Electron Beam Damage Studies on 6-Line Ferrihydrite

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Abstract. Electron energy loss near-edge structure (ELNES) combined with multiple linear least-square (MLLS) fitting and selected area electron diffraction (SAED) pattern analysis has been used to study electron beam damage in 6-line ferrihydrite. Initially all iron is Fe$^{3+}$ in octahedral coordination. Under increasing electron dose, an increasing percentage of octahedrally coordinated Fe$^{3+}$ migrates to tetrahedral sites. When the dose exceeds 3x10$^8$ electrons/nm$^2$, Fe$^{2+}$ was found to be present in the material.

1. Introduction
Ferrihydrite is a nanocrystalline hydrated ferric oxide that commonly forms in a near-surface environment in nature. Ferrihydrite samples are distinguished by the number of visible X-ray diffraction (XRD) peaks at \(d\)-spacings between approximately 0.15 and 0.25 nm, and subsequently are labelled as 6-line ferrihydrite (6LFh) and 2-line ferrihydrite (2LFh) respectively.

Typical 6LFh crystallites are 5-6 nm in diameter. Several models for the 6LFh structure have been proposed using different measurement techniques for bulk samples or individual crystallites: XRD, high-resolution transmission electron microscopy (HRTEM), or nanodiffraction, [1,2]. It is generally accepted that 6LFh contains Fe$^{3+}$ mostly in an octahedral coordination. However, under certain conditions, such as heating in an inert atmosphere, ferrihydrite can transform to hematite, maghemite, magnetite, or wüstite, [3,4]. In addition, it is well known that in the TEM the electron beam can affect a sample during examination in an electron microscope in various ways, such as atomic displacement, electron-beam sputtering, electron-beam heating, etc. Therefore, during irradiation of 6LFh in the TEM, there is the possibility of electron beam damage causing iron atoms to migrate from octahedral sites to tetrahedral sites, and even reducing Fe$^{3+}$ to Fe$^{2+}$, ultimately resulting in structural and chemical phase conversion. Ascertaining a ‘safe electron dose’ (defined as the electron dose above which significant changes to the structure of the specimen occur) to examine 6LFh is an essential step before characterization in a TEM.

Electron energy loss spectroscopy (EELS) in a TEM has been shown to be a reliable method for characterisation of materials with regard to their elemental composition and electronic structure (which is represented in the energy-loss near-edge structure (ELNES) of the core ionization edges). The Fe \(L_{2,3}\)-edges (known as ‘white lines’) are characterised by sharp maxima just above the edge onsets, which represent transitions to empty 3d states. The Fe \(L_{2,3}\)-edges of the iron oxides show a characteristic behaviour with changing Fe valence state. Fe$^{3+}$ containing minerals are characterised by an \(L_{2}\)-edge with a leading shoulder and a peak maximum at 709.5 eV, while Fe$^{2+}$ containing minerals are characterised by an \(L_{2}\)-peak maximum at 707.5 eV with no leading shoulder. Any reduction of iron is shown as an increase in the low-energy shoulder of the Fe \(L_{2}\)-edge and we have used this technique...
combined with multiple linear least-square (MLLS) fitting of reference spectra to investigate electron beam damage of 6LFh in a TEM with a range of electron doses.

2. Materials and Methods

2.1 Sample preparation

6LFh samples were prepared by following the method of Schwertmann and Cornell [5]. 2L of distilled water was preheated to 75°C in an oven, 20g of unhydrolyzed crystals of Fe(NO$_3$)$_3$·9H$_2$O were added with rapid stirring, and the solution was then returned to the oven and left for 10mins. The solution was subsequently cooled rapidly by plunging into ice water, transferred to a dialysis bag and dialysed for 7 days by changing the water several times each day. Finally the suspension was freeze dried producing ~5g of 6LFh. The 6LFh powder was characterized by XRD which yielded the standard 6 X-ray reflections (0.321nm, 0.252nm, 0.222nm, 0.196nm, 0.170nm, and 0.147nm) for 6LFh.

2.2 Instruments

TEM investigations were carried out with a FEI CM200 FEG TEM operating at 197kV and fitted with a Gatan Imaging filter (GIF 200).

Specimens were prepared by dispersing the 6LFh powder in ethanol and then drop-casting onto a standard holey carbon support film (Agar Scientific Ltd.). Bulk energy loss spectra were taken in diffraction mode (image coupled) with an approximately 0.18µm diameter selected area aperture (SAD) inserted, leading to a collection semi-angle of 6mrad, and a convergence semi-angle of approximately 1mrad. A thin area was examined in each sample (the relative sample thickness was estimated from the low-loss spectrum of each sample and all were less than 0.3*(inelastic mean free path)). EELS spectra were acquired with an energy dispersion of 0.1eV/channel and an energy resolution of 0.8eV. Measurements were taken at accumulated electron doses ranging from 3x10$^4$ up to 2.5x10$^9$electrons/nm$^2$ by adjusting the probe size (condenser 2). Electron dose was estimated using an FEI empirical calibration curve based on the measured brightness on the fluorescent viewing screen of the TEM. Selected area electron diffraction (SAED) patterns from the examined area were also obtained at each electron dose and compared to standard XRD tables of $d$-spacings for reference iron oxides.

2.3 Techniques

2.3.1 Multiple Linear Least-Square (MLLS) Fitting

MLLS fitting was undertaken in Gatan’s DigitalMicrograph software version 3.4, all the EELS spectra were energy calibrated, background subtracted, low loss deconvoluted, normalised by using an integration area in a 28eV energy window (702-730eV) that includes the two white lines and then MLLS fitted to iron oxide reference spectra.

The MLLS fitting program forms a model function consisting of a linear combination of the specified fitting references (at least two spectra) and then fits this model to the experimental spectrum by adjusting the fitting coefficients to minimize the square of the deviation between the model and the experimental spectrum (least-squares fit parameter, $\chi^2$). In our fitting procedure, each data point was set to be weighted equally. The reference spectra used in this study were haematite ($\alpha$-Fe$_2$O$_3$; Fe$^{3+}$ in octahedral coordination), maghemite ($\gamma$-Fe$_2$O$_3$; 62.5% octahedral Fe$^{3+}$ and 37.5% tetrahedral Fe$^{3+}$), and wüstite (FeO; octahedral Fe$^{2+}$) [6]. A fitting range 702-730eV was selected and the percentage of each iron valency (Fe$^{3+}$ and Fe$^{2+}$) and coordination (octahedral or tetrahedral) could then be estimated from the fitting model.

3. Results

An example MLLS fit to a 6LFh Fe $L_{2,3}$-edges EEL spectrum recorded at an accumulated electron dose of 3x10$^4$electrons/nm$^2$ is shown in Figure 1a. The spectrum is best fitted by a linear combination of all three reference spectra: haematite, maghemite, and wüstite (Figure 1b). The residual intensity after subtraction of the MLLS fit from the experimental spectrum is shown inset in Figure 1a.
Figure 1. (a) An example of the result of a MLLS fit. The experimental 6-line ferrihydrite spectrum the curve with square marks (□) and the best fit spectrum is the curve with circular marks (○). The insert shows the residual intensity following fitting. The scale of the residual plot is approximately the same as the fitting plot. (b) The relative proportions of the three reference spectra that, when combined, produce the best fit to the experimental spectrum.

For each fitted spectrum, the relative percentage of Fe$^{3+}$ (in octahedral or tetrahedral coordination) and Fe$^{2+}$ (in octahedral coordination) can be obtained from the weighting coefficient of each reference spectrum in the MLLS fit. The change in iron coordination and valence of 6LFh as a function of electron dose is shown in Figure 2. From the MLLS fitting analysis, it can be assumed that 6LFh is a ~100% Fe$^{3+}$ bearing mineral with all of the iron atoms sat in octahedral sites at very low electron doses. As the dose increases, Fe$^{3+}$ migrates from octahedral sites to tetrahedral sites (Figure 2a). For doses of 3x10$^8$ electrons/nm$^2$ and higher, some percentage of Fe$^{3+}$ is reduced to Fe$^{2+}$ (Figure 2b). This is confirmed with the corresponding SAED patterns taken at the same doses.

Figure 2. (a) The estimated percentage of octahedrally coordinated Fe$^{3+}$ in 6-line ferrihydrite at each electron dose. (b) The estimated percentage of Fe$^{3+}$ (octahedral + tetrahedral coordination) in 6-line ferrihydrite at each electron dose.

For doses less than 3x10$^8$ electrons/nm$^2$, the ring diffraction patterns give d-spacings consistent with previous electron diffraction work on 6Lfh (the major 8 d-spacings are 0.366nm, 0.3-0.32nm, 0.25-0.26nm, 0.227nm, 0.202nm, 0.186nm, 0.176nm and 0.145-0.158nm) [2]. When the dose is higher than 3x10$^8$ electrons/nm$^2$, extra rings could be observed and assigned to haematite or maghemite ($d=0.482$nm, 0.374nm, 0.208nm and 0.161nm), and wüstite ($d=0.128$nm and 0.123nm). This suggests that the 6Lfh becomes a mixture of ferrihydrite, haematite, maghemite and wüstite phases. The most intense reflections from these minor phases may also be present in the experimental diffraction
patterns taken at doses lower than $3 \times 10^4$ electrons/nm$^2$ but they are obscured by the strong reflections from the major, ferrihydrite, phase. Also, with low doses, each of the diffraction rings in the SAED patterns had even intensity; but as the dose increased, the rings became spotty. This indicates that the crystallites of 6LFh become larger with dose.

4. Discussion

Ideally, separate Fe L$_{2,3}$-edge reference spectra of Fe$^{3+}$ in octahedral coordination, Fe$^{3+}$ in tetrahedral coordination, Fe$^{2+}$ in octahedral coordination, and Fe$^{2+}$ in tetrahedral coordination should be used. For simplicity, haematite (100% Fe$^{3+}$ in octahedral coordination), maghemite (62.5% octahedral Fe$^{3+}$ and 37.5% tetrahedral Fe$^{3+}$), and wüstite (100% Fe$^{2+}$ in octahedral coordination) are used in this study and adequately fit the experimental 6LFh spectra. The coefficients generated from the MLLS fitting are not taken to represent the volume percentage of each reference material present in 6LFh but are taken as estimates of the valence and coordination of the Fe in 6LFh.

Extrapolation of the estimated percentage of Fe$^{3+}$ in octahedral coordination (Figure 2b) to an electron dose of 1 electron/nm$^2$ indicates that 6LFh should consist of 100% octahedral coordination. This is consistent with work presented by other groups (e.g. [7]) and, whilst this does not preclude the fact that the MLLS fits may not be unique it does indicate that they are physically plausible. An electron dose up to $10^6$ electrons/nm$^2$ results in a change in coordination of Fe$^{3+}$ from octahedral to tetrahedral but no reduction. Therefore, the dose=$10^6$ electrons/nm$^2$ could be termed as the maximum ‘safe’ dose. Above this maximum safe dose, iron reduction is observed. This change could be due to direct beam heating damaging the specimen as suggested by Drits et al [3] and/or radiation damage.

5. Conclusion

Electron beam damage of a hydrated ferric oxide has been demonstrated in this study. With a series of electron doses from as low as $3 \times 10^4$ electrons/nm$^2$ up to $2.5 \times 10^9$ electrons/nm$^2$, MLLS fitting of Fe L$_{2,3}$-edges spectra combined with SAED patterns suggests that a structural change (including changes in iron valency and coordination) is induced by high electron doses. This is an indication that electron beam damage could affect any structural characterization undertaken at a commonly used electron dose ($>10^6$ electrons/nm$^2$) and establishing a ‘safe’ electron dose is essential.

References and Acknowledgement

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