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Quantification of Fe-oxidation state in mixed valence minerals: a geochemical application of EELS revisited

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Abstract. The use of TEM and electron energy loss spectroscopy to determine levels of Fe³⁺ in solids at nanometre spatial resolution is well established. Here we assess this technique at the energy resolution of a monochromated electron source (0.3 eV) and with the capability of simultaneously acquiring core- and low-loss spectra for absolute energy calibration of core-loss chemical shifts. Fe *L*_{2,3}-edges of four oxide standards give a characteristic energy loss near edge structure (ELNES) and the *L*₃-peak maxima of the spectra exhibit an energy shift of ~ 1.8 eV between ferrous (709 eV) and ferric (710.8 eV) iron. We show that diagenetic chlorites present in iron oxide loaded 'red beds' contain predominately Fe³⁺, based on the absolute energy position of the low signal Fe *L*₃-edges (centred around 710.8 eV). We also fit our standard-spectra to Fe *L*_{2,3}-edges from magnetite and maghemite nanoparticles to investigate iron site occupancy. An additional chemical shift needs to be applied to the octahedral ferrous iron site component to achieve a plausible, linear fit to the magnetite spectrum which we speculate may be due to electron hopping between the mixed valence octahedral iron sites in magnetite.

1. Introduction

Geochemical applications of Electron Energy-Loss Spectroscopy (EELS) in the Transmission Electron Microscope (TEM) have shown a wide range of benefits, including elemental quantification, the determination of oxidation state, and local co-ordination of atomic species [1]. Of these, the determination and quantification of Fe oxidation state is of particular geochemical significance in terms of the information it provides on redox, fugacity, pressure and temperature conditions at crystallisation or alteration.

The TEM-EELS methods of Garvie and Buseck [2] and van Aken, Liebscher and Styrsa [3] allow quantification of ferric iron to total iron in a range of silicates and oxides with a total iron content of a few atom % or more. This work revisits similar analyses, originally reported by Pan et al. [4], but with the improved energy resolution of a monochromated electron source and additional, absolute edge energy measurement by dual EELS acquisition [5].

2. Methods

We present data from the iron valence and co-ordination standards used by Pan et al. [4] to provide a reference and then investigate measuring valence in low iron content diagenetic chlorites (provided by Stephen Hillier from Old Red Sandstone of the UK [FWW-5 and ED2], the Permian of Poland [ROT-1] and the Triassic of the North Sea [CHL-25 and -34]; all sieved to < 2 µm clay size fractions) and iron site occupancy in synthetic iron oxide nanoparticles (made in-house or purchased from Alfa-Aesar). We have used a FEI Titan³ Themis 300 kV G2 S/TEM at the University of Leeds which is equipped with a monochromator (tuned to 0.3 eV energy resolution), FEI SuperX EDX detectors, a Gatan Quantum ER 965 imaging filter (with Dual EELS; this enables energy calibration of a core-loss edge with a simultaneously acquired low loss spectrum) and a Gatan OneView CCD. Image coupled EEL spectra (~ 6.6 mrad collection and ~ 1.0 mrad convergence semi-angles) were acquired in TEM diffraction



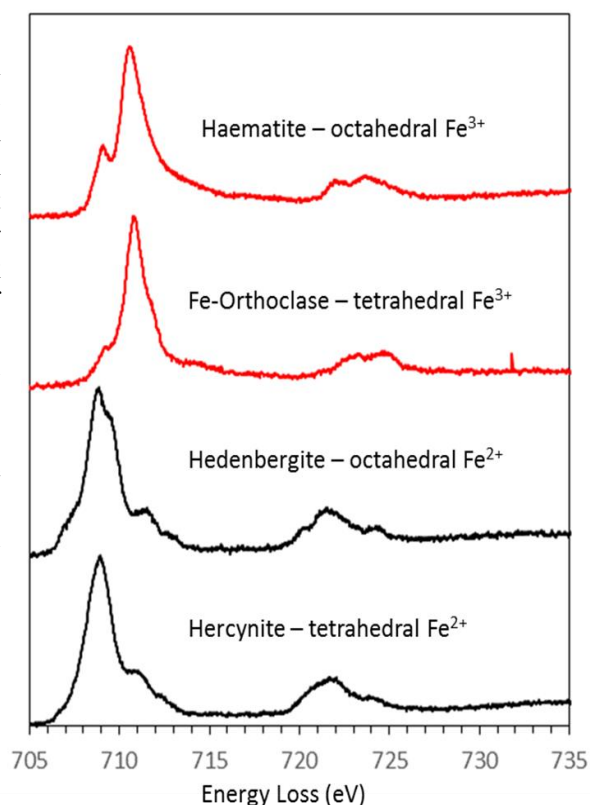
(using the smallest selected area electron diffraction aperture of ~ 200 nm diameter at the image plane) from crushed dispersions of minerals drop-cast on holey carbon films (Agar Scientific Ltd). Spectra were energy calibrated (to the simultaneously acquired low-loss) and background subtracted (power law) in Gatan's GMS software (version 3.1), t/λ values were generally < 0.35 .

3. Results

3.1. Iron Oxide Standards

Fe $L_{2,3}$ -edges of the four oxide standards exhibiting different iron valence and co-ordination give characteristic energy loss near edge structure (ELNES). Mineral details and EEL spectra recorded at 0.8 eV energy resolution are reported in Pan et al. [4]. Here, there are clear shoulders at high and low energies of the main L_3 peaks for ferrous and ferric iron respectively and the peak maxima of the spectra exhibit a chemical shift of ~ 1.8 eV between ferrous (709 eV) and ferric (710.8 eV) iron valence states (Figure 1). The energy-loss scale is now absolute due to the Dual EELS capability of the spectrometer. There was little change to the mineral morphologies or Fe edge shapes over the 30 s acquisition times (up to 1 min total exposure; at a screen current of 20 nA prior to insertion of the SAED aperture).

Figure 1. Reference Fe $L_{2,3}$ -edge energy loss spectra; from bottom up, hercynite (tetrahedral coordinated ferrous iron), hedenbergite (octahedral coordinated ferrous iron), Fe-orthoclase (tetrahedral coordinated ferric iron) and haematite (octahedral coordinated ferric iron).

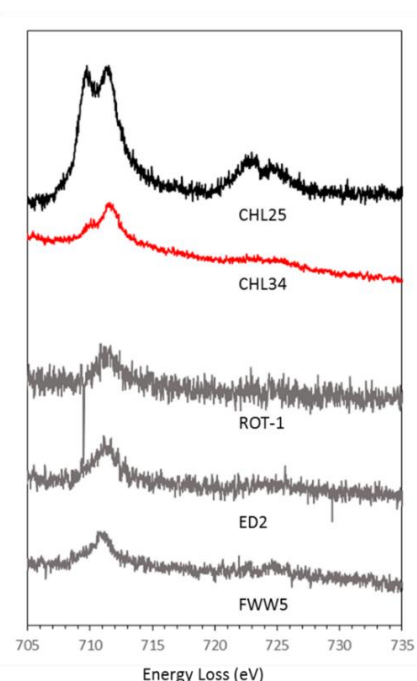


3.2. Dioctahedral Chlorites from Red Beds

Diagenetic chlorites are a common component of many sedimentary rocks. In most settings aluminous dioctahedral chlorites are rarer than ferro-magnesian trioctahedral types, however in some iron oxide-rich 'red beds' this trend may be reversed. It is hypothesised here that early formed hematite may play a crucial role as a buffer on the oxidation state of Fe in some red bed diagenetic systems. Under such conditions, it is postulated that the formation of dioctahedral chlorites (sудоite and tosудite) is favoured over that of the more common Fe^{2+} rich trioctahedral relatives because they can readily and preferentially accommodate Fe^{3+} [6].

Three dioctahedral chlorite samples provided by Hillier have clay particles present that are some type of sudoite (FWW5 and ROT-1) or tosудite (ED2) by powder X-ray diffraction (data not shown). Chlorites consist mainly of Si, Al, Fe and Mg and the presence of significant amounts of K, Na and Ca would indicate contamination with other clay minerals. Two reference chlorites, a tri- and dioctahedral form (CHL-25 and CHL-34) are also investigated and these are expected to be ferrous and ferric bearing respectively. Fe $L_{2,3}$ -edges taken from the sudoite (FWW5 and ROT-1) and tosудite (ED2) samples have low signal but are centred around 710.8 eV energy loss, indicating that they contain predominately Fe^{3+} while the tri- and dioctahedral chlorite references (CHL-25 and CHL-34) are mixed valence and Fe^{3+} -rich respectively (Figure 2).

Figure 2. Fe $L_{2,3}$ -edges of particles from the chlorite standards and unknowns. Iron levels are sufficiently low to make valence determination from Fe-ELNES difficult however the absolute edge energies of the peak maxima permit an estimate. The trioctahedral reference chlorite (CHL-25) is iron-rich and mixed valence whereas the dioctahedral reference (CHL-34) is lower in iron content and Fe³⁺-rich (the Fe L_3 peak maxima is at 710.8 eV). The sudoites (FWW5 and ROT-1) and tosudite (ED2) have even lower iron content but are clearly all Fe³⁺-rich (given that they too have Fe L_3 peak maxima centred around 710.8 eV). EDX spectroscopy of the unknowns was used to confirm the chlorite-like composition of the particles tested by EELS.



3.3. Fe_3O_4 (magnetite) and $\gamma-Fe_2O_3$ (maghemite)

Nanoparticulate forms of Fe_3O_4 (magnetite) and $\gamma-Fe_2O_3$ (maghemite) were synthesized in-house (following the method described in Brown et al. [7]) or purchased from Alfa-Aesar respectively. Fe_3O_4 and $\gamma-Fe_2O_3$ have the same crystal structure however the former contains mixed valence iron and the latter has only Fe³⁺ (with corresponding octahedral iron site vacancies to achieve stoichiometry). The unit-cell lengths of pure Fe_3O_4 and pure $\gamma-Fe_2O_3$ are given as 0.839 and 0.835 nm respectively (for example, Zhu et al., [8]).

Powder X-ray diffraction of the materials assessed here confirms both samples have the expected inverse spinel structure and Rietveld refinement suggests the unit-cell length of the magnetite sample is 0.838 nm and the maghemite sample is 0.833 nm (data not shown). The Fe $L_{2,3}$ -ELNES of these samples (Figure 3, black spectra) are consistent with Fe $L_{2,3}$ -X-ray Absorption Spectra reported by Zhu et al. [8].

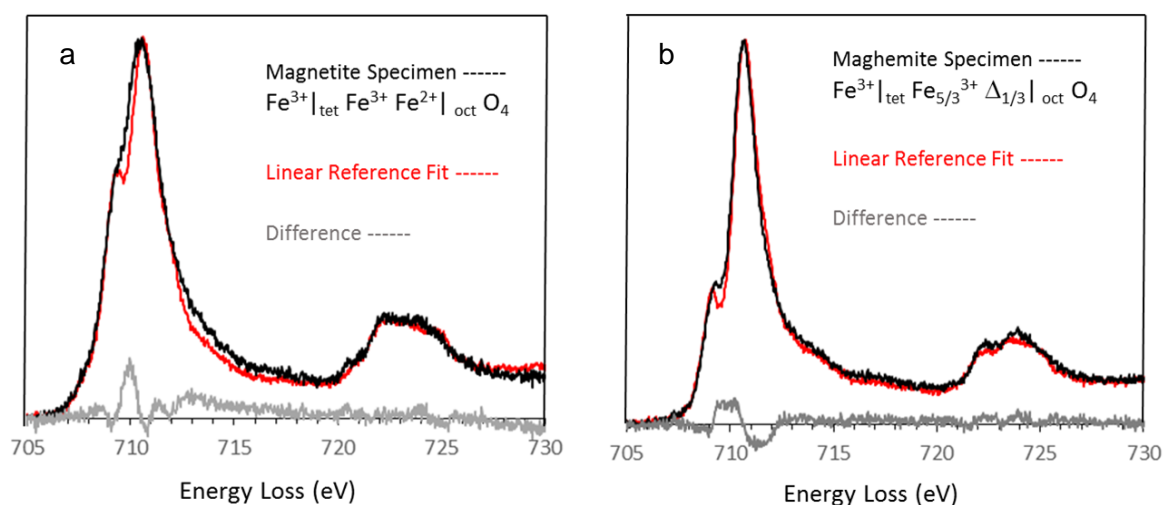


Figure 3. Fe $L_{2,3}$ -edges of magnetite (a) and maghemite (b) samples (black). Also shown are linear reference fits (red) and difference spectra (grey) obtained by combining the previously measured iron valence and site standards (Figure 1) in the intensity ratios indicated by the formulae given in the figure legend and subtracting these from the experimental spectra.

Linear reference fits to these energy loss spectra have been achieved by adding the appropriate, intensity normalised standard spectra (Figure 1) in the intensity ratios indicated by the formulae for stoichiometric magnetite and maghemite (given in figure legends, Figure 3). The magnetite fit spectrum (1:1:1 for tetrahedral ferric: octahedral ferric: octahedral ferrous iron), also requires the octahedral Fe²⁺ component to be given a 0.8 eV offset to higher energy loss whereas the maghemite fit is achieved with no adjustment in energy loss of the two components (1:5/3 for tetrahedral ferric : octahedral ferric iron); The required offset for the octahedral Fe²⁺ component in magnetite may be a result of the strong asymmetry of the hedenbergite standard spectrum (i.e., changes in octahedral site symmetry for ferrous iron in hedenbergite and magnetite) or could be due to electron hopping that is known to occur between the octahedral coordinated iron sites in magnetite (e.g., [9]).

4. Conclusion

Using TEM and electron energy loss spectroscopy to determine Fe³⁺ content of minerals has been revisited at the energy resolution of a monochromated electron source (0.3 eV) and with the ability to simultaneously acquire core- and low-loss spectra for absolute energy calibration of core-loss chemical shifts. We show a reproducible ~1.8 eV chemical shift between ferrous (709.0 eV) and ferric (710.8 eV) Fe L₃ core-EELS edges. This absolute edge energy position is then used here to identify the dominance of Fe³⁺ in low iron content diagenetic chlorite minerals. In addition, Fe L_{2,3}-edges from magnetite and maghemite nanoparticles have been acquired and fitted by our iron-site standard spectra to investigate iron site occupancy. We find an additional chemical shift needs to be applied to the octahedral ferrous iron site component to achieve a plausible, linear fit to the magnetite spectrum and we speculate that this may be due to electron hopping between the mixed valence octahedral iron sites in magnetite however this finding requires further investigation.

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Acknowledgements

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