Low-electron fluence STEM-EELS analysis of ferrihydrite nano-particles approaching the Ångstrom scale

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Abstract. We present here the preliminary results from a modified low electron-fluence (< 10^7 electron nm^-2) mode of electron energy-loss spectroscopy (EELS) combined with scanning transmission electron microscopy (viz. Smart-acquisition) as applied to ferrihydrite nanoparticles. Ferrihydrites of two different crystallinities (2-line and 6-line ferrihydrite) have been synthesised and characterised by bulk techniques and then comparing Fe-EELS from the surface and bulk of individual particles (crystallites of 2-6 nm diameter). Thus far we have been able to isolate the first 0.1-0.5 nm of surface EEL-signal specific to both oxygen and iron and detect no differences between the surface and bulk within a particle. The Fe-EEL signal of the 6-line ferrihydrite is consistent with previously published work however we do observe a broadening in the Fe-L3 peak of the less crystalline 2-line ferrihydrite and tentatively attribute this to distortion of the iron co-ordination in the more disordered structure.

1. Introduction
The aims of this study are, first, to establish a set of experimental parameters for the characterisation of the surface and bulk iron rich mineral cores of the ferritin protein complex. Second but by no means a less important goal, is it to thoroughly characterise ferrihydrite (FHY) nanoparticles which are thought to constitute the principle phase within ferritin mineral cores (FMCs) [1]. The main analytical technique employed in this study is scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS) as this allows us to probe structure and chemistry ultimately down to the Å scale. A modified mode of spectrum acquisition that continuously averages similar specimen regions as identified by prior high angle annular dark field imaging is used here. This technique limits the effects electron beam-damage and facilitates the comparison of average surface to bulk EELS analyses. The technique, termed smart-acquisition, is described in greater detail elsewhere in these precedings [Sader et al.].

Of the approximately 14 known iron oxyhydroxides, FHY is considered to be the most poorly crystalline (crystallite sizes of 2-6 nm). Its nominal bulk formula is typically quoted as Fe$_5$Ho$_8$·4H$_2$O following Towe & Bradley 1973 [2], however careful TEM analysis of single particles has shown the water contribution to this formula to be variable depending on both the synthesis route followed and subsequent handling of the sample prior to examination [3]. Analytical probes of atomic structure, such as X-ray diffraction (XRD), show FHY to be generally structurally disordered and to exhibit a

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range of crystallinities. There are generally accepted to be two forms of FHY which in order of increasing crystallinity are 2-(X-ray) Line FHY and 6-Line FHY (2LFHY and 6LFHY), based on their XRD profiles. It is the general consensus that 6LFHY is simply a more crystalline version of 2LFHY [4]. Within this structure iron is nominally ferric and octahedrally coordinated with neighbouring oxygen atoms. It has been suggested that perhaps the surfaces of individual crystallites are structurally different to the bulk [5].

One important factor to consider when attempting (S)TEM characterisation of FHY is that it is sensitive to the high energy beam-electrons. The damage mechanism is not well understood however it is apparent that both iron’s oxidation number and coordination number are reduced [6]. A full assessment of 2LFHY’s damage susceptibility to 100 keV electrons has not yet been carried out however, using 200 keV electrons preliminary results (unpublished) have shown it to be no more prone to damage than 6LFHY.

The Fe-L\textsubscript{2,3} electron energy-loss ionization edge is dominated by the dipole-allowed transitions (i.e. where \(\Delta l = \pm 1\)) of 2\(p\) initial-state electrons to 3\(d\) final-states. It is characterised by a peak-doublet at with an edge-onset of ca. 708-710 eV and peak-to-peak separation of 12.4 eV. Superimposed on this basic motif is a fine-structure (ELNES) which reflects the valence of iron as well as the coordination number, geometry and nature (e.g. chemical-species) of binding ligands. The intensity ratio of the two principle Fe-L\textsubscript{2,3} peaks has been show to be a sensitive probe of Fe(III)/ΣFe in mixed valence Fe-(oxy)hydroxides and Fe-silicates [7]. The nature of this ELNES is also affected by any distortions of coordination-sphere geometry since there will then exist multiple Fe-O bond lengths surrounding a given site.

2. Experimental methods
All STEM-EELS work has been carried out using a VG HB501 STEM retro-fitted with a Nion spherical aberration corrector and a Gatan Enfina electron energy loss spectrometer at the Daresbury Laboratories, UK (SuperSTEM1). Beam convergence angles of 24 mrad and probe diameters of 0.13nm were used. When performing EELS the spectrometer collection angle was 19 mrad. Beam currents are estimated to be approximately 100 pA. Using this set-up we have been able to acquire spatially resolved core-loss spectra at electron-fluences of ca. 10\textsuperscript{7} electrons.nm\textsuperscript{-2}.

Briefly the Smart-Acquisition EELS technique used here proceeds in the following manner; first regions of interest are identified in high-angle annular dark field STEM images and a binary mask image created; masked regions of interest, which can have arbitrary shapes and do not necessarily need to be connected, are then converted into a series of beam scan-coordinates; the beam is then scanned over these areas whilst collecting a single EEL spectrum. This modified technique spreads the electron-fluence over an extended area of sample thereby increasing the signal-to-noise ratio in the resulting spectrum for a given electron-fluence level when compared to traditional STEM-EELS.

The FHY samples used in this study were prepared following standard methods [8]. The success of the FHY synthesis has been confirmed by comparison of high-resolution TEM (HRTEM), X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR) results with those in the literature [8, 9].

3. Data analysis
We use here the linear least-squares fitting (LLS) of four well characterised reference minerals to our experimental Fe-L\textsubscript{2,3} edges to estimate the fractional compositions of octahedrally and tetrahedrally coordinated ferric and ferrous iron. Goodness of fit is determined by both visual inspection and by the \(\chi^2\) value (a measure of difference between experimental spectra and calculated fits) generated by the LLS fitting routine. This method and the reference standards used are described in greater detail in
In addition to LLS we obtain estimates of $Fe(III)/\Sigma Fe$ by analysis of the integrated white-line intensity ratio $I(L_3):I(L_2)$ as per van Aken et al [7].

The final data set used for surface to bulk analysis consists of the following: For analysis of 2LFHY, 7 surface-bulk mask pairs were selected for the measurement of the Fe $L_{2,3}$-ELNES and 9 surface-bulk pairs were selected for analysis of the O:Fe atomic ratio; For 6LFHY these corresponding numbers were 5 and 8 respectively. In all cases surface-bulk pairs have been chosen to allow for comparison on a particle-to-particle basis. Only Fe-L spectra having a SNR better than 5 were selected for ELNES analysis. A software routine generates an EELS scan-mask of each particle’s surface from an initial HAADF image and the quality of alignment has been assessed by overlaying the mask with the HAADF image from which it was derived. By analysing the pixel intensity distribution about the masked regions we have selected spectra which best isolate the surface signal. Masks sampling > 0.5 nm into the particle’s bulk were rejected. The same was true for those masks having a significant offset with respect the particle’s surface. Therefore we are confident that the surface spectra are taken from the outer 0.5 nm of the FHY particles and respective bulk spectra from further within.

4. Results

There little evidence of a difference between surface and bulk specific EEL signals for both 2LFHY and 6LFHY. Quantification of EELS gives iron to oxygen ratio of Fe:O $\approx 0.65 \pm 0.1$ for both 2LFHY and 6LFHY. This result is consistent, within experimental errors, with a dehydrated form of the generally accepted formula for FHY: Fe$_5$HO$_8$·4H$_2$O and previous EELS work on FHY [3].

Table 1. Average EELS-derived estimates and standard-deviations (STDEV) of coordination number and valence of iron in 2LFHY and 6LFHY. The STDEV has been quoted in lieu of measurement errors to illustrate the variability in the results.

| Fe ELNES fitting for both surface and bulk | Van Aken | EELS Quant. - Oxygen % |
|------------------------------------------|----------|------------------------|
| [Fe$^{3+}$]$^1$/[Fe$^{3+}$]$^2$ | [Fe$^{3+}$]$^1$/[Fe$^{3+}$]$^2$ | Fe$^{3+}$/ΣFe | Surface | Bulk |
| Haematite                                | Hedenbergite | Hercynite               | Fe$^{3+}$/ΣFe | Surface | Bulk |
| 2LFHY 36 ± 14%                           | 18 ± 12%   | 47 ± 17%               | 0.8 ± 0.10   | 65 ± 8%  | 63 ± 2%  |
| 6LFHY 93 ± 2%                            | 1 ± 2%    | 7 ± 2%                 | 0.93 ± 0.05  | 59 ± 6%  | 67 ± 3%  |

Fe-ELNES analysis reveals that for 6LFHY both the surface and bulk Fe is predominantly (i.e. 93% ± 10%) ferric in octahedral coordination with neighbouring oxygen atoms. The remaining Fe is also predominantly in $O_h$ symmetry but now in a reduced ferrous state. This observation is backed up by the results obtained using the Van Aken method.

Fe-ELNES analysis of the 2LFHY samples yields variable results. In general the ferric content is lower than that of 6LFHY for both surface and bulk measurements. This is confirmed by analysis using the Van Aken method. As for 6LFHY ligand coordination is predominantly $O_h$ however there a slight increase in both the $T_d$ and $O_h$ ferrous component.

5. Discussion

The lack of any clear evidence for differences between surface and bulk measurements may be interpreted in one of two ways. Firstly there may in fact be no (detectable) difference between these two cation locations or secondly there may be a deficiency in the current sampling capabilities (i.e. we are only isolating the first 0.5 nm) of surface-masks. In order to resolve this question we need to collect more data for which only the first few atomic layers (i.e. ca. 0.1 nm) are sampled in surface measurements and repeat the analysis.
The success of the LLS fitting, as assessed by the values of $\chi^2$, was found to be different for 6LFHY and 2LFHY. In the case of 6LFHY both surface and bulk spectra can be reasonably reproduced from a linear combination of the reference standards. However, in the case of 2LFHY fitting results have proved to be more variable and fits less satisfactory. In the case of 6LFHY, LLS fitting gave one distinct best-fit for a given experimental spectrum. For 2LFHY there were several similar LLS fit solutions with similar $\chi^2$ values. In each case the solution with the lowest $\chi^2$ value was chosen. This difficulty in fitting may be due to an observed increase in width of the $L_3$ peak for 2LFHY. This increase, which is of variable magnitude, forces the fitting algorithm to provide spurious fits to the data. Despite being a best-fit in the least squares sense (i.e. a global minimum in $\chi^2$) it is clear from visual inspection that the LLS fitting can reproduce ELNES features not present in the experimental spectra (at least at the current SNR levels).

The origin of this increased $L_3$ peak width is unclear and may be due to one of several reasons. First the damage susceptibility of 2LFHY has not yet been carefully assessed for 100 keV electrons and may be greater than for 6LFHY (which shows little or no propensity to damage at the fluences used here) [6]. If this susceptibility is significant our measured spectra may include some type of broadening due to alteration of the 2LFHY structure. Despite not being able to rule this possibility out we believe this not to be the case as we have shown (unpublished) 2LFHY to be no more damaging than 6LFHY for 200 keV electrons.

Second and probably more likely, the measured spectra may affected by genuine bond distortions in the octahedral symmetry about the ferric iron centre and/or an admixture of lower coordination Fe-O environments in the structure. Consequently, the variability in the $L_3$-width may reflect the inherent structural variability of 2LFHY; something which is hinted at by XRD albeit on a more bulk level. This result also suggests that the fitting of relatively well crystalline reference standards to systems in which there is a significant degree of distortion may be invalid. A series of experiments to investigate this effect on the $L_3$-edge could be envisaged using Fe-(oxy) hydroxides of more established valence and coordination (such as goethite or lepidocrocite) with a range of fine-particle sizes and so varying degrees of structural distortion.

6. Conclusion
We have successfully applied a novel low-electron fluence STEM-EELS acquisition technique to the spatially resolved ($\leq$0.5nm) structural and chemical characterisation of FHY nanoparticles. We do not observe a difference between the surface and bulk specific signals and results are consistent with previous work on FHY. This method and the subsequent data analysis used herein have been shown to be suitable for characterisation of morphologically irregular nanoparticles such as FHY and FMCs.

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