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|---|---|---|
|  | **Experiment title: Local coordination of Fe(III) in HFO synthesized in the presence of citrate and/or arsenate** | **Experiment number**:<br>**01-01-750** |
| **Beamline**:<br>BM01B | **Date of experiment**:<br>from: 25/02/2008 to: 29/02/2008 | **Date of report**:<br>16.07.2008<br>*Received at ESRF:* |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Wouter VAN BEEK |  |

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## Report:

*Introduction:*

Poorly crystalline hydrous ferric ($Fe^{III}$) oxides (HFO) are omnipresent in terrestrial environments. Due to their high specific surface areas HFOs are one of the most important adsorbents for both nutrients and pollutants. The presence of oxyanions (e.g., arsenate (As(V)) (*1*)) or organic matter (*2, 3*) has been shown to significantly affect the chemical and physical properties of HFO relative to HFO synthesized in pure systems, which has a pronounced influence on geochemical reactivity. Our aim is to systematically study the structure and reactivity of HFO formed in the presence of organic ligans and oxyanions as a proxy for HFO formed in microsites in natural soil and sediment environments. Below we report first results on the local coordination of Fe(III) in HFO formed in the presence of citrate and/or As(V) obtained from Fe K-edge extended X-ray absorption fine structure (EXAFS) analyses performed at BM01B.

*Methods and Results:*

We synthesized HFO by titrating 10 mM $Fe(NO_3)_3$ solutions with NaOH to pH 7. The solutions contained 0, 0.5, 2.5 and 5 mM citrate, respectively. The synthesis was carried out either in the absence or presence of 0.5 mM As(V). EXAFS spectra of freeze-dried samples prepared as pellets were collected at BM01B at room temperature in transmission mode. At high citrate concentrations only a fraction of the iron contained in the synthesis solution forms polymers large enough to be separated by centrifugation while a considerabe fraction of the Fe is still contained in the supernatant as soluble complexes and nanocolloidal particles, respectively. Aliquotes of the supernatant solutions were therefore analyzed in fluorescence mode.

*Results:*

The Fourier-transformed EXAFS spectra of HFO synthesized in absence of both citrate and arsenate (Cit0-As0), in the presence of 2.5 mM citrate (Cit2.5-As0), and in the presence of 2.5 mM citrate and 0.5 mM arsenate (Cit2.5-As0.5) are shown in Figure 1. The spectra were structurally interpreted by shell fitting. All spectra were fit simultaneously, constraining several fit-parameter (e.g. Debye-Waller parameters) to be the same for all spectra in order to reduce the number of adjustable parameters and parameter correlation (as in ref. (*2*)). Fit results for second-shell Fe are listed in Table 1. Both citrate and arsenate decreased the extent of polyhedral linkage of Fe(III) in the HFO, as reflected in lower coordination numbers for second-shell edge-sharing and corner-sharing Fe neighbors (Fe1 and Fe2, respectively), but did not affect the distances of second-shell Fe neighbors. These preliminary results provide first important information regarding the effect of citrate and As(V) on HFO structure and serve as a basis for further structural studies. Continuing work also addresses the reactivity of different types of poorly crystalline HFO towards ligand promoted dissolution, affecting also the fate of nutrients and contaminants associated with HFO.

***Table 1:*** *Fit results for edge-sharing and corner-sharing second-shell Fe. The samples are labled according to the concentration (mM) of citrate (Cit) and arsenate (As) in synthesis solutions (containing 10 mM Fe).*

| **Sample** | **Edge-sharing Fe1** | | **Corner-sharing Fe2** | |
|---|---|---|---|---|
| | CN | R (Å) | CN | R (Å) |
| **Cit0-As0** | 3.3 ± 1.5 | 3.06 ± 0.02 | 1.8 ± 1.7 | 3.46 ± 0.03 |
| **Cit2.5-As0** | 2.8 ± 1.3 | 3.06 ± 0.02 | 1.3 ± 1.3 | 3.47 ± 0.03 |
| **Cit2.5-As0.5** | 2.6 ± 1.1 | 3.06 ± 0.02 | 1.0 ± 1.0 | 3.47 ± 0.03 |

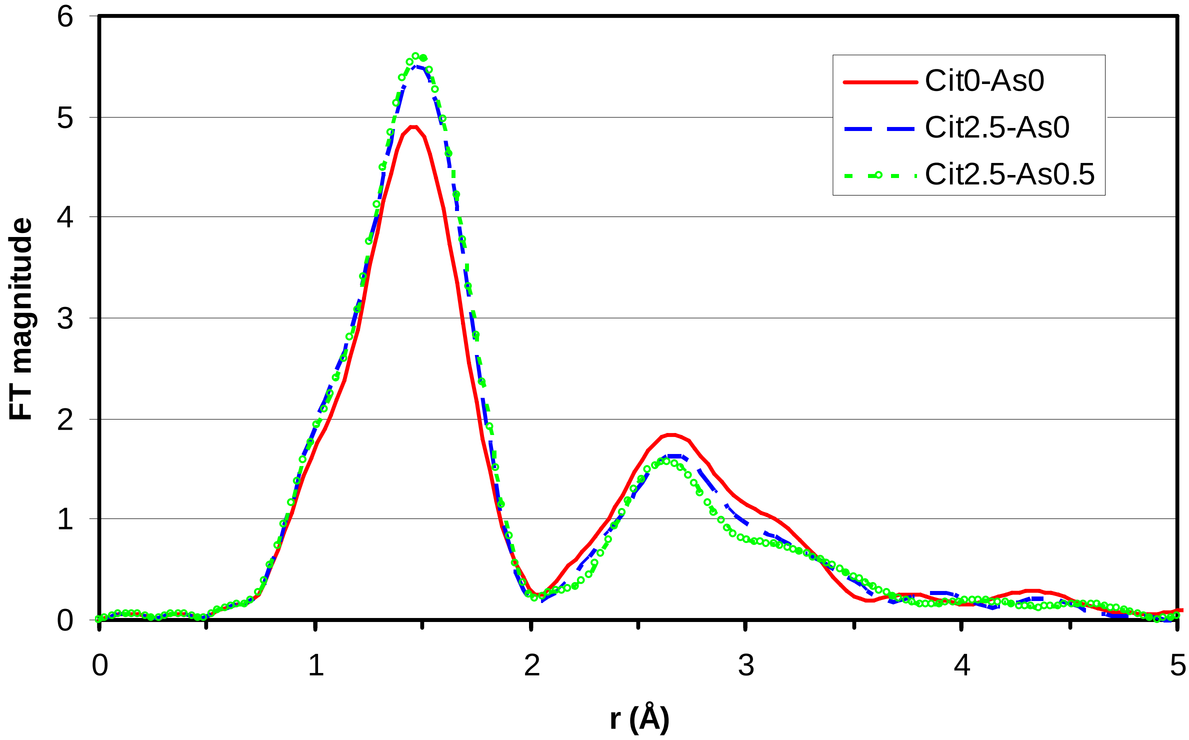

***Figure 1:*** Fourier transform magnitude ($k^3$-weighted data; k-range: 2-11.5$Å^{-1}$) of selected EXAFS spectra.

*Literature:*

(1) Waychunas, G. A.; Fuller, C. C.; Rea, B. A.; Davis, J. A. Wide angle X-ray scattering (WAXS) study of "two-line" ferrihydrite structure: Effect of arsenate sorption and counterion variation and comparison with EXAFS results. *Geochimica et Cosmochimica Acta* **1996**, *60*, 1765-1781.

(2) Mikutta, C.; Mikutta, R.; Bonneville, S.; Wagner, F.; Voegelin, A.; Christl, I.; Kretzschmar, R. Synthetic coprecipitates of exopolysaccharides and ferrihydrite. Part I: Characterization. *Geochimica et Cosmochimica Acta* **2008**, *72*, 1111-1127.

(3) Liu, C.; Huang, P. M. Atomic force microscopy and surface characteristics of iron oxides formed in citrate solutions. *Soil Science Society of America Journal* **1999**, *63*, 65-72.