Characterisation of Synthetic Two-line Ferrihydrite by Electron Energy Loss Spectroscopy

To cite this article: G Vaughan et al 2012 J. Phys.: Conf. Ser. 371 012079

View the article online for updates and enhancements.

Related content
- Low-electron fluence STEM-EELS analysis of ferrihydrite nano-particles approaching the Angstrom scale
  G Vaughan, R Brydson, A Brown et al.
- EELS from organic crystalline materials
  R Brydson, M D Eddleston, W Jones et al.
- Stability of nanoparticles in an oxide dispersion strengthened alloy
  V de Castro, S Lozano-Perez and M L Jenkins

Recent citations
- Structure of naturally hydrated ferrihydrite revealed through neutron diffraction and first-principles modeling
  Helen F. Chappell et al
- Interaction of polyhydroxy fullerenes with ferrihydrite: adsorption and aggregation
  Jing Liu et al
Characterisation of Synthetic Two-line Ferrihydrite by Electron Energy Loss Spectroscopy

G. Vaughan1,2, R Brydson1, and A. Brown1

1Institute for Materials Research, SPEME, University of Leeds, Leeds, LS2 9JT, UK.
2Johnson Matthey Tech. Centre, Blount’s Court, S. Common, Reading, RG4 9NH

pmgmv@leeds.ac.uk / vaughgm@matthey.com

Abstract. The precise atomic structure of the nanocrystalline iron oxyhydroxide mineral, ferrihydrite is currently under intense debate concerning two proposed models. We have synthesized two and six line ferrihydrite and concentrated on the characterisation of the two line form. We show that X-ray scattering data for the two-line form are consistent with the most recent reports and that assessment of the octahedral iron content by electron energy loss spectroscopy in the transmission electron microscope suggests some 90% of the iron is ferric with octahedral co-ordination. We also identify nitrate contamination that has not apparently affected the X-ray scattering and so we infer that it is surface adsorbed.

1. Introduction

Ferrihydrite (Fh) is a highly disordered iron (oxy)hydroxide which exists exclusively in nanocrystalline form (ranging from 2-6 nm in crystallite size). It occurs widely in natural waters, sediments, is a constituent of a wide variety of soils and is similar in form to the iron-rich mineral core of the iron-storage protein, ferritin [1]. Generally formed by rapid hydrolysis of dissolved iron in solution, Fh is often found co-present with other chemisorbed species such as arsenic, lead, phosphate and some organic molecules. The high sorption-capacity makes it an ideal candidate for use in water purification since it is capable of regulating the concentration and distribution of a host of impurities. First described in 1967 [2], there still exists considerable controversy over the precise atomic structure of Fh since its size and defective nature make a definitive characterization challenging. One structural model, based principally on simulation of powder XRD patterns, describes Fh as three intermixed phases for which iron occupies octahedral interstices only [3]. Recently, a new model challenging the standard view has been proposed, based predominantly on structural refinement of atomic pair-distributions measured in the synchrotron using total X-ray scattering methods [4,5]. In this model Fh is described as a single phase in which iron occupies both tetrahedral (<= 20%) and octahedral interstices. This new model has received some criticism [6,7] however the potential identification of ‘under saturated’ iron coordination sites has re-invigorated the structural debate.

In this study we have produced 2- and 6-line ferrihydrite (2LFh and 6LFh) and concentrated on the characterization of the 2LFh. In particular we present transmission electron microscope (TEM) based electron energy loss spectroscopic (EELS) characterization since this permits the assessment of iron valence and co-ordination at the nanometre scale [8].
2. Experimental
The Fhs used in this study were prepared following standard methods [9]. Briefly, for the synthesis of 2LFh, 10 g of Fe(NO$_3$)$_3$·9H$_2$O was added to 125 ml of distilled water and the pH of the resulting solution was raised to 7.2 by the addition of a 1 M solution of NaOH. Washing of the product was achieved by first centrifuging the solution, in order to separate the precipitate from the supernatant, and then re-dispersing the sediment in distilled water. This process was repeated 5 times before the product was freeze-dried and stored. For the preparation of 6LFh, 10 g of Fe(NO$_3$)$_3$·9H$_2$O were added to 1 L of distilled water which had been preheated to a temperature of 70 ºC. The resulting solution was held at this temperature for 10 minutes before being quenched in an ice bath. Washing was done by dialysis over several days. The cleaned product was then freeze-dried. Both Fhs have been stored as dry powders at 4 ºC.

Powder X-ray Diffraction was carried out using a Philips X´pert (PW 3040/60) diffractometer, high angle annular dark field scanning TEM (HAADF-STEM) imaging was undertaken using the VG HB501 STEM retro-fitted with a NION spherical aberration corrector (SuperSTEM 1, Daresbury, UK). Pair distribution functions (PDFs) were kindly produced by Marc Michel (Stanford University) who acquired the total X-ray scattering data for the 2LFh at the Advanced Photon Source (Argonne, USA) following a similar procedure to that reported in [4,5]. Fourier Transform Infrared Spectroscopy (FTIR) was conducted using a Thermoscientific Nicolet iS10 spectrometer run in ‘SMART’ attenuated total reflectance (ATR) mode with a diamond disc. Each spectrum is a background subtracted sum of 36 scans at 1.92 cm$^{-1}$ data spacing.

TEM investigations were carried out with a FEI/Philips CM200 FEG TEM operating at 197 kV and fitted with a Gatan Imaging filter (GIF 200). EELS Fe-L$_{2,3}$ edges were acquired in diffraction mode (image-coupled) on the microscope using the procedure described in [8]. We use here the linear least-squares fitting (LLS) of four well characterized reference minerals to our experimental Fe-L$_{2,3}$ edges to estimate the fractional compositions of octahedrally and tetrahedrally coordinated ferric and ferrous iron. The method and reference standards are detailed in [8].

3. Results and discussion
Powder X-ray diffraction (Figure 1a) and STEM-HAADF imaging (Figure 1b) of the 2LFh confirm the phase purity and nanocrystalline nature of the Fh. The XRD patterns for both 6LFh and 2LFh are consistent with those reported by Drits et al., [3]

Figure 1 a) Powder XRD patterns for 2 and 6LFh, the corresponding $d$-spacings listed above each peak are consistent with [3]. b) STEM-HAADF image of the 2LFh confirming the nanocrystalline nature of the powder. Inset is a power spectrum of the image demonstrating that the imaged region is polycrystalline.
The experimental pair distribution function (PDF) for the 2LFh can be compared with that of an equivalent Fh (Fhdy2) synthesized by the same protocol used here and reported in [4] (Figure 2).

![Figure 2](image1.png)

Figure 2. Comparison of the total X-Ray scattering PDF data for 2LFh and Fhdy2 from [4]. The atom-atom separations of the first three correlations, are labeled in units of Å. The profiles of the two samples are very similar.

Besides the high-frequency noise in the region \( r < 1.7 \text{ Å} \), which is an artifact resulting from the Fourier transformation and the finite \( Q \)-range used to obtain the PDF, the PDFs of the two samples are essentially identical. The positions and relative intensities of the correlation peaks, which extend out to approximately \( r \approx 20 \text{ Å} \), when overlaid are practically indistinguishable. The first correlation peak at \( r = 1.98 \text{ Å} \) is typically assigned to the Fe-(O, OH) distances, the next two at \( r = 3.05 \text{ Å} \) and 3.45 Å can be assigned to Fe-Fe distances and, as alluded to in the Introduction, the precise structure that describes this PDF is currently under intense debate [5, 7].

FTIR spectra for 2 and 6LFh are broadly similar to those previously published [10,11] (Figure 3).

![Figure 3](image2.png)

Figure 3. Infrared spectra obtained from 2 and 6LFh. The 2LFh has a steeper background and a sharp peak at 1385 cm\(^{-1}\) that can be attributed to nitrate.

The background in the range 2,000 to 4,000 cm\(^{-1}\) can be attributed to the strong scattering of the IR radiation which results from the “small sized” particles and aggregates of Fh. The background in this region is more pronounced for the 2LFh probably reflecting the smaller average crystallite sizes; however, this also may be in part due to the extent of hydration of this sample. This last point is supported by the increased intensity of the band around 1622 cm\(^{-1}\) (OH bending) for the 2LFh. This band, along with one at 3450 cm\(^{-1}\) (OH stretching), was noted by Towe and Bradley [2] to be associated with molecular water in “hydrogen-bonded association”. Cornell and Schwertmann [11] attribute bands at 3615 cm\(^{-1}\), 3430 cm\(^{-1}\) and 650 cm\(^{-1}\) to be due to free surface OH, bulk OH stretch and bulk OH deformations respectively.
The sharp spike at 1385 cm\(^{-1}\) observed for the 2LFh sample can be attributed to NO\(_3^–\) which is due to the ferric nitrate reagent used during synthesis [11]. The absence of this feature in the 6LFh spectrum highlights the efficacy of the dialysis method of washing over that used for the 2LFh.

The amount of iron in ferrihydrite that is ferric and in octahedral co-ordination was assessed by Fe L\(_3\) ELNES fitting and it decreases as a function of accumulated electron-fluence for 2LFh (Figure 4). Error bars shown have been derived from the reported errors in the fitting coefficient values provided by the fitting routine.

![Figure 4. Fe-L\(_3\) ELNES analysis of the ferric (a) and octahedral (b) iron content of 2LFh as a function of cumulative electron fluence. The extrapolated ferric and octahedral content at very low fluence are 91 and 93% respectively.](image)

There is a slight decrease in the amount of ferric and octahedrally coordinated iron that can be fitted by a characteristic exponential ‘dose-response’ function. When extrapolated back to the zero fluence limit the exponential function estimates 91 and 93% of the total iron is ferric and in octahedral coordination. This is consistent with the values measured by the same method for 6LFh [8].

Overall, the results show that probes of the ‘bulk’ structure of 2LFh are insensitive to nitrate contamination. This indicates that the nitrate is surface adsorbed rather than co-precipitated and this has implications for how other contaminants such as phosphate and arsenate bind to Fh. The TEM-EELS results confirm the beam sensitive nature of Fh and suggest that 2LFh contains some 10% less tetrahedral iron than proposed by the revised Michel model (which suggests 20% tetrahedral iron) [4].

4. Conclusions
X-ray scattering profiles of synthetic 2LFh are consistent with other reports however the measurement of ~93% octahedrally co-ordinated ferric iron by TEM-EELS is not in complete agreement with the most recently proposed structural model. Nitrate has also been detected and identified as a surface contaminant because its presence does not apparently affect the bulk structure.

References