



	Experiment title: Structure of ternary complexes of arsenate and ferric iron complexes of natural organic matter: Effect of iron loading and pH	Experiment number: EC-999
Beamline: BM23	Date of experiment: From 13.06. to 19.06.2012	Date of report: 2 September 2012
Shifts: 18	Local contact(s): Cornelius Strohm	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Christian Mikutta* Martin Hoffmann* Prof. Dr. Ruben Kretzschmar <u>All:</u> Institute of Biogeochemistry and Pollutant Dynamics (Soil Chemistry) Swiss Federal Institute of Technology Zurich (ETH Zürich) ETH Zentrum CHN Universitätsstrasse 16, CH-8092 Zurich, Switzerland		

1. Introduction

The fate of the toxic trace element arsenic (As) in aquatic and terrestrial ecosystems is strongly controlled by its interaction with solid phases.¹ While As sorption to mineral matter, notably Fe(III)-oxyhydroxides,² has been extensively studied in the past, sorption reactions with natural organic matter (NOM) are still poorly understood. Several mechanisms have been proposed for As-NOM interactions. Among those the formation of ternary complexes in which a polyvalent metal cation forms a bridge between a negatively charged As oxyanion and an organic ligand is most frequently invoked to explain As binding to NOM.^{3,4} Based on As and Fe K-edge X-ray absorption spectroscopy (XAS) measurements conducted at ESRF (Exp. No. EC-818), we recently succeeded in providing the first spectroscopic evidence for ternary complex formation between arsenate, As(V), and Fe(III) complexes of humic substances.⁵ Yet, there is no spectroscopic evidence for ternary complex formation between arsenite, As(III), and Fe(III)-NOM complexes. For this reason we performed Fe K-edge XAS measurements at beamline BM23 (Exp. No. EC-999) in order to explore the local coordination environment of Fe in As(III)- and Fe(III)-enriched particulate NOM. These measurements were complemented by As K-edge XAS measurements at beamline BM26A (Exp. No. EC-1005).

2. Materials and Methods

Peat was collected from a natural ombrotrophic peatland near Bad Buchau, Germany. For our sorption experiments, we used its 40-250- μm size fraction as a proxy for particulate NOM. The peat was spiked with varying amounts of Fe(III) as FeCl_3 at pH <2. After filtration and washing of the Fe(III)-loaded peat with doubly deionized (DDI) water, As(III) (0.3 mmol/mol C) was added under anoxic conditions ($p\text{O}_2$ <10 ppm). After equilibration of the peat with As(III) for 72 hours in 0.1 M NaCl solution at pH 7.0, 8.4 and 8.8, respectively, the peat was filtered, rinsed with DDI water, freeze-dried, and homogenized in an anoxic glove box. For Fe K-edge XAS analysis the samples were filled into Al sample holders and sealed with Kapton® tape. Iron K-edge (7,112 eV) X-ray absorption near

edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded in fluorescent-yield mode at ~ 80 K (and room temperature) using a 13-element Ge detector and a $N_2(l)$ cryostream. The monochromator was calibrated to the first maximum in the first derivative of the K-edge absorption spectrum of a metallic Fe foil (7,112 eV), which was continuously monitored to account for slight energy shifts during the sample measurements. For each sample 8-12 scans were averaged. Spectral processing was done according to standard procedures using the IFEFIT program suite.⁶ Fourier transforms of the $\chi(k)$ data were calculated over a k -range of 3.0-12.5 \AA^{-1} using a Kaiser-Bessel apodization window with a sill width of 3 \AA^{-1} .

3. Results and Discussion

First derivatives of the Fe K-edge XANES spectra of Fe(III)-peat complexes reacted with As(III) are shown in **Figure 1**. They exhibit maxima at $\sim 7,126$ eV, which are consistent with Fe(III) reference compounds. Accordingly, a significant reduction of Fe(III) was not observed in our experiments.

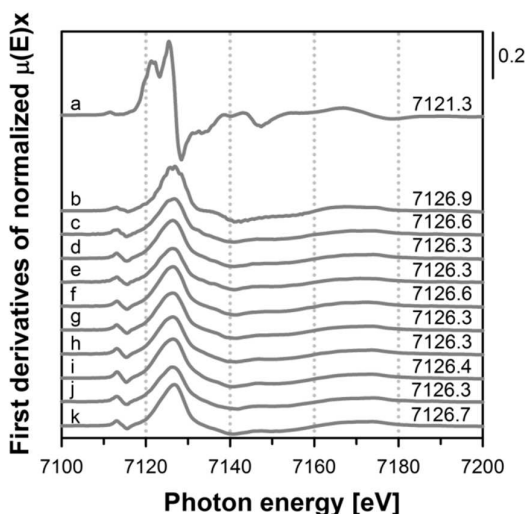


Figure 1. First derivatives of normalized Fe K-edge XANES spectra of (a) Fe(II)-oxalate, (b) Fe(III)-citrate, and peat samples with increasing Fe(III) loadings, which were reacted with As(III) at pH 7.0 (c-g), pH 8.4 (h, i), and pH 8.8 (j, k). Energy values indicate the maximum of the first derivatives.

At times, the cryostream cooling system led to ice formation on our samples, resulting in loss of signal intensity in some spectra. To avoid spectral quality deterioration, the cooling system was shut off. A spectrum comparison for a sample measured at 80 K and 298 K showed no significant difference in the signal-to-noise ratio (**Figure 2**) and no shift in the edge position (not shown). For these reasons, we continued our XAS measurements without cooling.

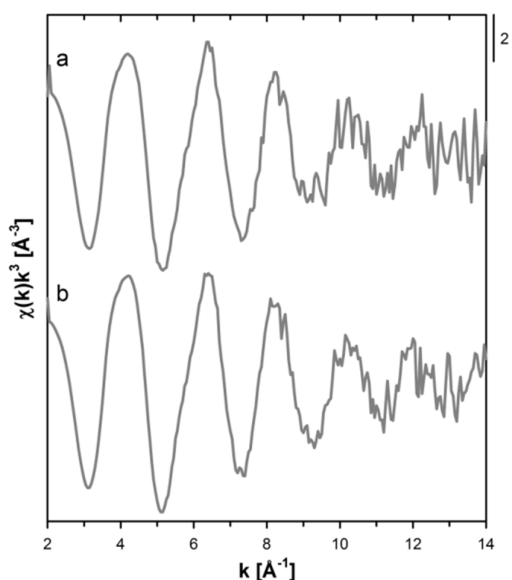


Figure 2. k^3 -weighted Fe K-edge EXAFS spectra of an Fe(III)-peat complex (~ 10 mg Fe/g peat) reacted with As(III) at pH 7.0 taken at (a) 80 K and (b) 298 K

Figure 3 depicts the k^3 -weighted Fe K-edge EXAFS spectra of Fe(III)-peat complexes reacted with As(III) and Fe reference compounds, as well as the magnitudes and real parts of the corresponding Fourier transforms. All peat samples showed a Fourier-transform peak at $R + \Delta R \sim 1.6$ \AA , which is related to O/N backscatterers in the first coordination shell of Fe.⁷ The samples also exhibited a Fourier-transform peak at $R + \Delta R \sim 2.2$ \AA typical of C neighbors in the second coordination shell of Fe.⁸ A clear trend of its occurrence, however, either with increasing Fe(III) loading or pH, was not apparent.

The peaks in the real part of the Fourier transform of goethite (α -FeOOH) at $R + \Delta R \sim 2.6$ \AA and ~ 2.9 \AA (**Figure 3**) are indicative of edge- and double corner-sharing $Fe(O,OH)_6$ octahedral linkages in the structure of Fe(III)-oxyhydroxides. The absence of these spectral features in the Fe(III)-peat samples implies a generally low degree of Fe

polymerization, and suggests the predominance of Fe species of low nuclearity in the peat. In order to further explore the local coordination environment of Fe in our samples, we currently evaluate the spectra shown in **Figure 3** by means of shell fitting and wavelet-transform analyses.

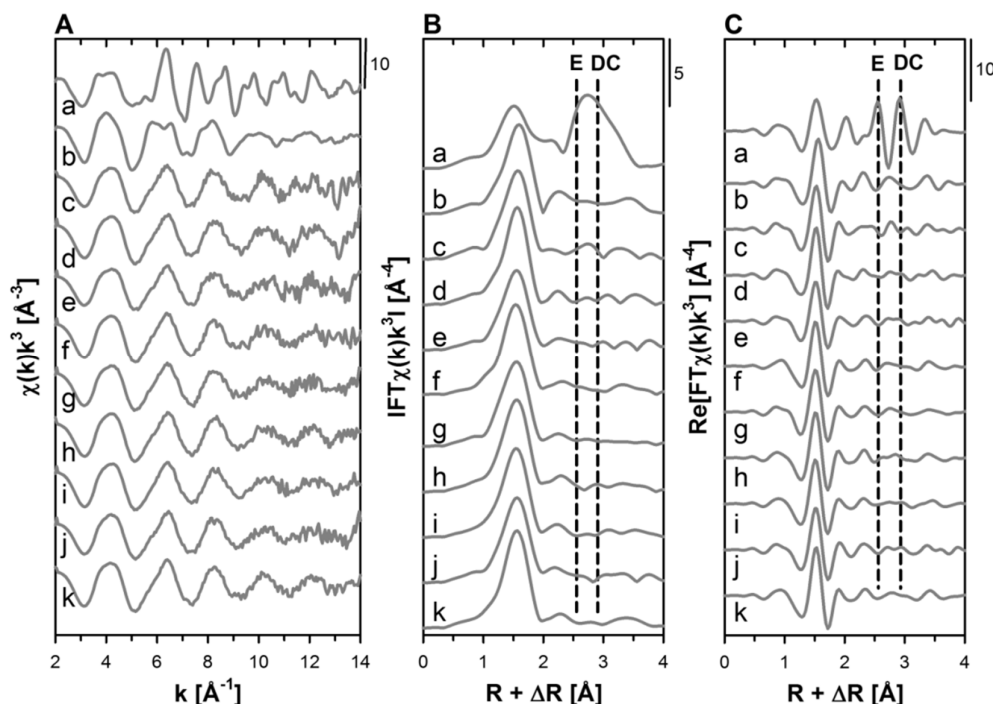


Figure 3. (A) k^3 -weighted Fe K-edge EXAFS spectra, (B) Fourier-transform magnitudes, and (C) real parts of the Fourier transforms of (a) goethite, (b) Fe(III)-oxalate, and peat samples with increasing Fe(III) loadings, which were reacted with As(III) at pH 7.0 (c-g), pH 8.4 (h, i), and pH 8.8 (j, k). The dashed vertical lines indicate the position of Fe in edge- (E) and double corner-sharing (DC) $\text{Fe}(\text{O},\text{OH})_6$ octahedra in the structure of goethite.

4. References

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