

Improved Discrimination of Synthetic Iron Oxyhydroxides Using XAFS

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Introduction

The growth and fate of iron oxides and (oxy)hydroxides depend strongly on their (bio)geochemical evolution, potentially making them strong indicators of present and past environments and climate [1,2]. Physical properties such as crystallography, composition, and microstructure play critical roles in determining chemical and physical behavior of such nanoparticles. Chemists from our group examine the impact of these parameters on particle growth, reduction/oxidation rates, and phase transformations through controlled experiments involving abiotic and microbially-mediated chemical reactions. In these studies, analytical chemistry and nanoparticle synthesis are often combined with low-temperature magnetometry and susceptibility, high-resolution transmission electron microscopy (HRTEM), Mössbauer spectroscopy, and x-ray diffraction (XRD).

Our recent research focus has been the magnetic properties of goethite (α -FeOOH) and ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), which are commonly found in soils, lake sediments, and loess. These minerals often occur as nanoparticles that can easily escape detection using traditional methods such as XRD. Magnetic measurements are highly sensitive to iron oxides and oxyhydroxides, even when they occur as extremely fine particles, making them ideal tools for the characterization of these materials [3]. Measurements of remanent and induced magnetizations at temperatures lower than 300K have been particularly useful when working with heterogeneous samples. Recent results from our group demonstrated the growth of goethite nanorods (rod-shaped nanoparticles of a few tens of nanometers) through oriented aggregation of smaller, 3-5 nm spherical nanoparticles. Magnetic measurements enabled us to follow this growth by aggregation because of the substantial differences in the magnetic properties of the two kinds of nanoparticles [4]. Similar particles of nanogoethite, as well as nanoparticles of ferrihydrite, are currently being used in experiments simulating natural biotic (e.g., bacterial) and abiotic reduction of ferric to ferrous ion. One goal of this research is to improve the magnetic tools used for their detection in natural samples. A good knowledge of the composition and structure of these nanoparticles is required for such studies and was the major motivation for the use of synchrotron radiation at the Advanced Photon Source (APS).

Methods and Materials

Samples Synthesis

Eight samples of iron oxyhydroxide nanoparticles were prepared. The goal was to vary the goethite to ferrihydrite ratio (from 0 to 100%) and vary the particle size of the ferrihydrite nanoparticles (100% ferrihydrite samples). All precursor solutions were prepared using 18 M Ω cm resistivity water (Millipore Corporation, Q-H₂O). The synthesis procedure for each sample is summarized below:

Starting Suspension: Equal volumes of 0.40 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.48M NaHCO_3 were prepared. The

NaHCO_3 solution was added dropwise via peristaltic pump using a flow rate of 3.5mL/min.

NanoGt: The starting suspension was dialyzed for 5 days using Q-H₂O at 4 °C with dialysis water changed 3 times per day. The pH was adjusted to 12 with NaOH and aged at 90 °C for 24 h.

FhA: The starting suspension was dialyzed for 3 weeks using Q-H₂O at 4 °C with dialysis water changed 3 times per day.

FhB: The starting suspension was dialyzed for 3 weeks using Q-H₂O at room temperature with dialysis water changed 3 times per day.

FhC: The starting suspension was microwaved to boil and then boiled in a hot water bath for an additional 40 minutes. The suspension was then dialyzed for 5 days using Q-H₂O at 4 °C with dialysis water changed 3 times per day.

FhD: The starting suspension was microwaved to boil and then cooled in ice bath to room temperature. The suspension was then dialyzed for 5 days using Q-H₂O at 4 °C with dialysis water changed 3 times per day.

FhD24: The pH of a portion of the FhD suspension was adjusted to 4 using nitric acid. This suspension was then aged at 90 °C for 24 h.

Two other samples were prepared using methods described by Schwertmann and Cornell [5]:

FhE: A 1M solution of KOH was added dropwise to a 0.2 M $\text{Fe}(\text{NO}_3)_3$ solution until the pH reached 7-8. The resulting suspension was centrifuged, decanted, and placed in dialysis bags. The suspension was dialyzed for 3 days using Q-H₂O at room temperature with dialysis water changed 3 times per day.

FhF: 20 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to 2 L of Q-H₂O preheated to 75 °C, with rapid stirring. The solution was then placed in an 75 °C oven for 15 minutes. The resulting suspension was cooled in an ice bath and dialyzed at room temperature for 3 days using Q-H₂O. The dialysis water was changed 3 times per day.

TEM and XRD characterization of the samples indicated that sample NanoGt was composed of goethite nanorods (10x50 nm). Samples FhA, FhB, FhC, FhD, and FhF were mostly isolated nanoparticles (ranging 2-6 nm in diameter, depending on the sample) with XRD patterns showing 6 broad peaks characteristic of 6-line ferrihydrite. A few rods, presumably of goethite, were also detected in these samples. Sample FhD24 contained significantly more goethite nanorods. The XRD pattern for sample FhE showed 2 broad peaks characteristic of 2-line ferrihydrite.

XAFS Experiments

Synchrotron work was performed using the GSECARS beamline 13-BMD. X-ray absorption fine structure (XAFS) spectra were taken in transmission at the iron K-edge, on finely powdered samples that were uniformly spread on commercial tape and mounted on photographic slides. Energy calibration

was achieved using a 7.5 μm thick iron foil. Four sets of measurements were taken for each sample in favor of data averaging. Data analysis was performed using the utility ATHENA developed by Bruce Ravel (freely available at <http://leonardo.phys.washington.edu/~ravel/software/exafs>), which is based on the IFFEFIT program library [6]. The reader will find reviews of XAFS data analysis pertinent to earth sciences in Fendorf et al. (1994) [7] and Waychunas (2001) [8].

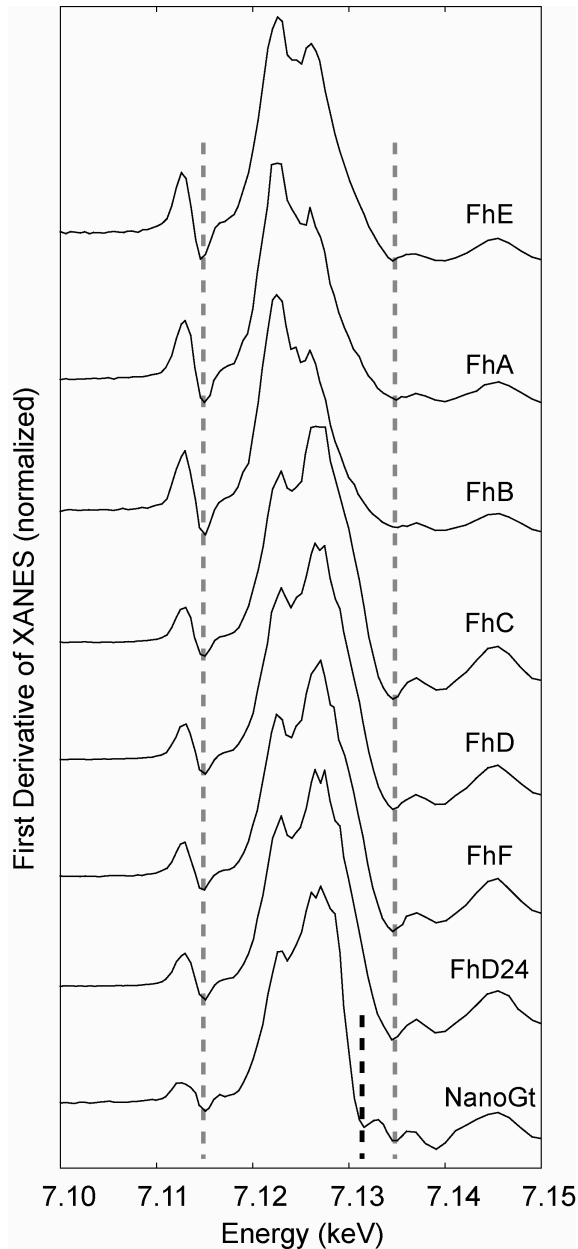


Fig.1. First derivatives of normalized XANES. Derivatives have been normalized to their maximum values before drawing the figure. Gray and black vertical lines demarcate the upper and lower energy range of the main peak for the ferrihydrate and goethite samples, respectively.

Results and Discussion

First derivatives of the normalized x-ray absorption near-edge spectra (XANES) are shown in Fig.1. All ferrihydrate samples display similar XANES derivatives, essentially characterized by a broad peak between ~ 7115 and ~ 7135 eV. The peak of the nano-goethite sample NanoGt is however narrower, with its

high-energy side being more abrupt than for ferrihydrate. These XANES derivatives are similar to previously published data on ferrihydrate and goethite [9], where the broad peak has been interpreted as a characteristic of octahedral coordination of iron atoms in Fe(III) minerals. Only a slight effect of the presence of goethite in sample FhD24 can be observed. Additional substructures of lower amplitudes can be seen in the data, such as the presence of two secondary peaks on the top of the major peak. These appear to be real features, although their relative amplitudes may be modulated by experimental imperfections such as variable sample thickness [9].

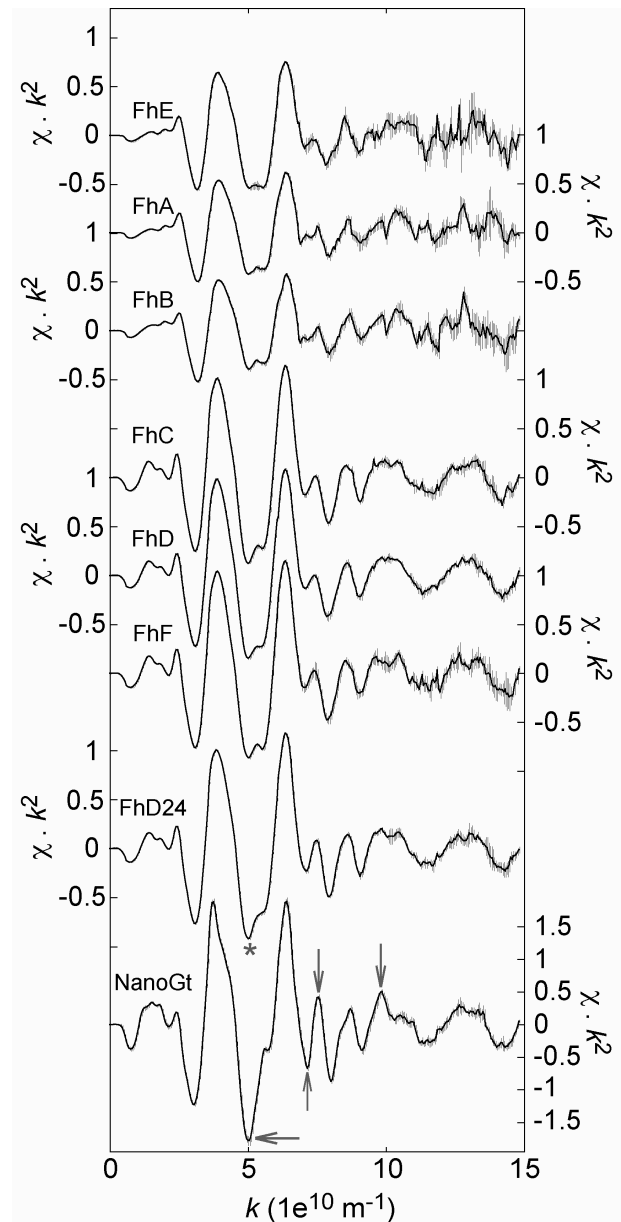


Fig.2. Amplitudes of the EXAFS oscillations weighted by k^2 . Thin vertical lines represent the standard deviation. The gray arrows emphasize some of the features that are different between ferrihydrate and goethite. The gray star indicates one effect of the presence of goethite nanorods in the EXAFS oscillations of sample FhD24.

Extended x-ray absorption fine structure (EXAFS) spectra are represented in Fig.2 as a function of wave number k . Values of the EXAFS amplitude χ have been weighted by k^2 to enhance

the signal at high k . All ferrihydrite samples possess the same global oscillatory pattern, displaying in particular two broad maxima centered at ~ 3.9 and $\sim 6.35 \times 10^{10} \text{m}^{-1}$, separated by a minimum at $\sim 5.3 \times 10^{10} \text{m}^{-1}$. The oscillatory patterns of samples FhC, FhD, and FhF display more similarities among each other than with the other samples. EXAFS data for FhE, FhA, and FhB have lower amplitudes and are noisier above $10 \times 10^{10} \text{m}^{-1}$. Significant differences exist with the EXAFS spectrum of goethite sample NanoGt, some of which are pointed out by gray arrows on Fig.2. The large minimum in amplitude, for instance, is much more pronounced than for ferrihydrite and occurs at lower k . Some effects of the presence of goethite nanorods in the aged sample FhD24 can also be observed, like for instance the secondary minimum around $5 \times 10^{10} \text{m}^{-1}$ (pointed out by a star on Fig.2).

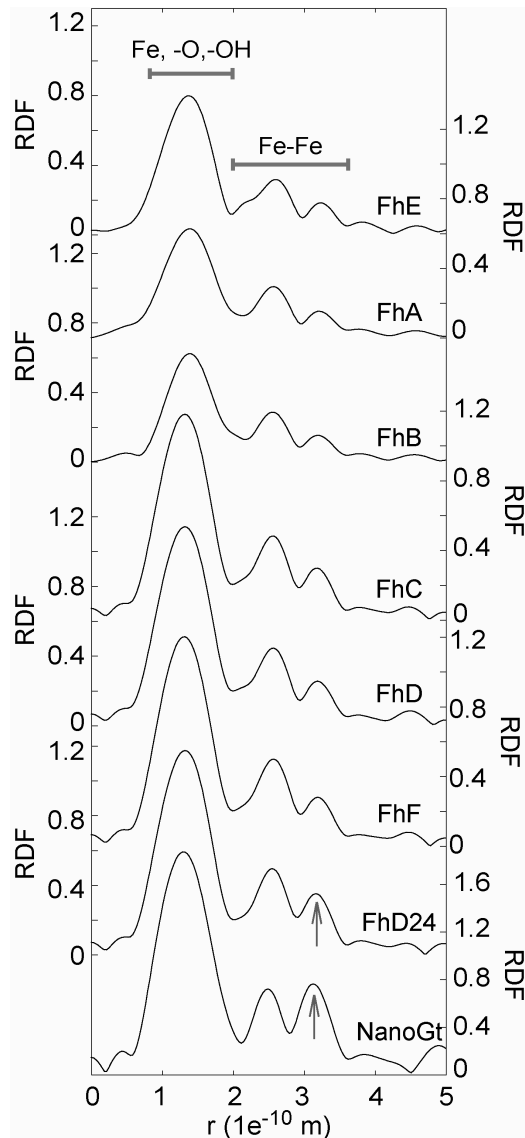


Fig.3. Radial distribution functions (RDF). The first peak corresponds to Fe-O and Fe-OH distances, and the following peaks to Fe-Fe distances [10]. The RDFs are not phase-corrected, and therefore the peaks occur at lower values than the actual inter atomic distances. A significant difference exists between goethite and ferrihydrite distributions. It is particularly visible in the height of the second Fe peak, as pointed out by an arrow.

In order to extract information about inter atomic distances, radial distribution functions (RDF) of the EXAFS amplitudes were calculated using a windowed Fourier transform over the k interval $2.0\text{-}9.5 \times 10^{10} \text{m}^{-1}$ (Fig.3). Ferrihydrite samples have very similar radial distributions, with peak positions that are nearly identical owing to similarities in local structures. The amplitudes of the peaks for samples FhE, FhA, and FhB are significantly lower, which could be due to long-range disorder. The EXAFS amplitudes of these samples are also significantly lower (Fig.2). Interestingly, these three samples have been synthesized at low temperature, contrary to the other samples. Little difference in the global shape of the spectra is found between the 2-line and the 6-line ferrihydrite samples, but the first Fe peak appears wider in the 2-line sample, particularly at low Fe-Fe distances. This may simply be an effect of the reduced height of the main Fe peak. Nonetheless, smaller Fe-Fe distances in oxyhydroxides have been interpreted by some authors as resulting from the existence of face-sharing Fe-octahedra (hematite-like) in the crystal structure [10]. Mean Fe-Fe distances and coordination are different for pure goethite sample NanoGt. In particular, the second Fe peak is relatively higher. This results in a relative increase of the second Fe peak height in the RDF of mixed sample FhD24 (arrow on Fig.3).

Based on these XAFS experiments, samples FhF, FhC, and FhD were found to be the most coherent in terms of composition and crystal structure. HRTEM study of the same three samples showed significant differences in average particle sizes (average diameters of 5.4, 4.1, 3.0 nm for FhF, FhC, FhD, respectively). For these reasons, FhF, FhC and FhD have been selected for a comprehensive study of the particle size dependency of the magnetism of 6-line ferrihydrite nanoparticles.

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