before filtering and was found to be 6.0±0.1 for all samples. The remaining solutions were filtered through 0.2 μm membranes (Millipore Corp., Bedford, MA). Dissolved PO_4 in filtrates was measured using the molybdate colorimetric (Murphy-Riley) procedure[6] on a Shimadzu Model UV 2101PC spectrophotometer.

Phosphorus K-edge XANES

Phosphorus *K*-edge XANES data were collected at TLS beamline 16A1 at the NSRRC in Hsinchu, Taiwan. The synchrotron radiation, which passes through focusing mirrors, was detuned by 50% at 200 eV above the P *K*-edge. The channel-cut Si(111) monochromator energy was calibrated to 2222.3 eV based on the first inflection point in the L3-edge derivative spectra from a Zr foil. Spectra were collected in fluorescence mode between -50 to +300 eV relative to the P(V) *K*-edge energy at 2151 eV, using a step size of 0.1 eV across the absorption edge region (-5 to +10 eV). A $He_{(g)}$-purged flight path and a $N_{2(g)}$-filled Lytle detector were used. Self-absorption effects were considered to be insignificant because no decrease in the white-line peak intensity was observed with increasing sorbed PO_4 concentration.

Multiple XANES spectra for each sample were aligned, merged, baseline corrected, and normalized using the approach described above for Fe XAS analysis. The distribution of PO_4 bonding between Al and Fe in AlG samples was determined by LCF analyses across the pre-white-line region from -7 to -2 eV using the Athena program. Samples of PO_4 sorbed on goethite (0-AlG) and boehmite were used as end-member standards in LCF analyses.

Table S1. Al and Fe used in synthesis and the chemical composition of synthesized Al-substituted goethite.

Sample	$Fe(NO_3)_3$•9 H_2O (g)	$Al(NO_3)_3$•9 H_2O (g)	$Al(NO_3)_3$•9 H_2O in 2 N KOH (g)	Precipitated Al/(Al+Fe) (mol %)[a]
0-AlG	20.0	0.0	0.0	0.0
3-AlG	20.0	0.0	3.5	2.9
10-AlG	17.5	2.5	8.8	10.4
17-AlG	15.0	5.0	15.0	17.4

[a] Precipitated Al/(Al+Fe) molar proportions were derived by calculating the contents of Al and Fe in acid digestates of individual precipitates.

Table S2. Structural parameters obtained from Fe *K*-edge EXAFS fitting analyses for Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG).[a]

Path	CN	R (Å)	σ^2 (Å^2)
	------------------- 0-AlG -------------------		
Fe-O1	6	2.01 (0.00)	0.012 (0.002)
Fe-Fe1	2.02 (0.18)	3.04 (0.01)	0.004 (0.001)
Fe-Fe2	3.12 (0.25)	3.30 (0.01)	0.005 (0.001)
Fe-Fe3	4.84 (0.58)	3.46 (0.01)	0.006 (0.001)
	--------------- 3-AlG ---------------		
Fe-O1	6	2.00 (0.00)	0.013 (0.001)
Fe-Fe1	1.85 (0.24)	3.03 (0.01)	0.005 (0.001)
Fe-Fe2	3.07 (0.38)	3.30 (0.05)	0.005 (0.002)
Fe-Fe3	5.05 (0.59)	3.46 (0.03)	0.005 (0.002)
	--------------- 10-AlG ---------------		
Fe-O1	6	1.98 (0.01)	0.010 (0.000)
Fe-Fe1	1.39 (0.19)	3.00 (0.01)	0.006 (0.001)
Fe-Fe2	-/-	-/-	-/-
Fe-Fe3	1.44 (0.25)	3.56 (0.03)	0.004 (0.001)
Fe-Al1	0.48 (0.27)	3.00 (0.05)	0.005 (0.001)
Fe-Al2	4.24 (0.34)	3.24 (0.01)	0.005 (0.001)
	--------------- 17-AlG ---------------		
Fe-O1	6	1.98 (0.00)	0.010 (0.001)
Fe-Fe1	1.15 (0.28)	2.99 (0.03)	0.005 (0.002)
Fe-Fe2	-/-	-/-	-/-
Fe-Fe3	1.05 (0.44)	3.56 (0.04)	0.004 (0.003)
Fe-Al1	0.55 (0.45)	3.00 (0.14)	0.007 (0.002)
Fe-Al2	4.63 (0.57)	3.28 (0.02)	0.007 (0.002)

[a] Fitting was done across the k range of 2.5 to 11.5 Å^{-1} and an R range of 1.0 to 3.6 Å. Numbers in parentheses are uncertainties calculated for the EXAFS model. All samples were fit simultaneously, yielding a normalized sum of squared residuals [*R-factor* = $\sum(\text{data-fit})^2/\sum\text{data}^2$)] of 0.010 (1.0%) for all samples. Values of other EXAFS model parameters not shown above were either fixed or fit to a common value across all samples as follows: S_0^2 = 0.68 (0.08) (fixed amplitude reduction factor based on first-shell fitting of goethite); ΔE = 0.25 eV (fitted energy shift parameter).

Table S3. Fitting parameters of the Langmiur model for phosphate sorption isotherms on Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG) at pH 6.0.

Sample	q_{max} (mmol kg^{-1})	K_L (L μmol^{-1})	r^2
0-AlG	134.7 ± 2.8	1.12 ± 0.28	0.99
3-AlG	209.0 ± 6.1	0.64 ± 0.13	0.99
10-AlG	283.8 ± 9.6	0.42 ± 0.07	0.99
17-AlG	583.7 ± 29.2	0.27 ± 0.09	0.98

q_{max}: maximum adsorption capacity

K_L: Langmuir constant

Table S4. Phosphate associated with Fe(III) vs. Al(III) calculated using linear combination fitting to normalized P *K*-edge XANES spectra for Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG).[a]

Sample	Sorbed PO_4 (mmol kg^{-1})	% Associated with Fe	% Associated with Al	R-factor[b]
3-AlG	111	95.6 (2.4)	4.4 (2.4)	0.0184
	197	68.0 (1.8)	32.0 (1.8)	0.0069
10-AlG	151	48.6 (1.9)	51.4 (1.9)	0.0120
	220	78.5 (2.2)	21.5 (2.2)	0.0070
	264	74.3 (2.0)	25.7 (2.0)	0.0058
17-AlG	156	81.4 (2.7)	18.6 (2.7)	0.0061
	312	51.1 (1.5)	48.9 (1.5)	0.0025
	454	76.9 (2.2)	23.1 (2.2)	0.0036
	551	55.9 (1.7)	44.1 (1.7)	0.0015

[a] Standards used for linear combination fitting were goethite (0-AlG) and boehmite with sorbed PO_4 concentration of 135 and 400 mmol kg^{-1} at pH 6.0 and in a 0.01 M KCl background electrolyte. Deviations in parentheses represent uncertainties in fitting parameters as calculated by Athena. The sum of fitted Fe and Al proportions ranged from 95% to 108% and were normalized to sum to 100%.

[b] Normalized sum of the squared residuals of the fit (R-factor = $\sum(\text{data-fit})^2/\sum \text{data}^2$).

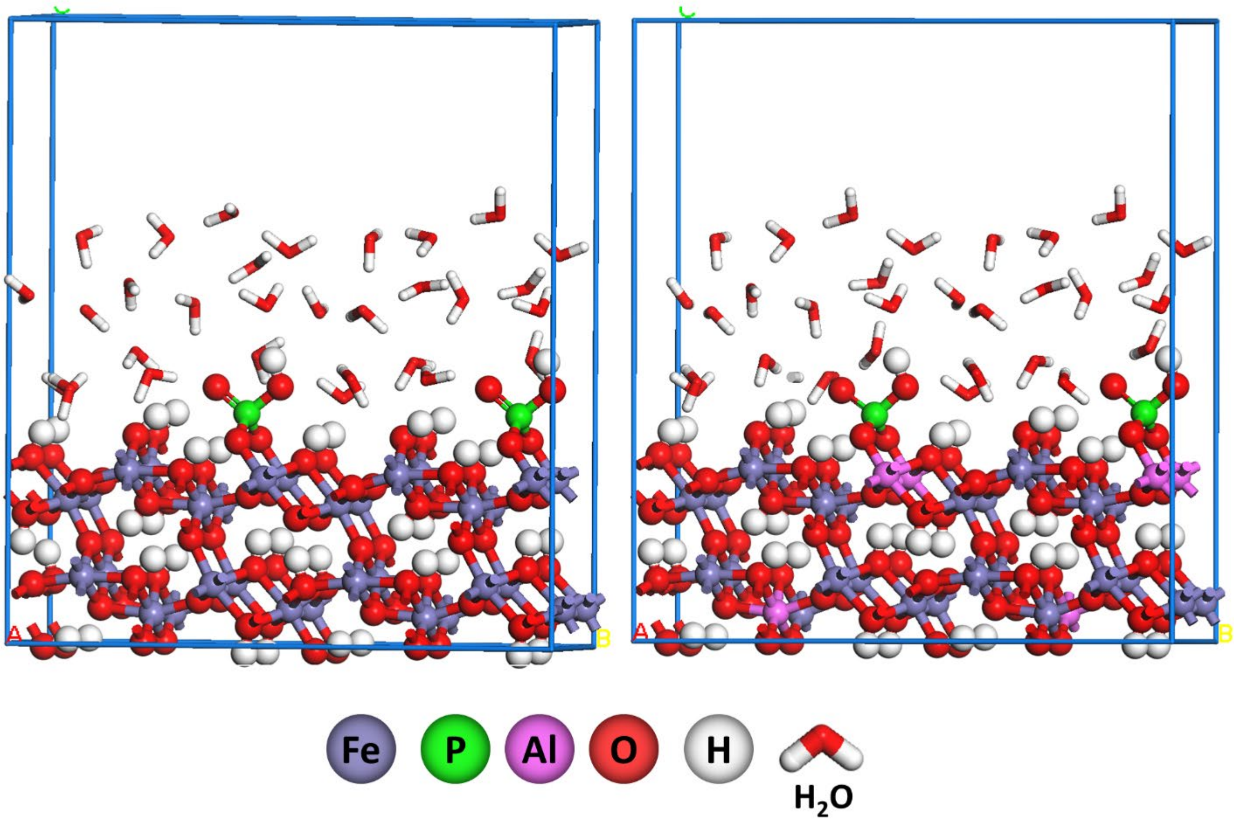

Fig. S1. Models of (a) goethite and (b) Al-substituted goethite with sorbed PO_4, which were used to perform the density functional theory (DFT) simulation. The Al-substituted goethite contains 12.5 mol% of Al.

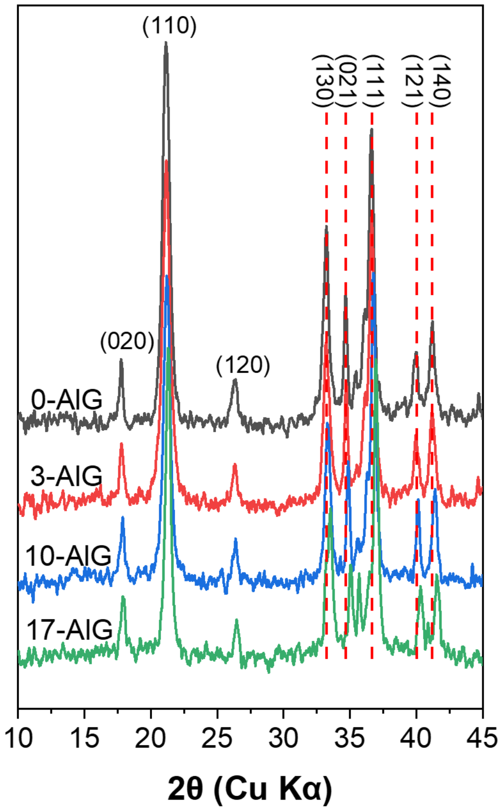

Fig. S2. X-ray diffraction patterns for Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG).

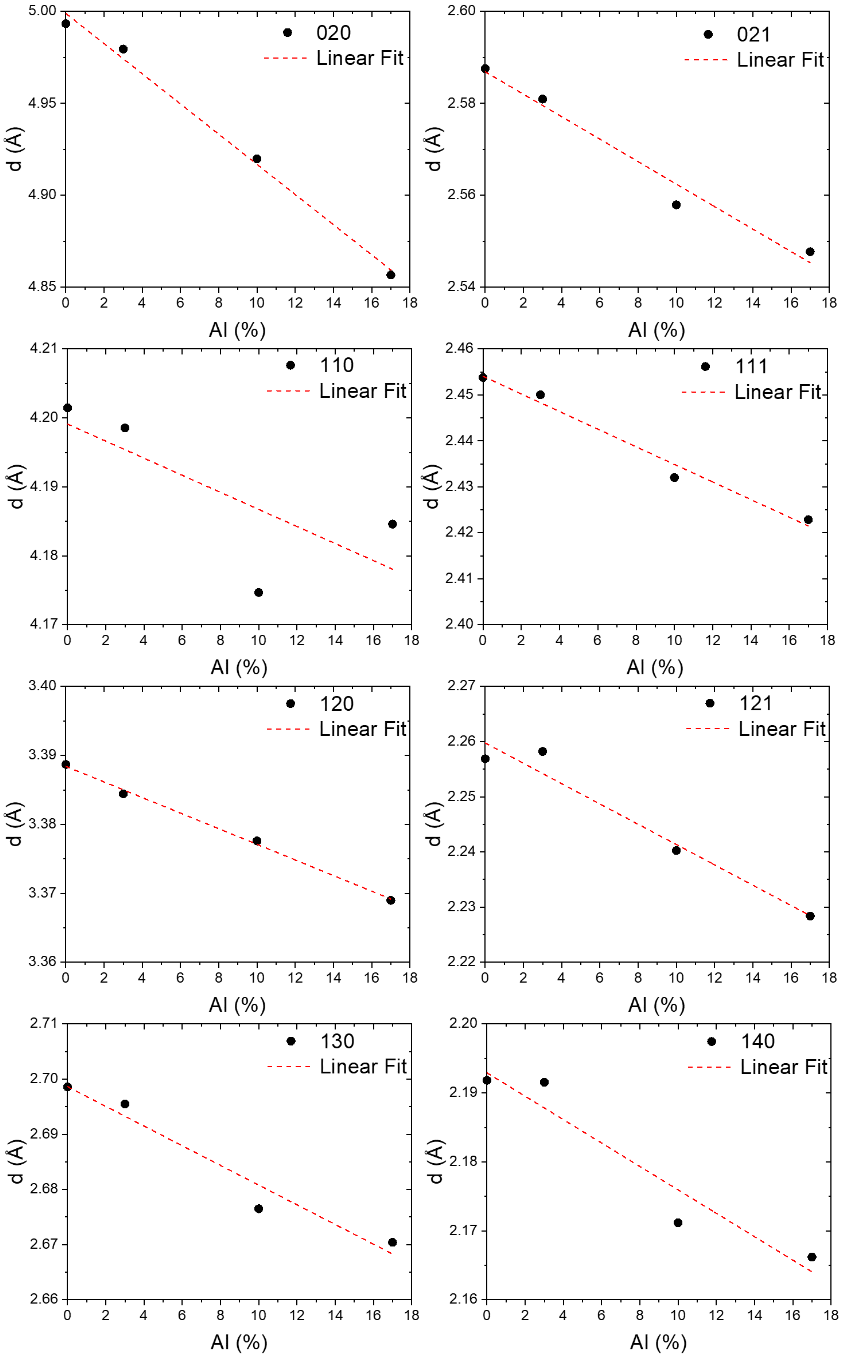

Fig. S3. The d value for individual planes of Al-substituted goethite as the function of Al substitution.

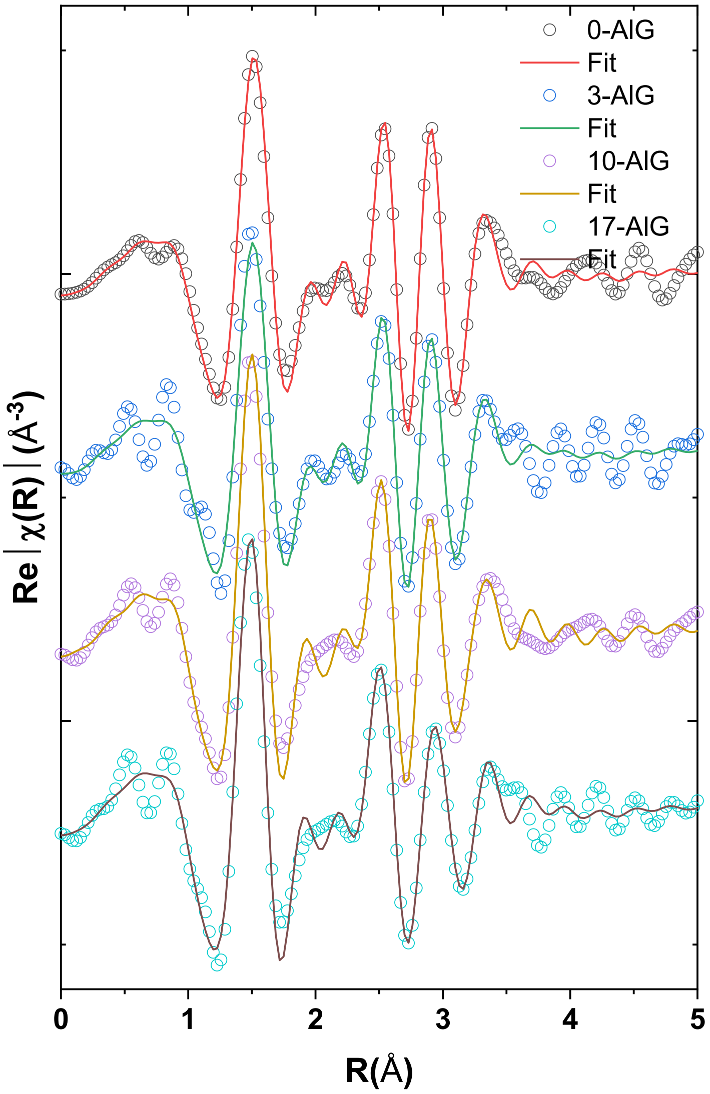

Fig. S4. Real part of Fourier transformed Fe *K*-edge EXAFS data (open circles) with model fits (solid lines) for Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG).

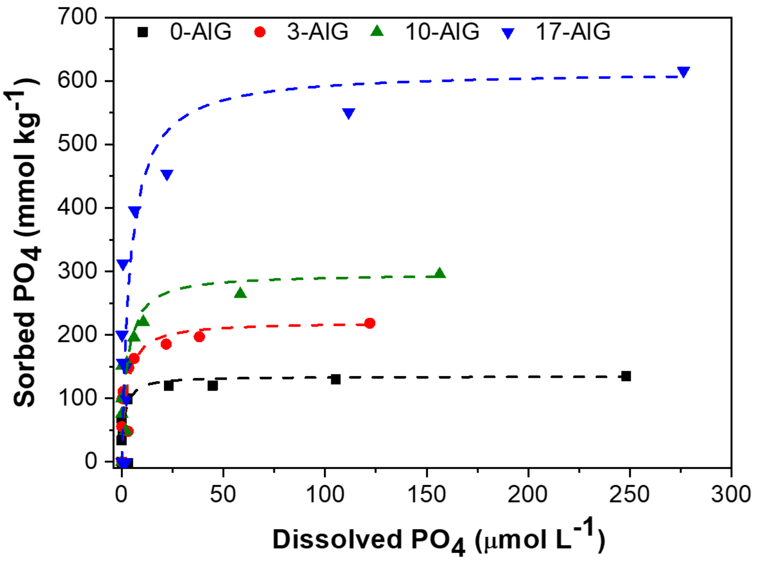

Fig. S5. Phosphate sorption isotherms at pH 6.0 and corresponding Langmiur model fits (dashed lines) for Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG).

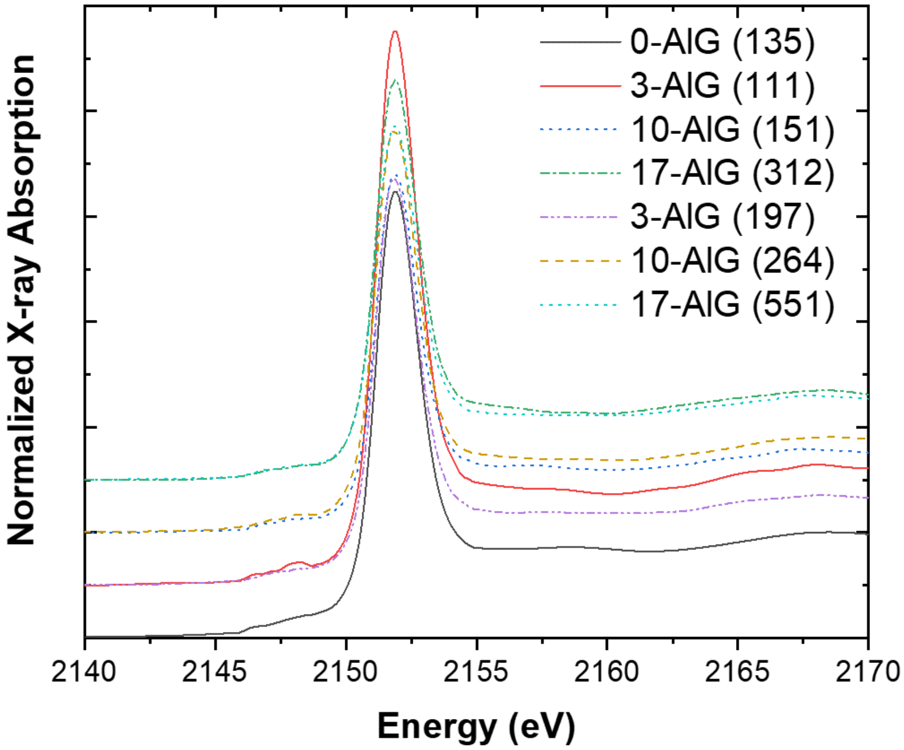

Fig. S6. Normalized P *K*-edge XANES spectra for PO_4 sorbed at various concentrations on Al-substituted goethite with Al/Al+Fe mol% of 0 (0-AlG), 2.9 (3-AlG), 10.4 (10-AlG), and 17.4 (17-AlG). The numbers after sample names are the sorbed PO_4 concentrations (mmol kg^{-1}) at pH 6.0 and in a 0.01 M KCl background electrolyte.

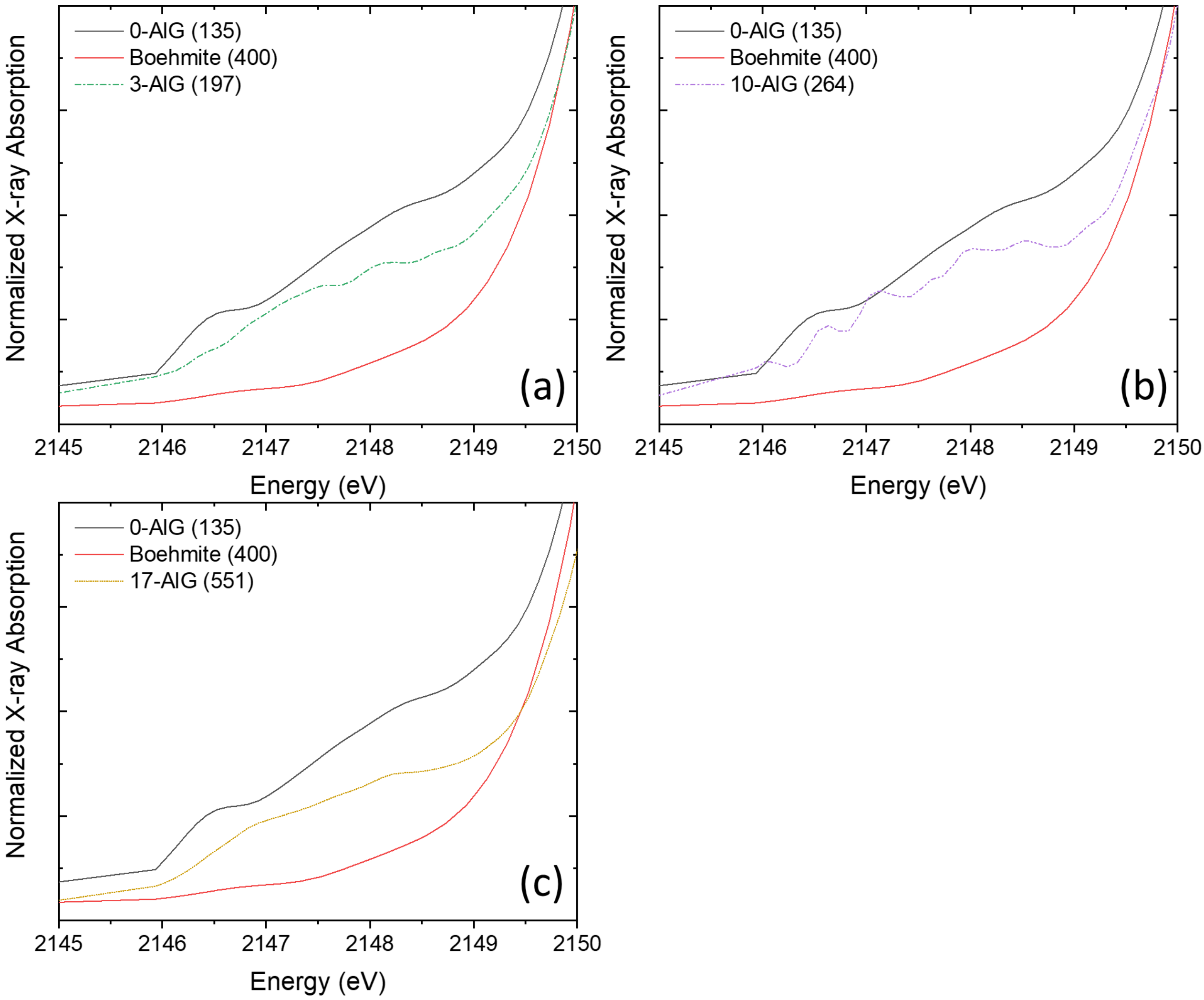

Fig. S7. Pre-white-line region of normalized P *K*-edge XANES spectra for PO_4 sorbed at various concentrations on Al-substituted goethite with Al/Al+Fe mol% of (a) 2.9 (3-AlG), (b) 10.4 (10-AlG), and (c) 17.4 (17-AlG). Spectra for end-member samples of PO_4 sorbed on goethite (0-AlG) or Al-hydroxide (boehmite) were shown in all figures. The numbers in parentheses after sample names are the sorbed PO_4 concentrations (mmol kg^{-1}) at pH 6.0 and in a 0.01 M KCl background electrolyte.

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