
Article:
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TABLE 1: Cu k-edge EXAFS fits for Cu adsorbed to humic acid, ferrihydrite and goethite, and ferrihydrite and goethite organo-mineral composites. (Fit to ferrihydrite reproduced from Moon and Peacock, 2012).

(a) EXAFS fits for spectra fit by refinement of a single model cluster

pH	N_O $R(Cu\text{-}O_1)$ $2\sigma^2$ θ, φ	N_O $R(Cu\text{-}O_2)$ $2\sigma^2$ θ, φ	N_O $R(Cu\text{-}O_3)$ $2\sigma^2$ θ, φ	N_O $R(Cu\text{-}O_4)$ $2\sigma^2$ θ, φ	N_O $R(Cu\text{-}O_{ax})$ $2\sigma^2$ θ, φ	N_{Fe} $R(Cu\text{-}Fe_1)$ $2\sigma^2$ θ, φ	N_{Fe} $R(Cu\text{-}Fe_2)$ $2\sigma^2$ θ, φ	N_C $R(Cu\text{-}C)$ $2\sigma^2$ θ, φ	N_O $R(Cu\text{-}O_5)$ $2\sigma^2$ θ, φ	EF	R (%)	Fit Index	Reduced Chi^2
Humic acid end-member model sample: HA_51wt%C_0.7wt%Cu_pH5													
5.00	1.0 1.96 0.008 90, 0	1.0 1.92 0.011 90, 90	1.0 1.95 0.023 90, 180	1.0 2.00 0.024 90, 270	1.0 2.31 0.019 0, 0	-	-	1.0 2.79 0.023 90, 24	1.0 4.12 0.016 90, 19	-1.79	20.4	0.36	30.3
Ferrihydrite end-member model sample: Fh_0.7wt%Cu_pH6.25													
6.25	1.0 1.91 0.009 90, 0	1.0 1.90 0.007 90, 90	1.0 1.95 0.003 90, 180	1.0 2.03 0.006 90, 270	-	0.8 3.01 0.023 90, 45	-	-	-	-5.49	17.1	0.20	4.35
Goethite end-member model sample: Gt_0.7wt%Cu_pH6													
6.00	1.0 1.89 0.017 90, 0	1.0 1.97 0.005 90, 90	1.0 1.92 0.003 90, 180	1.0 2.00 0.013 90, 270	-	1.0 3.03 0.013 130, 0	1.0 3.28 0.013 130, 90	-	-	5.09	18.7	0.30	25.0
Ferrihydrite organo-mineral composite: Fh_HA_8wt%C_0.7wt%Cu													
4.30	1.0 1.96 0.007 90, 0	1.0 1.93 0.009 90, 90	1.0 2.00 0.019 90, 180	1.0 1.97 0.020 90, 270	1.0 2.35 0.017 0, 0	-	-	1.0 2.79 0.026 90, 24	1.0 4.11 0.020 90, 19	2.16	21.2	0.35	29.8
Ferrihydrite organo-mineral composite: Fh_HA_12wt%C_0.7wt%Cu													
4.30	1.0 1.97 0.005 90, 0	1.0 1.92 0.007 90, 90	1.0 2.00 0.020 90, 180	1.0 1.99 0.020 90, 270	1.0 2.35 0.017 0, 0	-	-	1.0 2.79 0.025 90, 24	1.0 4.11 0.020 90, 21	1.82	21.9	0.35	29.2
Goethite organo-mineral composite: Gt_HA_7wt%C_0.7wt%Cu													
4.30	1.0 1.94 0.005 90, 0	1.0 1.94 0.012 90, 90	1.0 1.99 0.016 90, 180	1.0 1.98 0.015 90, 270	1.0 2.34 0.019 0, 0	-	-	1.0 2.79 0.020 90, 24	1.0 4.11 0.013 90, 19	2.03	22.7	0.38	31.5

N is the number of atoms in a shell. R is the distance of the atom in a shell from the Cu central absorber. σ is the Debye-Waller factor. θ and φ are the spherical coordinates of each atom in a shell. EF is the correction to the Fermi energy value set in ATHENA. Values in italics were held constant during optimisation.

(b) EXAFS fits for ferrihydrite and goethite organo-mineral composites fit by linear combination of two model clusters

pH	N $Cu_{mineral}$	N Cu_{HA}	EF	R (%)	Fit Index	Reduced Chi^2
Ferrihydrite organo-mineral composite: Fh_HA_8wt%C_0.7wt%Cu						
5.00	0.49±0.09	0.51±0.09	2.41	25.5	0.52	3.13
6.00	0.70±0.12	0.30±0.12	3.71	26.9	0.59	3.51
Ferrihydrite organo-mineral composite: Fh_HA_12wt%C_0.7wt%Cu						
5.00	0.50±0.10	0.50±0.10	1.90	24.7	0.51	3.05
6.00	0.68±0.11	0.32±0.11	2.69	28.1	0.65	3.87
Goethite organo-mineral composite: Gt_HA_7wt%C_0.7wt%Cu						
5.00	0.49±0.10	0.51±0.10	0.07	26.1	0.64	3.80
6.00	0.63±0.10	0.37±0.10	3.46	27.5	0.67	4.03

N $Cu_{mineral}$ is the number of Cu atoms (Cu site occupancy) adsorbed to the ferrihydrite or goethite fraction of the organo-mineral composite via bidentate edge-sharing or corner-sharing complexation, respectively. N Cu_{HA} is the number of Cu atoms (Cu site occupancy) adsorbed to humic acid fraction of the organo-mineral composite. EF is the correction to the Fermi energy value set in ATHENA. In the linear combination analysis, N $Cu_{mineral}$ + N Cu_{HA} was constrained to equal 1.

TABLE 2: Input parameters for the surface complexation models for Cu adsorbed to ferrihydrite (reproduced here from Moon and Peacock, 2013), goethite and humic acid.

Ferrihydrite (reproduced from Moon and Peacock, 2013)		
Surface area (m^2/g)[a]		300
Site density $\equiv FeOH^{-0.5}(e)$ (sites/nm^2)[b] / (mol sites/g x10^{-3})[c]		2.5 / 1.25
Site density $\equiv FeOH^{-0.5}(c)$ (sites/nm^2)[b] / (mol sites/g x10^{-3})[c]		3.5 / 1.74
Site density $\equiv Fe_3O^{-0.5}$ (sites/nm^2)[b] / (mol sites/g x10^{-3})[c]		1.2 / 0.598
C_{stern} (F/m^2)[d]		1.10
[e]log $K_{FeOH(e)}$	$\equiv FeOH^{-0.5}(e) + H^+ = \equiv FeOH_2^{+0.5}(e)$	7.99
[d]log $K_{FeOH(e)\_Na}$	$\equiv FeOH^{-0.5}(e) + Na^+ = \equiv FeOH^{-0.5}(e)$ - - Na^+	-1.00
[d]log $K_{FeOH2(e)\_NO3}$	$\equiv FeOH_2^{+0.5}(e) + NO_3^- = \equiv FeOH_2^{+0.5}(e)$ - - NO_3^-	-1.00
(where equations above are repeated for ($\equiv FeOH^{-0.5}(c)$)		
[e]log K_{Fe3O}	$\equiv Fe_3O^{-0.5} + H^+ = \equiv Fe_3OH^{+0.5}$	7.99
[d]log K_{Fe3O_Na}	$\equiv Fe_3O^{-0.5} + Na^+ = \equiv Fe_3O^{-0.5}$ - - Na^+	-1.00
[d]log K_{Fe3OH_NO3}	$\equiv Fe_3OH^{+0.5} + NO_3^- = \equiv Fe_3OH^{+0.5}$ - - NO_3^-	-1.00
Goethite		
Surface area (m^2/g)[a]		103
Site density $\equiv FeOH^{-0.5}$ (sites/nm^2)[b] / (mol sites/g x10^{-3})[c]		3.45 / 0.59
Site density $\equiv Fe_3O^{-0.5}$ (sites/nm^2)[b] / (mol sites/g x10^{-3})[c]		2.70 / 0.46
C_{stern} (F/m^2)[d]		1.00
[e]log K_{FeOH}	$\equiv FeOH^{-0.5} + H^+ = \equiv FeOH_2^{+0.5}$	9.20
[d]log K_{FeOH_Na}	$\equiv FeOH^{-0.5} + Na^+ = \equiv FeOH^{-0.5}$ - - Na^+	-1.00
[d]log K_{FeOH2_NO3}	$\equiv FeOH_2^{+0.5} + NO_3^- = \equiv FeOH_2^{+0.5}$ - - NO_3^-	-1.00
[e]log K_{Fe3O}	$\equiv Fe_3O^{-0.5} + H^+ = \equiv Fe_3OH^{+0.5}$	9.20
[d]log K_{Fe3O_Na}	$\equiv Fe_3O^{-0.5} + Na^+ = \equiv Fe_3O^{-0.5}$ - - Na^+	-1.00
[d]log K_{Fe3OH_NO3}	$\equiv Fe_3OH^{+0.5} + NO_3^- = \equiv Fe_3OH^{+0.5}$ - - NO_3^-	-1.00
Humic acid		
Surface area (m^2/g)[a]		200
Site density $\equiv RCOO^-$ (sites/nm^2)[c] / (mol sites/g x10^{-3})[d]		6.20 / 2.06
Site density $\equiv RO^-$ (sites/nm^2)[c] / (mol sites/g x10^{-3})[d]		4.49 / 1.49
C_{stern} (F/m^2)$_d$		8.00
[d]log K_{RCOO}	$\equiv RCOO^- + H^+ = \equiv RCOOH^+$	3.67
[d]log K_{COO_Na}	$\equiv RCOO^- + Na^+ = \equiv RCOO^-$ - - Na^+	-1.00
[d]log K_{RO}	$\equiv RO^- + H^+ = \equiv ROH^+$	7.11
[d]log K_{RO_Na}	$\equiv RO^- + Na^+ = \equiv RO^-$ - - Na^+	-1.00

[a]Determined from BET analysis (Fh and Gt: this study; HA: Bujak et al., 1995). [b]Determined from a crystallographic consideration of the mineral surface (Fh: Hiemstra and van Riemsdijk, 2009; Gt: Hiemstra and van Riemsdijk, 1996). [c]Determined using the surface area. [d]Determined from fitting potentiometric titration data (Fh: Moon and Peacock, 2013; Gt: Otero-Fariña, 2017; HA: López et al., 2012). [e]Determined according to log $K_{group} = pH_{PZC}$ (Hiemstra et al., 1996).

TABLE 3: Input parameters for the surface complexation models for Cu adsorbed to ferrihydrite and goethite organo-mineral composites.

Organo-mineral composite		**Ferrihydrite**				
wt% C		**2**	**5**	**8**	**12**	**16**
mineral:humic acid % mass ratio		**96:4**	**90:10**	**84:16**	**77:23**	**69:31**
Surface area (m^2/g)[a]		296	290	284	277	269
Site density $\equiv FeOH^{-0.5}(e)$ (mol sites/g $x10^{-3}$)[b]		1.200	1.125	1.050	0.963	0.863
Site density $\equiv FeOH^{-0.5}(c)$ (mol sites/g $x10^{-3}$)[b]		1.670	1.566	1.462	1.340	1.201
Site density $\equiv Fe_3O^{-0.5}$ (mol sites/g $x10^{-3}$)[b]		0.574	0.538	0.502	0.460	0.413
Site density $\equiv RCOO^-$ (mol sites/g $x10^{-3}$)[b]		0.082	0.206	0.330	0.474	0.639
Site density $\equiv RO^-$ (mol sites/g $x10^{-3}$)[b]		0.0560	0.149	0.238	0.343	0.462
C_{stern} (F/m^2)[c]		1.38	1.79	2.20	2.69	3.24
[d]log $K_{FeOH(e)}$	$\equiv FeOH^{-0.5}(e) + H^+ = \equiv FeOH_2^{+0.5}(e)$	7.99	7.99	7.99	7.99	7.99
[d]log $K_{FeOH(e)\_Na}$	$\equiv FeOH^{-0.5}(e) + Na^+ = \equiv FeOH^{-0.5}(e) - - Na^+$	-1.00	-1.00	-1.00	-1.00	-1.00
[d]log $K_{FeOH2(e)\_NO3}$	$\equiv FeOH_2^{+0.5}(e) + NO_3^- = \equiv FeOH_2^{+0.5}(e) - - NO_3^-$	-1.00	-1.00	-1.00	-1.00	-1.00
(where equations above are repeated for ($\equiv FeOH^{-0.5}(c)$)						
[d]log K_{Fe3O}	$\equiv Fe_3O^{-0.5} + H^+ = \equiv Fe_3OH^{+0.5}$	7.99	7.99	7.99	7.99	7.99
[d]log K_{Fe3O_Na}	$\equiv Fe_3O^{-0.5} + Na^+ = \equiv Fe_3O^{-0.5} - - Na^+$	-1.00	-1.00	-1.00	-1.00	-1.00
[d]log K_{Fe3OH_NO3}	$\equiv Fe_3OH^{+0.5} + NO_3^- = \equiv Fe_3OH^{+0.5} - - NO_3^-$	-1.00	-1.00	-1.00	-1.00	-1.00
[d]log K_{RCOO}	$\equiv RCOO^- + H^+ = \equiv RCOOH^+$	3.67	3.67	3.67	3.67	3.67
[d]log K_{RCOO_Na}	$\equiv RCOO^- + Na^+ = \equiv RCOO^- - - Na^+$	-1.00	-1.00	-1.00	-1.00	-1.00
[d]log K_{RO}	$\equiv RO^- + H^+ = \equiv ROH^+$	7.11	7.11	7.11	7.11	7.11
[d]log K_{RO_Na}	$\equiv RO^- + Na^+ = \equiv RO^- - - Na^+$	-1.00	-1.00	-1.00	-1.00	-1.00
[d]log K_{CuFh}	$2\equiv FeOH^{-0.5}(e) + Cu^{+2} = (\equiv FeOH(e))_2Cu^+$	8.61	8.61	8.61	8.61	8.61
[d]log K_{CuHA}	$\equiv RCOO^- + Cu^{+2} = \equiv RCOOCu^+$	2.49	2.49	2.49	2.49	2.49
Organo-mineral composite		**Goethite**				
wt% C		**7**				
mineral:humic acid % mass ratio		**86:14**				
Surface area (m^2/g)[a]		116				
Site density $\equiv FeOH^{-0.5}$ (mol sites/g $x10^{-3}$)[b]		0.507				
Site density $\equiv Fe_3O^{-0.5}$ (mol sites/g $x10^{-3}$)[b]		0.396				
Site density $\equiv RCOO^-$ (mol sites/g $x10^{-3}$)[b]		0.288				
Site density $\equiv RO^-$ (mol sites/g $x10^{-3}$)[b]		0.209				
C_{stern} (F/m^2)c		1.98				
[d]log K_{FeOH}	$\equiv FeOH^{-0.5} + H^+ = \equiv FeOH_2^{+0.5}$	9.20				
[d]log K_{FeOH_Na}	$\equiv FeOH^{-0.5} + Na^+ = \equiv FeOH^{-0.5} - - Na^+$	-1.00				
[d]log K_{FeOH2_NO3}	$\equiv FeOH_2^{+0.5} + NO_3^- = \equiv FeOH_2^{+0.5} - - NO_3^-$	-1.00				
[d]log K_{Fe3O}	$\equiv Fe_3O^{-0.5} + H^+ = \equiv Fe_3OH^{+0.5}$	9.20				
[d]log K_{Fe3O_Na}	$\equiv Fe_3O^{-0.5} + Na^+ = \equiv Fe_3O^{-0.5} - - Na^+$	-1.00				
[d]log K_{Fe3OH_NO3}	$\equiv Fe_3OH^{+0.5} + NO_3^- = \equiv Fe_3OH^{+0.5} - - NO_3^-$	-1.00				
[d]log K_{RCOO}	$\equiv RCOO^- + H^+ = \equiv RCOOH^+$	3.67				
[d]log K_{RCOO_Na}	$\equiv RCOO^- + Na^+ = \equiv RCOO^- - - Na^+$	-1.00				

[d]log K_{RO}	$\equiv RO^- + H^+ = \equiv ROH^+$	7.11
[d]log K_{RO_Na}	$\equiv RO^- + Na^+ = \equiv RO^- - - Na^+$	-1.00
[d]log K_{CuGt}	$2\equiv FeOH^{-0.5} + Cu^{+2} = (\equiv FeOH)_2Cu^+$	12.93
[d]log K_{CuHA}	$\equiv RCOO^- + Cu^{+2} = \equiv RCOOCu^+$	2.49

[a]Calculated using the surface areas of the end-member mineral and humic acid weighted to the mineral:humic acid mass ratio of each composite. [b]Calculated using the surface site densities of the end-member mineral and humic acid weighted to the mineral:humic acid mass ratio of each composite. [c]Calculated using the C_{stern} values of the end-member mineral and humic acid weighted to the mineral:humic acid mass ratio of each composite. [d]Fixed at those determined for the end-member ferrihydrite (Moon and Peacock, 2013), goethite and humic acid (both this study).

TABLE 4: Distribution of adsorbed Cu between the iron (hydr)oxide and humic acid fractions in the ferrihydrite and goethite organo-mineral composites predicted from the surface complexation model and obtained by EXAFS.

Organo-mineral composite	pH	Distribution of Cu between iron (hydr)oxide and humic acid					
		End-member model fit		Optimised model fit		EXAFS	
		$logK_{CuHA}$2.49	$logK_{CuFh}$8.61	$logK_{CuHA}$3.31	$logK_{CuFh}$9.27		
		% HA	% Fh	% HA	% Fh	% HA	% Fh
Fh_HA_8wt%C_0.7wt%Cu	4.3	75	25	90	10	100	0
	5.0	34	66	54	46	51±9	49±9
	6.0	7	93	20	80	30±12	70±12
Fh_HA_12wt%C_0.7wt%Cu	4.3	90	10	88	12	100	0
	5.0	69	31	55	45	50±10	50±10
	6.0	23	77	22	78	32±11	68±11
		$logK_{CuHA}$2.49	$logK_{CuGt}$12.93	$logK_{CuHA}$4.86	$logK_{CuGt}$12.10		
		% HA	% Gt	% HA	% Gt	% HA	% Gt
Gt_HA_7wt%C_0.7wt%Cu	4.3	20	80	97	3	100	0
	5.0	12	88	78	22	51±10	49±10
	6.0	3	97	46	54	37±10	63±10