



**Experiment title:** Local coordination of Fe(III) in systems comprising hydrous ferric oxide, arsenate, and citrate

**Experiment number:**  
**01-01-776**

<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 19/02/2009 to: 24/02/2009	<b>Date of report:</b> 07.03.2009
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## Report:

### Introduction

Field and laboratory research has shown that the partitioning of arsenic (As) between solution and soils or sediment solids in aqueous systems is often controlled by the cycling of Fe. Under oxic conditions, the dominating inorganic As species is arsenate (As(V), which is often found in association with hydrous ferric oxides (HFO). The principal immobilization mechanisms for As(V) by HFO may be twofold: Arsenate may become sequestered from solution during precipitation of HFO (coprecipitation) or become immobilized by HFO after its formation (adsorption). The latter mechanism is considered as being less effective in As removal from solution on a molar Fe basis compared to coprecipitation [1]. The extent of sequestration of As during formation of HFO depends on the presence of competing species that have a similar or higher affinity toward HFO. Low molecular weight organic acid (LMWOA) anions are important examples of competing species typically found in environmental systems. Plants, fungi, and bacteria excrete LMWOA anions, which may then reach millimolar concentrations in (micro)environments such as the soil rhizosphere or biofilms [2, 3]. LMWOA anions may, at high concentrations, impair or inhibit the formation of crystalline Fe(III)-(hydr)oxides. Because (re)crystallization of HFO involves the polymerization of  $\text{Fe}(\text{O},\text{OH})_6$  octaeder which in turn decreases the number of available sorption sites for As, high concentrations of LMWOA anions may eventually favor the sequestration of As on a molar Fe basis. In addition, LMWOA anions may effectively stabilize HFO particles against aggregation, thus reducing the aggregation-induced loss of ligand-accessible surface area. The objective of our research was to study the speciation of Fe (and As) in systems where HFO is formed in the presence of As(V) and LMWOA anions.

## Methods

We synthesized HFO in the presence of citrate and As(V). In these syntheses we varied the initial citrate/Fe ratio from 0 to 0.5 (Table 1). The syntheses were conducted by titrating a 200 mM Fe(NO<sub>3</sub>)<sub>3</sub> solution containing 10 mM As(V) and increasing amounts of citrate with 1 M KOH at a rate of 0.3 mL/min up to a final pH of 6.5. Afterwards, the suspensions were centrifuged at 5000 × *g* for 1 h. The supernatants were decanted and subsequently ultrafiltered through 3.5-kDa membranes to separate colloidal HFO from dissolved Fe (As) species. The centrifugate was shock-frozen in liquid N<sub>2</sub> and freeze-dried. In all three fractions, we measured the total content of Fe and As. The freeze-dried solids were analyzed by powder X-ray diffractometry and for their C and N contents. Iron K-edge X-ray absorption spectra of the centrifugates, the supernatants, and the ultrafiltrates were measured in both transmission and fluorescence mode at the BM01B beamline.

## Results

At molar citrate/Fe ratios >0.05, only a fraction of the initial Fe forms HFO particles large enough to be separated by centrifugation, whereas a considerable fraction of the Fe remains in solution as soluble complexes and fine colloidal particles, respectively (Table 1). Increasing amounts of citrate in the synthesis had no effect on the molar As/Fe ratio of the solids formed (Table 1, column 4). A similar molar As/Fe ratio found for the centrifugates and the supernatants in treatments 3 and 4 suggests that the supernatant is mainly composed of colloiddally stabilized HFO with a similar molar As/Fe ratio as the solids that were sedimented by centrifugation. This finding was surprising given that in treatment 4 the dissolved Fe fraction comprised a significant portion of the total Fe with a much lower As/Fe ratio (Table 1, last two columns). To clarify the speciation of Fe in the supernatants containing HFO colloids and dissolved Fe species by means of linear combination fit (LCF) analysis, the supernatant samples and the 3.5-kDa ultrafiltrates were analyzed for their X-ray absorption fine structure.

**Table 1. Molar As/Fe and citrate/Fe ratios in synthesis protocols and in synthesis products.**

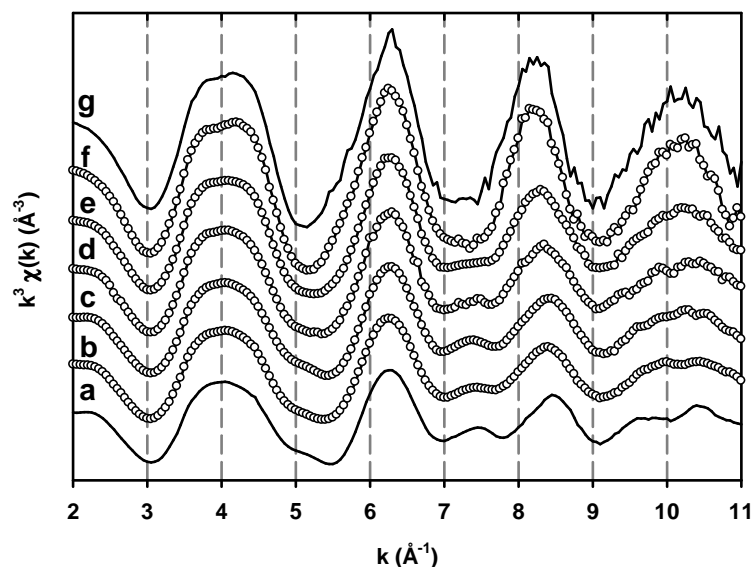
Treatment No.	Synthesis		% of Fe remaining in sol. after centrifugation	Centrifugate		Supernatant	% of total Fe in 3.5-kDa ultrafiltrate	3.5-kDa Ultrafiltrate
	As/Fe	citrate/Fe		As/Fe	citrate/Fe	As/Fe		As/Fe
1	0.05	0.00	bdl <sup>a</sup>	0.05	0.00	0.00 <sup>b</sup>	0.0	0.00
2	0.05	0.05	bdl	0.05	0.05	0.00 <sup>b</sup>	0.0	0.00
3	0.05	0.25	63	0.04	0.17	0.05	8.3	0.04
4	0.05	0.50	95	0.05	0.21	0.05	39	0.01

<sup>a</sup> below detection limit with ICP-OES (<5 μM); <sup>b</sup> all Fe could be settled by means of centrifugation.

Figure 1 shows selected  $k^3$ -weighted  $\chi(k)$  spectra of the solids and supernatants analyzed. As can be noticed by mere visual inspection of Fig. 1, spectra of the supernatants of treatments 3 and 4 (d, e) fall in between the two endmembers: pure As-containing HFO and soluble Fe(III)-citrate complexes (Fig. 1, solid black lines), whereas the  $\chi(k)$  spectrum of the 3.5-kDa ultrafiltrate (f) resembles that of the Fe(III)-citrate reference. Linear combination fit analysis over a  $k$ -range of 2.5-11 Å<sup>-1</sup> using the two endmembers revealed that in the supernatants of treatment 3 and 4, respectively, 26% and 43% of the Fe can be ascribed to soluble Fe(III)-citrate complexes. The R-factors of the fits were always less than 0.02. Based on the fitted values and our solution data, we conclude that approximately 50% of Fe(III)-citrate complexes formed during synthesis of HFO in treatment 3 are readsorbed to the solid, while at higher initial citrate concentrations (treatment 4) only 5% of the Fe(III)-citrate complexes become readsorbed to HFO, presumably due to competition for sorption sites with As(V) and citrate molecules. Our data show that, in agreement with our introductory reasoning, at an initial molar citrate/Fe ratio of 0.50, the suspended HFO particles in the supernatant comprise a significant higher molar As/Fe ratio than the precipitated particles.

Based on our earlier EXAFS experiments at beamline BM01B (Exp. No. 01-01-750) and our recent results, we are now able to show convincingly (i) that increasing citrate concentrations in the presence or absence of As(V) lead to an increased disorder in the HFO structure, (ii) that a significant portion of HFO is stabilized in suspension by citrate at initial molar citrate/Fe ratios >0.05, (iii) that the HFO particles in the supernatant are less crystalline than those of the centrifugate, and (iv) that a significant portion of Fe(III)-citrate complexes formed during HFO synthesis can become readsorbed onto the solids. These valuable information, in conjunction with As K-edge EXAFS data obtained at ANKA (Karlsruhe, Germany), have

important implications for our understanding of the sequestration of As in oxic environments where poorly crystalline Fe(III)-(hydr)oxides form in the presence of low molecular weight organics.



**Figure 1.**  $k^3$ -weighted  $\chi(k)$  spectra of Fe in the solids, suspensions, and solutions analyzed: (a) As-HFO (molar citrate/Fe = 0), (b) As-HFO (molar citrate/Fe = 0.25), (c) As-HFO (molar citrate/Fe = 0.5), (d) suspension of treatment 3, (e) suspension of treatment 4, (f) 3.5-kDa filtrate of treatment 4, (g) Fe(III)-citrate complex (pH 5.05).

In summary, our data suggest that despite HFO precipitation, As(V) remains mobile at high LMWOA anion concentrations because HFO colloids to which As(V) is sorbed do not coagulate. In addition, our EXAFS data indicate that in the supernatants ternary complexes of As(V), that is, complexes composed of As(V), Fe(III), and citrate, are negligible compared to As(V) adsorbed to suspended HFO colloids. Our results provide new important insights into the effect of low molecular weight organics on the mobility and potential bioavailability of pollutants like As(V) in soils and sediments. The excellent results obtained at ESRF will aid in establishing the link between the structure and biogeochemical reactivity of poorly crystalline Fe(III)-(hydr)oxides formed in the presence of ubiquitous organic matter in natural systems.

### Acknowledgements

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### References

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