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Names and affiliations of applicants (* indicates experimentalists):

Dr. Christian Mikutta*
Martin Hoffmann*
Prof. Dr. Ruben Kretzschmar

All:
Institute of Biogeochemistry and Pollutant Dynamics (Soil Chemistry)
Swiss Federal Institute of Technology Zurich (ETH Zürich)
ETH Zentrum CHN F 23.2
Universitätstrasse 16, CH-8092 Zurich, Switzerland

1. Introduction

While the interactions of both As species with mineral matter have received much attention in the past, natural organic matter (NOM) as a ubiquitous sorbent for As has long been neglected by geochemists. However, a growing body of direct evidence now suggests that both As(V) and As(III) can bind to NOM. Several binding mechanisms have been hypothesized for As(V) and As(III), which include (i) the formation of ternary complexes with a polyvalent metal cation forming a bridge between negatively charged As oxyanions and organic ligands, (ii) the formation of outer-sphere complexes with protonated amino groups of NOM, and (iii) the formation of covalent bonds between phenolate/carboxylate groups of NOM and As(III) or As(V). Ternary As complex formation is by far the most popular binding mechanism invoked to explain As binding to NOM[1-4], suggesting that it is universally accepted and pointing towards its environmental relevance. Perusal of these studies, however, revealed a complete lack of direct evidence for ternary As complexes because neither were spectroscopic methods employed in these studies nor could the presence of particulate Fe be ruled out. The main objective of this study was therefore to test the formation of ternary complexes between As(V) and Fe(III)-NOM complexes. To this end, we reacted As(V) with Fe(III)-humate and –fulvate complexes at pH 7 and studied the local coordination environments (<5 Å) of As and Fe by means of K-edge X-ray absorption spectroscopy in fluorescence mode at ~80 K. The XAS spectra were analyzed by Wavelet-transform analysis and shell-fitting.

2. Results and Discussion

Iron K-edge EXAFS spectroscopy. Shell-fits were performed on the Fourier-transformed k^3-weighted Fe K-edge EXAFS spectra (k-range: 1-12 Å^{-1}, fit k-weight = 3). The final model fits are illustrated in Fig. 1A and EXAFS parameters are summarized in Table 1. Evidently, all features in the Fe K-edge EXAFS and the Fourier transforms are adequately described by a structural motif in which three corner-sharing $Fe(O,OH)_6$ octahedra linked by a single μ_3-O bridge form a planar Fe trimer. Oxygen coordination numbers close to six and average

Fe-O bond distances of 1.99 Å are in agreement with those determined for humic acid.[5] Likewise, Fe-C interactions in the second scattering shell at ~2.95 Å are in the range of reported values for humic acid and organic soils.[5, 6] The fitted Fe-Fe bond distance of approximately 3.46 Å accords well with corner-sharing $Fe(O,OH)_6$ octahedra and is consistent with the fitted average Fe-O bond distances and an Fe-O(μ_3)-Fe bond angle of 120°. The compliance of our EXAFS data with a trimeric Fe model indicates that the majority of Fe in Fe(III)-HS complexes is hydrolyzed at neutral pH and exists in the form of small oligomeric Fe(III) species.

Arsenic K-edge EXAFS spectroscopy. Shell-fits were performed on the Fourier-filtered k^3-weighted As K-edge EXAFS spectra (Fig. 2). All EXAFS parameters (Table 1) determined for As accord with previous studies on As(V) sorption to Fe(III) oxyhydroxides: Four O were found at a mean distance of 1.70 Å with an average Debye-Waller parameter of 0.003 Å^2, which were followed by 0.5-0.7 Fe atoms at ~3.30 Å. The observed As-Fe bond distance is commonly explained by a monodentate binuclear (^{2}C) As(V) complex in which As(V) shares two oxygens with two edge-sharing $Fe(O,OH)_6$ octahedra.[7] Since the predominance of such octahedral linkages was ruled out for the HS samples, As(V) is likely bridging two corner-sharing $Fe(O,OH)_6$ octahedra. Classical monodentate mononuclear (^{1}V) complexes of As(V) and bidentate mononuclear (^{1}E) complexes can be excluded because the As-Fe distances of these complexes would be considerably longer (>3.6 Å for ^{1}V) or shorter (<2.9 Å for ^{1}E) than those determined for a ^{2}C complex.[7] The fact that the coordination number of second-shell Fe is less than unity may suggest that a portion of As(V) is adsorbed in a mononuclear ^{1}V complex stabilized by a H-bond to a singly coordinated OH group of an adjacent $Fe(O,OH)_6$ octahedron as was proposed for As(V) adsorption to goethite (α-FeOOH).[8] Other reasons for the low Fe coordination numbers could be sodium arsenate precipitation upon lyophilization and/or outer-sphere complexation of As(V) to oligomeric Fe clusters[9] and/or protonated amino groups of HS molecules.[10] The fitted Fe coordination numbers imply that between 25 and 70% of total As(V) formed an inner-sphere complex with oligomeric Fe clusters. Based on the wavelet-transform analyses and shell-fits of Fe and As K-edge EXAFS spectra, we conclude that at neutral pH As(V) is bound to Fe(III)-HS complexes predominantly as inner-sphere, bridging-binuclear complex with oligomeric Fe(III) clusters, in which octahedral corner linkages predominate.

Table 1. Iron and As K-edge EXAFS shell-fit results for Fe(III)-HS complexes reacted with As(V). Values in bold were fixed in the fit. Parameters in italics were defined in terms of single scattering paths and subsequently covaried in the fits. Fit uncertainties are given for the last significant figure. The passive amplitude reduction factor, S_0^2, was fixed to 0.71 for Fe and 1.00 for As. (FA = fulvate, HA = humate)

Sample	Path	CN (-)[a]	R (Å)[b]	σ^2 (Å^2)[c]	ΔE (eV)[d]	R-factor (-)[e]
			Iron			
FA	Fe-O	5.7 (3)	1.99 (0)	0.007 (1)	3.9 (6)	0.003
	Fe-C	2.9 (13)	2.96 (2)	0.009 (6)		
	Fe-Fe	**2**	3.46 (1)	0.014 (1)		
	Fe-O-Fe-O (collinear)	*5.7*	4.45 (2)	0.009 (4)		
	Fe-O-Fe-O (non-collinear)	*5.7*	3.84 (6)	0.014 (12)		
HA	Fe-O	5.7 (3)	1.99 (0)	0.006 (1)	4.2 (6)	0.003
	Fe-C	3.0 (16)	2.94 (3)	0.011 (7)		
	Fe-Fe	**2**	3.47 (1)	0.014 (2)		
	Fe-O-Fe-O (collinear)	*5.7*	4.46 (2)	0.006 (3)		
	Fe-O-Fe-O (non-collinear)	*5.7*	3.83 (5)	0.013 (11)		
			Arsenic			
FA	As-O	**4**	1.70 (0)	0.003 (0)	4.7 (12)	0.007
	As-Fe	0.7 (1)	3.29 (1)	**0.007**		
	Fe-O-O (triangular)	**12**	*3.08*	*0.003*		
	As-O-As-O (collinear)	**4**	*3.40*	*0.012*		
	As-O-As-O (non-collinear)	**12**	*3.40*	*0.006*		
HA	As-O	**4**	1.70 (0)	0.003 (0)	4.6 (11)	0.006
	As-Fe	0.5 (1)	3.30 (1)	**0.003**		
	Fe-O-O (triangular)	**12**	*3.09*	*0.003*		
	As-O-As-O (collinear)	**4**	*3.40*	*0.011*		
	As-O-As-O (non-collinear)	**12**	*3.40*	*0.006*		

[a] coordination number, [b] mean half path length, [c] Debye-Waller parameter, [d] energy-shift parameter

[e] R-factor = $\sum_i(\mathrm{data}_i-\mathrm{fit}_i)^2/\sum_i \mathrm{data}_i^2$

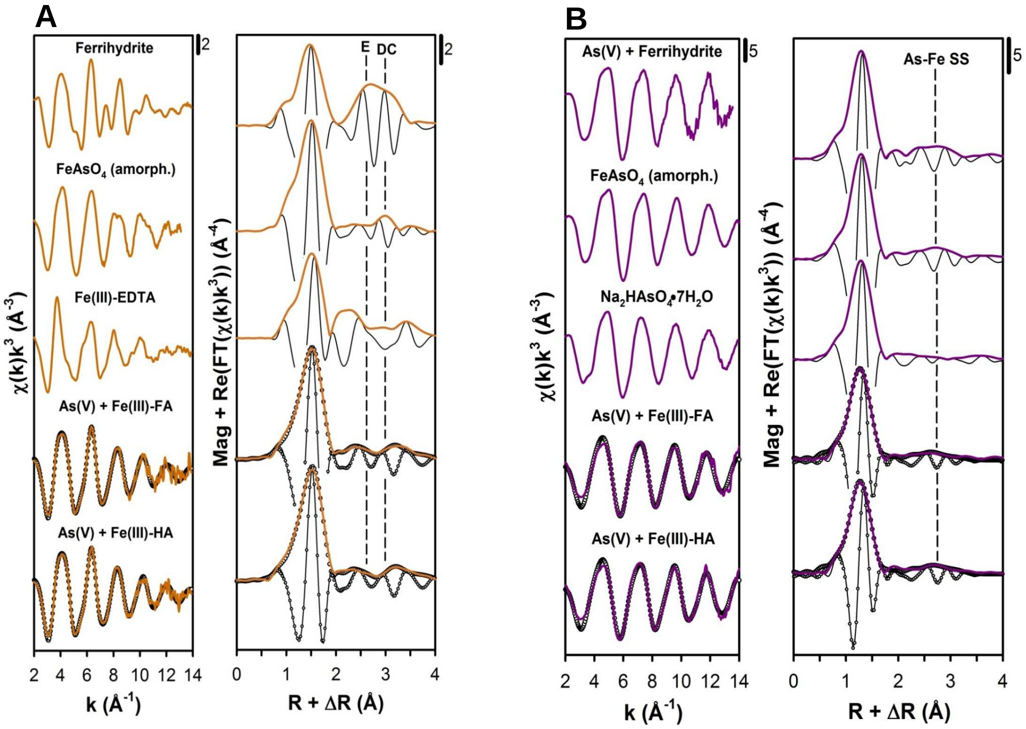

Figure 1. Iron **(A)** and As **(B)** K-edge EXAFS spectra (left), and magnitude as well as real part of the Fourier transform (right) of reference compounds and Fe(III)-HS complexes reacted with As(V). Dotted lines represent the model fits in *k*-space (left) and *R*-space (right). In **A** the dashed vertical lines indicate the position of Fe in edge- (E) and double corner-sharing Fe(O,OH)$_6$ octahedra (DC) in the structure of ferrihydrite. In **B** the dashed vertical line marks the position of the As-Fe single scattering (SS) path at $R + \Delta R$ ~2.8 Å. (FA = fulvate, HA = humate)

3. References

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4. Study output

Mikutta C. and Kretzschmar R. (2011) Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances (*submitted*)

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