Investigating nanoscale mineral compositions: Iron L$_{3}$-edge spectroscopic evaluation of iron oxide and oxy-hydroxide coordination

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ABSTRACT

The iron (Fe) L$_{3}$-edge X-ray absorption near-edge structure (XANES) spectrum is sensitive to the local coordination environment around the Fe metal center, making it a useful probe for understanding Fe mineral speciation. The two dominant spectral peaks in the Fe L$_{3}$-edge are parameterized according to the difference in the energy position (ΔE), and the quotient (intensity ratio) of the two peaks’ maxima. Variations in the ΔE value and intensity ratio values were found to be anti-correlated with respect to the various distortion measures considered in this study (e.g., polyhedral volume distortion percentage). This two-parameter plot could be explained by considering the Fe valence state, the ligand chemistry and the site symmetry of the Fe polyhedra. Furthermore, the ΔE and intensity ratio values were found to be anti-correlated with respect to the various distortion measures considered in this study (e.g., polyhedral volume distortion percentage). This two-parameter plot is thus presented as a standard-phase less specific identification tool for use in Fe speciation studies, applicable to both natural systems (e.g., aerosols, aquatic colloids) as well as to engineered systems (e.g., nanoparticle synthesis). A major advantage of this technique is that it is applicable to both crystalline and poorly crystalline phases, thus enhancing our ability to study amorphous and nano-crystalline phases that are typically difficult to characterize using X-ray diffraction techniques.

Keywords: Fe, iron, L-edge, XANES, iron oxide, iron oxy-hydroxide, ferrihydrite

INTRODUCTION

Iron L$_{3}$-edge X-ray absorption spectroscopy (XAS) provides important electronic information about the local atomic structure around the Fe center and this technique has thus been utilized in a considerable number of studies; ranging from biogeochemistry (Wang et al. 1997; Calvert et al. 2005; Benzerara et al. 2007; Chan et al. 2009; Miot et al. 2009) and mineralogy (van Aken et al. 1998; Miyajima et al. 2004), to materials chemistry (Labatut et al. 1998; Grandjean et al. 1999; Mikhlin et al. 2005; Augustsson et al. 2005; Chen et al. 2007; Shirakawa et al. 2007). Much of this work, especially in hydrated systems, is possible because of the advancements in soft X-ray instrumentation (Cramer et al. 2005; Padmore and Warwick 1994) and because of the volumes of early vacuum-based work devoted to developing a fundamental understanding of the L-edge spectral features (van der Laan and Kirkman 1992; Cressey et al. 1993; Crocombette et al. 1995; de Groot 2005). The Fe L-edge represents the probability and occurrence of dipole-allowed electronic transitions from the 2p ground state to 3d-like molecular orbitals, and variations in the resultant spectra are interpreted as a function of valence state, site occupation, symmetry, spin state, and degree of distortion (van der Laan and Kirkman 1992; Schofield et al. 1995; de Groot 2005; Miedema and de Groot 2013). The chemical information contained in the Fe L-edge complements the information obtained from Fe K-edge analyses and the L-edge technique has been chosen for use in this study because of its better resolution of fine structure, higher absorption cross section (important in spectro-microscopy), and lower intrinsic lifetime broadening (e.g., de Groot 2005).

The 2p electronic transitions of Fe L-edge can be probed either by using XAS techniques at a synchrotron light source, or by electron energy-loss spectroscopy (EELS) using a transmission electron microscope (TEM). A comprehensive evaluation of these two techniques suggests that XAS is superior over EELS particularly when environmentally relevant hydrated samples are considered (e.g., Dyne et al. 2006; Bluhm et al. 2006). The foremost reason for this is that XAS allows for the
molecular level investigation of samples in their pristine state, without the need for sample drying, which can alter the chemical state of the elements of interest and can induce shrinkage, aggregation, and water loss from the chemically important hydration shells. In addition, the spectral resolution that can be achieved using XAS is superior to the spectral resolution associated with EELS techniques.

Application of the Fe $L_{\text{eq}}$-edge XAS for speciation and mineralogical studies, especially in samples of environmental significance, have thus far largely been limited to valence state quantification studies (Cressey et al. 1993; van Aken and Liebscher 2002; Miyajima et al. 2004; Calvert et al. 2005; Cavé et al. 2006; Dynes et al. 2006; Bourdelle et al. 2013). Fe oxidation state is undoubtably a fundamental parameter governing the Fe behavior in biogeochemical systems, as well as the Fe properties in material science and engineering applications. However, given that the Fe $L_{\text{eq}}$-edge probes local electronic structure (van der Laan and Kirkman 1992; Cressey et al. 1993); the resultant spectrum is also sensitive to variations in coordination and ligand bonding. Although a recent study has made use of fine differences in the Fe $L_{\text{eq}}$-edge XAS to investigate ferrihydrite structure (Peak and Regier 2012), to our knowledge, there has not as yet been a systematic experimental study investigating the changes in XAS spectral features in response to varying Fe speciation. Several studies have used the Fe $L_{\text{eq}}$-edge as a speculation probe for investigating Fe phases, primarily the Fe-oxidation state, in environmental samples. Chan et al. (2004) use Fe $L_{\text{eq}}$-edge scanning transmission X-ray microscopy (STXM) mapping and Fe $L_{\text{eq}}$-edge X-ray photoelectron emission spectromicroscopy to infer that mineralized bio-filaments consist of amorphous Fe oxy-hydroxide. Interactions with biology have further been investigated by Miot and co-workers (2009), who used the Fe $L_{\text{eq}}$-edge XAS to measure the rates and the extent of Fe oxidation by bacteria; and Liu et al. (2015) who confirm pyrite transformation to Fe$^{3+}$ phases during biodegradation. Other studies have utilized the Fe $L_{\text{eq}}$-edge to understand and characterize the mineral-organic associations in soils (Chen and Sparks 2015) and marine particles (Von der Heyden et al. 2014) and the Fe $L_{\text{eq}}$-edge XAS has also been used to conclude that the observed Fe$^{3+}$ in hydrothermal systems is not present as finely dispersed Fe$^{2+}$ minerals, but rather that the Fe$^{3+}$ is stabilized by complexation with particulate organic matter (Toner et al. 2009).

In this study, we synthesize high-purity Fe mineral standards that we analyze using high-resolution Fe $L_{\text{eq}}$-edge experimental XANES to extract detailed chemical information from their spectral features. These data are further compared to an extensive compilation of Fe $L_{\text{eq}}$-edge XANES spectra published in the literature (Von der Heyden et al. 2012; see their supplementary material). In particular, we parameterize the $L_{\text{eq}}$-edge peak splitting (ΔE) and the intensity (peak height) ratio associated with these split peaks (Fig. 1a), and use these parameters to explore the changes in Fe coordination environment as a function of Fe mineral structure and chemistry. Although additional information can be derived from the Fe $L_{\text{eq}}$-edge, this parameterization approach benefits from its ease of use, consistency in peak identification and quantification, and a lack of a need for mineral standards for energy calibration. The $L_{\text{eq}}$-edge peak-splitting can largely be attributed to the ligand field splitting of Fe d-orbitals into $t_{2g}$ and $e_g$ subsets, which are further divisible into molecular orbitals formed by ligand coordination (Todd et al. 2003a; de Groot 2005). The ΔE value is thus strongly linked to the energy levels of these molecular orbitals, whereas the intensity ratio value is also affected by the respective orbital compositions—with selection rules governing the likelihood of electronic transitions. By interpreting high-resolution $L_{\text{eq}}$-edge X-ray absorption near-edge structure (XANES) spectra, this study investigates the factors that influence the ΔE and intensity ratio values of the Fe $L_{\text{eq}}$-edge for the polymorphs of the Fe oxide and oxy-hydroxide system. Fe mineral phases, particularly Fe oxides and oxy-hydroxides, play an integral role in soil and sediment biogeochemical reactions (Cornell and Schwertmann 2003) and in contaminant transport and transport processes (Appelo and Postma 2004; Hochella et al. 2005; Von der Heyden and Roychoudhury 2015), and they are often small and difficult to differentiate in environmental samples by using traditional methods. The advantages of the Fe $L_{\text{eq}}$-edge X-ray spectro-microscopic technique is that it has a spatial resolution of down to 10 nm and that it is able to evaluate the chemical and structural properties of both amorphous and crystalline phases. It is thus an ideal tool for examining the properties of sub-micrometer-sized environmental samples—such as aquatic colloids (Lead and Wilkinson 2006; Wigginton et al. 2007; Von der Heyden et al. 2012, 2014) and aerosols (Krueger et al. 2004; Majestic et al. 2007; Takahama et al. 2008).

**Experimental details**

**Synthesis of standards**

Fe oxide and Fe (oxy-) hydroxide mineral standards [goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), hematite (α-Fe$_2$O$_3$), maghemite (γ-Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), and amorphous iron oxy-hydroxide] were prepared following the methods outlined in Schwertmann and Cornell (2000). The purities of the prepared standards were confirmed by X-ray diffraction (Rigaku XRD) and infrared spectroscopy (Bruker IFS 66v/s).

**X-ray data collection**

The scanning transmission X-ray microscopy (STXM) studies were conducted at the Molecular Environmental Sciences (MES) beamline 11.0.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory, U.S.A. (see Bluhm et al. 2006). A few microliters of the mineral suspension was placed on a 100 nm thick Si$_3$N$_4$ sample window and allowed to air-dry before being placed in the end-station for X-ray analysis. All X-ray scans were conducted in transmission mode in a 1 atm He environment and at ambient temperature. The end-station specifications; for X-ray analysis. All X-ray scans were conducted in transmission mode in a 1 atm He environment and at ambient temperature. The end-station specifications; for X-ray analysis. All X-ray scans were conducted in transmission mode in a 1 atm He environment and at ambient temperature. The end-station specifications; for X-ray analysis. All X-ray scans were conducted in transmission mode in a 1 atm He environment and at ambient temperature. The end-station specifications; for X-ray analysis.
were tested, and found to be negligible relative to the real spectral differences caused by differences in Fe mineralogy. Because transmission X-ray spectrometry is sensitive to saturation effects, only the normalized spectra with a maximum peak intensity (i.e., ~709.8 eV peak) in the range of 0.17 to 0.83 were interrogated further in this study (magnetite = 57 spectra; hematite = 48 spectra; akaganeite = 66 spectra; goethite = 42 spectra; lepidocrocite = 32 spectra; and amorphous Fe oxy-hydroxide = 53 spectra). This intensity range matched the intensity range that we have observed in natural samples (Von der Heyden et al. 2012, 2014); and limits X-ray saturation effects from thicker particles. The collected spectra did thus not require mathematical smoothing.

The spectral parameters (ΔeV and intensity ratio) were calculated from the background-subtracted spectra using the “Search Min-Max” function in WinXAS (Ressler 1998). This approach, based on evaluating the first derivative of the spectra, excludes the possibility for human-induced bias when evaluating the spectra and ensures consistency across the 299 standard Fe oxide and oxy-hydroxide spectra considered in this study. The “Search Min-Max” function returns the energy position and the maximum peak absorbance intensity data for all peaks contained within the Fe L-edge spectra. The ΔeV value was calculated by subtracting the energy position of the low energy peak in the L3-edge (~708.2 eV) from the energy position of the high energy peak in the L3-edge (~709.8 eV). Similarly the intensity ratio of the split peaks in the Fe L-edge was calculated as the quotient (or peak ratio) of the low energy peak’s maximum absorbance intensity and the high energy peak’s maximum absorbance intensity.
absorbance intensity (Fig. 1). The nature of these operations ensures that the X-ray spectra do not require energy calibration and that the ΔE vs. intensity ratio tool thus represents a standard-less method for characterizing Fe mineralogy. Spectral information for additional Fe-rich phases was compiled from published literature. Peak height and energy data were obtained either by contacting the corresponding author directly or by digitizing the published figures.

Theoretical XANES calculations

The charge-transfer multiplet program CTM4XAS (Stavitski and de Groot 2010) was used to further validate the experimental observations made using Fe L-edge XANES spectroscopy. Theoretical spectral calculations can accurately reproduce the observed splitting of the Fe L-edge [e.g., by stipulating in CTM4XAS that 10Dq = 1.45, Slater integrals = 0.7 (after Miedema and de Groot 2013)]. However, certain software limitations (e.g., complexity in modeling covalency associated with bonding to oxygen and hydroxyl ligands [Miedema and de Groot 2013], the limited number of symmetry options available, and the sheer number of variables that can impact on ΔE and intensity ratio values (Fig. 2) complicate the accurate calculation of the subtle, observed variations in the ΔE and intensity ratio values when applied to the Fe oxide and -oxy-hydroxide system. Accurate calculation of spectra is further complicated by the presence of more than one Fe coordination site in some minerals (e.g., maghemite is characterized by Fe in tetrahedral and octahedral coordination).

Local structure evaluations

Additional comparisons were made between our spectral data set and various physical parameters of the respective Fe-oxide and -oxy-hydroxide coordination polyhedra. Structural details for the different Fe phases were obtained from the published crystal structure data [akaganite (Post and Buchwald 1991), ferricyanide (Michel et al. 2007), aegirine (Gualtieri and Venturelli 1999), hematite (Blake et al. 1966), lepidocrocite (Weykoff 1963), maghemite (Shmakov et al. 1995), and magnetite (Fleet 1986)]. The investigations into their coordination environments were conducted using the crystallographic programs IVTON (Balić-Žunić and Vicković 1996) and XSeed (Atwood and Barbour 2003).

Results and Discussion

Theoretical influences of Fe L-edge spectral parameters

Although the L\textsubscript{2}- and L\textsubscript{3}-edges contain the same chemical information; the L\textsubscript{2}-edge, representing the dipole-allowed 2p\textsubscript{3/2} electronic transitions to the valence orbitals, shows sharper and better resolved spectral features than the corresponding L\textsubscript{3}-edge. The splitting in the L\textsubscript{3}-edge peak is largely due to the crystal field interaction; however, the spectral shape of the L\textsubscript{3}-edge can also be influenced by inter-electronic repulsions, spin-orbit coupling, electrostatic multiplet effects, orbital covalency, and core-hole effects (de Groot et al. 1990; Hocking et al. 2010; Miedema and de Groot 2013). The split peaks of the L\textsubscript{3}-edge can be parameterized by their peak intensity ratio value and a ΔE value, representing the energy difference between the two peak positions (Fig. 1). Here we investigate the structural factors and bonding interactions that influence the ΔE and intensity ratio values, thus determining the effects of mineralogical speciation on L\textsubscript{3}-edge spectral features.

ΔE. The interaction between Fe orbitals and a ligand field removes Fe 3d orbital degeneracy and gives rise to ligand field splitting parameters such as Δ\textsubscript{A} and Δ\textsubscript{C}. A measure of the ligand field splitting is given by the relativistic term 10Dq, which is derived from UV-visible spectroscopy. Charge transfer multiplet calculations (using CTM4XAS software) reveals that the XANES L\textsubscript{3}-edge ΔE has a strong positive correlation (r\textsuperscript{2} = 0.98, data not shown) with the ligand field splitting 10Dq parameter, indicating that factors that increase the ligand field splitting (e.g., 10Dq) will similarly increase the X-ray ΔE value. This relationship is further supported by the positive correlation between measured optical 10Dq values (Sherman and Waite 1985) and the measured ΔE values for the Fe oxide and -oxy-hydroxide minerals with Fe in octahedral coordination (r\textsuperscript{2} = 0.64, Table 1). The differences between the optical 10Dq value and the X-ray ΔE value (Table 1; 10Dq greater than ΔE by ~12–25%) do not agree well with the theoretical calculations that predict that for 10Dq values less than 1.98; the 10Dq value should be less than the ΔE value. This offset does, however, agree well with previous work conducted on the high-spin Mn\textsuperscript{2+} system (Cramer et al.
1991), which showed that the X-ray data reflects the crystal field strength in the final state (i.e., not the ground state). The decreased splitting measured by X-ray techniques may be attributed to core-hole effects (Cramer et al. 1991).

Because of their strong impacts on the ligand field splitting parameter and because of the positive relationship between 10Dq and ΔEv, Fe valence state and Fe coordination number represent first-order impacts on the magnitude of the ΔEv value. Fe2+ phases show a larger degree of variability in their ΔEv value [1.1–2.8 eV (Fig. 3a)], with Fe3+ silicates in particular showing the highest values (2.2–2.8 eV). The Fe3+ system is relatively more constrained; comprising of ΔEv values ranging between 1.3–2.0 eV, with the majority of common Fe-oxides in the range of 1.4–1.7 eV. The coordination environment, specifically the coordination number (CN), is known to impact directly on the degree of ligand field splitting (e.g., Δ = 1/eD; Fig. 1c); and is thus expected to impact on the magnitude of the ΔEv value. This is confirmed by an analysis of the polymorphs of the Fe3+PO4 system. Heterosite, the octahedral-coordinated Fe3+PO4 polymorph (CN = 6), has a measured ΔEv value of 1.59 (Augustsson et al. 2005), whereas its tetrahedral counterpart (CN = 4), rodolicoite, has a much lower ΔEv value (0.34; de Groot 2005) and is characterized by a weak low energy feature.

**TABLE 1.** Comparison between various methods for determining d-orbital splitting

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔEv (STXM)</th>
<th>Optical 10Dq</th>
<th>Oxygen K-edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>1.54</td>
<td>1.90</td>
<td>–</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>1.65</td>
<td>1.98</td>
<td>–</td>
</tr>
<tr>
<td>Hematite</td>
<td>1.53</td>
<td>1.74</td>
<td>1.41</td>
</tr>
<tr>
<td>Maghemite</td>
<td>1.43</td>
<td>1.91</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Notes: 1 Our data, 2 Sherman and Waite (1985), 3 Sherman (2005), 4 Gilbert et al. (2010). Data set limited to the Fe-oxide and oxy-hydroxide system because of the scope of this study and because 10Dq values for Fe-silicate species are difficult to estimate due to low symmetry and trace impurities (Burns 1970). Data for maghemite (γ-Fe2O3) may be complicated by the presence of Fe in both octahedral (O3) and tetrahedral (t2) sites. 5 Presence of both oxo- and hydroxyl ligands prevents direct determination of orbital splitting from the oxygen K-edge.

Ligand effects, which can influence the extent of ligand field splitting, play a second-order role in impacting spectral ΔEv values. Specifically, the spectrochemical series can be used as a semi-quantitative measure in determining the relative ligand field splitting with strong field ligands such as SO42− [ΔEv = 1.58–1.65 (Shirakawa et al. 2007; Peak et al. 2012)] displaying the high ΔEv, whereas weak field ligands such as NO3− [ΔEv = 1.41 (Peak et al. 2012)] have lower values. To exclude ligand-specific effects, additional comparisons were made using only the spectral parameters of the polymorphs of the Fe oxide and oxy-hydroxide system, where the only ligands are O2− and OH−. Despite the chemical similarities between these two ligands (i.e., both form partially covalent Fe-O bonds through hybridization of O 2p and Fe 3d orbitals), the hydrogen present in the hydroxyl (OH−) ligand significantly affects the electron density around the bonding oxygen (Welsh and Sherwood 1989), and thus the ionicity of metal-ligand bonds (Sherman 1985). This effect has a stronger impact on the binding energies associated with O 1s or 2s electronic transitions to valence orbitals (Welsh and Sherwood 1989; Gilbert et al. 2007), yet it also affects the structure of the valence orbitals, notably leading to an increase in the ligand field splitting (Fig. 1c). These small-scale shifts in the spectral parameters (e.g., ΔEv) due to subtle changes in the covalency of the oxygen-metal bonds could not be precisely reproduced using the CTM4XAS software.

Because Fe L-edge spectroscopy probes only the local coordination environment (van der Laan and Kirkman 1992); additional differences in the measured ΔEv values in the iron oxide and iron oxy-hydroxide system must be related to variations in the coordination polyhedra. The crystal structure of the different polymorphs dictate the geometry (and thus site symmetry), and number and type (face-, edge-, or point-sharing) of linkages associated with the local Fe coordination polyhedra (Fig. 4). Several of the minerals consist of multiple Fe coordination sites (Fig. 4: akaganeite, ferrihydrite, maghemite, magnetite) and each polyhedron is associated with its own degree of distortion and

**FIGURE 3.** (a) ΔEv vs. intensity ratio plot of spectral parameters of various published Fe phases. An intensity ratio of −1 can be used to distinguish between Fe2+–rich and Fe3+–rich phases (adapted from Von der Heyden et al. 2012—see original for all references). (b) ΔEv vs. intensity ratio plot for the Fe oxide and Fe oxy-hydroxide system, showing how characteristic spectral features can be used to differentiate between phases with differing structure and chemistry. Error bars reflect one times standard deviation.
decline in symmetry away from perfect octahedral symmetry. The experimental XANES spectrum (from the bulk Fe oxide or oxy-hydroxide) reflects the spectral contributions from each of these polyhedra. Although theoretical calculations can reproduce the splitting of the Fe L$_3$-edge, accurate theoretical calculation of the fine structure associated with structural variations and symmetry declines across multiple Fe sites will be challenging to calculate as each distorted polyhedron will be characterized by its own multiplicity, peak shifts and line-broadenings. The experimental spectra, however, show the net effects of all of the structurally controlled distortions and these third-order effects result in $\Delta$E shifts of around 0.12 eV (Figs. 3b and 4).

Figure 5 summarizes the relationship between spectral parameters and several properties of Fe coordination polyhedra in Fe oxides and oxy-hydroxides (averaged if more than one Fe site was present). Angle variance and quadratic elongation are distortion measures relating, respectively to the deviations in ligand bond angle and bond length away from those associated with an ideal polyhedron (Robinson et al. 1971); whereas volume distortion percentage is measured relative to the volume of an ideal polyhedron (Makovicky and Balić-Žunić 1998; Balić-Žunić 2007). The $\Delta$E spectral parameter displays a strong positive correlation with bond-angle variations and volume distortion of the polyhedron while it exhibits a strong negative correlation with variability in ligand bond length. Comparison between the polyhedral volume distortion and the $\Delta$E value yields a strong positive correlation. The number and types of polyhedral linkages also influence the local bonding environment within the Fe coordination polyhedron. The $\Delta$E value shows only moderate and negative correlation to the total number of polyhedral linkages with the prevalence of edge-sharing linkages over corner-sharing linkages favoring higher $\Delta$E values. Finally, additional distortion effects can occur for example, with the presence of trace impurities. These distortion effects can exert profound influence the geometry and point group symmetry of coordination polyhedra, with the ability to remove degeneracy of molecular orbitals (Fig. 1c; Sherman 1985a). Such multiplet effects can lead to spectral peak broadening and shifts in the $\Delta$E value, depending on the composition of the orbitals resulting from distorted symmetry.

**Intensity ratio.** The intensity ratio of the constituent split peaks of the Fe L$_3$-edge spectrum have traditionally been used in the determination and quantification of Fe valence state (Cressey et al. 1993; van Aken et al. 2002; Miyajima et al. 2004; Calvert et al. 2005; Cavé et al. 2006; Dynes et al. 2006; Liu et al. 2015). This is because the Fe oxidation state, and the corresponding number of vacancies in the valence orbitals, exert the strongest control on Fe L$_3$-edge intensity ratio (Fig. 3a). An intensity ratio of $\sim$1 can be used to clearly differentiate between the Fe$^{2+}$ species and Fe$^{3+}$ species, the former having an intensity ratio around 0.51 ($\pm$0.18), whereas the latter averages around 2.00 ($\pm$1.50). Mixed valence species have an intensity ratios closer to 0.7 ($\pm$0.30). From theoretical calculations, the strength of the ligand field (as measured by the 10Dq value) also has a strong influence on the intensity ratio value (i.e., for O$_6$ symmetry with Slater integrals set to 70% (e.g., Miedema and de Groot 2013) the correlation coefficient ($r^2$) between the intensity ratio and 10Dq is 0.99). Additional first-order influences on the number of orbital vacancies, and thus the L$_3$-edge intensity ratio, include the coordination number (O$_6$ vs. T$_5$) and the spin state (high spin vs. low spin) of the Fe species.

Second-order influences on the intensity ratio value are attributed to ligand effects on the chemical character of available singly occupied and unoccupied molecular orbitals. In accordance with the Laporte selection rule (Burns 1970), it is particularly the amount of Fe d-character (or conversely, the amount of ligand p-character) in these valence orbitals that determines the likelihood of dipole-allowed $2p \rightarrow 3d$ electronic transitions. In their work on differential orbital covalency in Fe chelators, the L-$\text{\chi}$-edge splitting data of Hocking et al. (2010) showed good correlation with both the bond length (affected by bond covalency/ionicity) and the percent of d-character (versus high spin) in valence orbitals (Table 2). Bond covalency is closely tied to n-bonding interaction that occurs exclusively between ligand p-orbitals and the Fe 3d $t_{2g}$ subset of orbitals. If the low- and high-energy peaks in the Fe L$_3$-edge spectrum are tentatively assigned $t_{2g}$ and $e_g$ character, respectively, then changes in the overall bond covalency, a ligand-specific effect, will impact on the observed spectral intensity ratio. Ligand effects influence the intensity ratio by up to a value of 0.2 when ligands are similar (e.g., $O_2^-$ vs. $OH^-$, Fig. 3b), and this influence can exceed 0.4 when ligands are vastly different [S$^{2-}$: 0.8 (Bormite (Miklín et al. 2005)) vs. NO$_2^-$: 0.4 (Peak and Regier 2012)].

Polyhedral distortion also affects the orbital composition by inducing multiplet structure in which the ligand p-character is further split among orbitals at different energy levels. Applying the Robinson et al. (1971) scheme that uses quadratic elongation and variance of bond angles to measure polyhedral distortion; we find that the intensity ratio values for species from the Fe-oxide and oxy-hydroxide do not correlate with variations in bond angle and show only relatively weak positive correlation with the changes in bond length (Fig. 5a). The correlation between intensity ratio value and the volume distortion percentage is negative ($r^2 = 0.59$, Fig. 5c), indicating that high ratios result from low polyhedral distortions. The intensity ratio shows better correlation with the number and type of polyhedral linkages experienced between adjacent Fe coordination polyhedra. Large intensity ratios are strongly favored as the number of polyhedral linkages increases, particularly when the proportion of corner-sharing linkages increases preferentially (Fig. 5a). Figure 5 additionally alludes to the inverse relationship between $\Delta$E and intensity ratio, indicative that the third-order impacts that lead to high $\Delta$E also typically result in lower intensity ratio values.

**Application of L$_3$-edge XAS to Fe-oxide and oxy-hydroxide speciation**

The sensitivity of the Fe L$_3$-edge to local coordination (i.e., variations in ligand arrangement and type) renders it an ideal probe to investigate Fe mineralogy and to derive chemical and structural information from amorphous Fe phases. Figure 3b plots the spectral parameters ($\Delta$E and intensity ratio) of Fe oxide and oxy-hydroxide mineral standards ranging in size between 20 and 400 nm. The spectral parameters did not show any size-dependent trends in their magnitudes. The plot is limited to the Fe-O and Fe-OH system to limit any additional ligand-specific effects on the spectral parameters (e.g., electronegativity, ionic
Figure 4. Iron polyhedra with local coordination for the Fe oxide and oxy-hydroxide mineral phases analyzed in this study. Polyhedral distortions are the result of chemical and mineralogical (i.e., number and type of polyhedral linkages) properties of the respective phases. Inset octahedra are relative to a perfect octahedron and give an idea of the bond angle distortions and volume distortion (percent volume distortion measure indicated in bold). All bond lengths are in angstrom units (Å) and all images were generated using XSeed (Atwood and Barbour 2003) and crystallographic data from published references: 1 = Gualtieri and Venturelli (1999); 2 = Wycoff (1963); 3 = Post and Buchwald (1991); 4 = Michel et al. (2007); 5 = Blake et al. (1966); 6 = Fleet (1986); 7 = Shmakov et al. (1995).

(Continued on next page)
size and charge, and specific bonding interaction). Each solid square represents the average ΔE_{v} and intensity ratio value for each standard phase, and these averages were calculated by considering only the 299 environmentally relevant spectra (i.e., only spectra with an L_{3}-edge high energy peak maximum of between 0.17 and 0.83), to limit saturation effects associated with transmission mode XANES. Despite constraining this range, some saturation was still observed and resulted in the broader horizontal error bars associated with the intensity ratio averages (Fig. 3b) relative to the error bars associated with the ΔE_{v} values (both sets of error bars represent 1× standard deviation).

The measured spectral parameters for the various phases are reported in the format intensity ratio (±intensity ratio standard deviation): ΔE_{v} (±ΔE_{v} standard deviation) and are amorphous Fe oxy-hydroxide (0.51 ± 0.02: 1.50 ± 0.02); goethite (0.52 ± 0.04: 1.54 ± 0.02); akaganeite (0.47 ± 0.02: 1.54 ± 0.04); lepidocrocite (0.48 ± 0.03: 1.65 ± 0.03); hematite (0.66 ± 0.06: 1.52 ± 0.06); and maghemite (0.55 ± 0.07: 1.43 ± 0.06). The magnetite point is plotted from data collected from a single standard spectrum (intensity ratio = 0.72; ΔE_{v} = 1.14) and the associated error bars are estimated from the average of the standard deviations found in the other six data points. The magnetite spectral shape and position of this field on the plot matches well with other published data (Kendelewicz et al. 2000; Regan et al. 2001; de Smit et al. 2009; Zhu et al. 2015). A series of two-tailed t-tests (95% confidence limit) was conducted on these averages, and all data points are significantly different from one another in terms of the combinations of their ΔE_{v} and intensity ratio values.

The most noticeable controls on the phase distribution in the plot are the first-order and second-order effects of coordination number and ligand type, respectively. Mineral phases characterized by the presence of tetrahedral iron (magnetite; Fig. 4j), maghemite (Fig. 4m), and possibly ferrihydrite (Fig. 4g; Michel et al. 2007; Peak and Regier 2012; Guyodo et al. 2012) typically have the lowest values for ΔE_{v}. This is in agreement with the generalized chemical trend for ligand field splitting in which Δ_{0} = 4/9Δ_{O} (e.g., Burns 1970) (Fig. 1c). Although the number of different types of ligands has been limited in this data set, the presence of hydroxyl ligands causes marked shifts in the molecular orbital structure of Fe polyhedra [Fig. 1c: FeO_{4}(OH)_{2} octahedron]. The presence of the hydroxyl ligands in the FeOOH mineral structure also results in lower intensity ratio values (<0.55), relative to pure oxide phases (intensity ratio greater than 0.55; Fig. 3). The lower intensity ratio values in Fe oxy-hydroxide phases indicate that bonding to hydroxyl groups results in modifications to the valence orbital compositions, making transitions to the high energy orbitals relatively more favorable. For example, Sherman (1985) found that hydroxyl ligands appear to promote the covalency between Fe^{3+} centers and O^{2−} atoms. Following the discussion in section 1.2., this
will result in more O 2p character in the t2g valence orbital subset making the electronic transitions less allowable, and thus decreasing the observed intensity ratio in Fe oxy-hydroxides (Fig. 3b).

On account of their polymorphism, the Fe oxy-hydroxides have equivalent chemical stoichiometry and are closely grouped on the ΔE vs. intensity ratio diagram. Third-order distortion effects need to be invoked to explain the small differences in their distribution on the plot. Goethite (α-FeOOH) has a tunnel structure (Cornell and Schwertmann 2003) characterized by a single type of Fe octahedron showing only moderate percentage volume distortion (Fig. 4a). Distortion in the goethite octahedron is caused by differences in the coordinating ligand (e.g., Fig. 4a: longer hydroxyl oxygen bond distances: 2.072–2.097 Å vs. shorter oxygen group bond distances 1.928–1.955 Å) and by variations in the type of linkages to adjacent Fe octahedra (e.g., the longest bonds are between the Fe center and hydroxyl ligands that are shared by two adjacent edge-sharing octahedra).

Akaganeite is structurally similar to its polymorph goethite as they both have equal number and types of polyhedral linkages between adjacent octahedra. It is thus not surprising that their fields in the ΔE vs. intensity ratio plot are close and partially overlap. There is insignificant difference in the degree of splitting in the valence orbitals (both ΔE values ~1.54) and their plotted fields are thus only offset by a difference in intensity ratio of ~0.05. Although the spectral interpretation of akaganeite may be slightly complicated by the presence of chloride ions and two structurally different Fe sites, the relationships shown in Figure 5 should still be explored when explaining the observed shift in intensity ratio. The relationship between goethite intensity ratio (0.52) and akaganeite intensity ratio (0.47) does not conform to the trends in the either the angle variance or the quadratic elongation distortion parameters, both of which are only weak to moderate trends. The higher averaged volume distortion in the akaganeite octahedra relative to the goethite octahedron is in good agreement with the strong negative correlation between intensity ratio and percentage volume distortion (Fig. 5c). The effect of volume distortion may be larger than alluded to by the average value reported for the akaganeite structure, as the resolved values for each center show that the akaganeite Fe1 octahedron has the highest degree of volume distortion for any of the Fe oxide or oxy-hydroxide polyhedra (Fig. 4c).

Lepidocrocite differs from its polymorphs in that it has a layered structure and each Fe octahedron consists of only two hydroxyl groups. Mineral stoichiometry is achieved by the linkage arrangement between adjacent polyhedra, as each hydroxyl group is only shared by one edge-sharing octahedron, whereas each oxygen ligand is shared by two adjacent edge-sharing octahedra. Akaganeite is structurally similar to its polymorph goethite as they both have equal number and types of polyhedral linkages between adjacent octahedra. It is thus not surprising that their fields in the ΔE vs. intensity ratio plot are close and partially overlap. There is insignificant difference in the degree of splitting in the valence orbitals (both ΔE values ~1.54) and their plotted fields are thus only offset by a difference in intensity ratio of ~0.05. Although the spectral interpretation of akaganeite may be

Table 2. Intensity ratio correlation to bond length and orbital character in organic Fe3+ chelates

<table>
<thead>
<tr>
<th>Species</th>
<th>Intensity ratio</th>
<th>Average bond length (Å)</th>
<th>Average % d-character in valence orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(ox)3]3–</td>
<td>0.49</td>
<td>2.008</td>
<td>84</td>
</tr>
<tr>
<td>[Fe(pha)3]</td>
<td>0.43</td>
<td>2.013</td>
<td>68</td>
</tr>
<tr>
<td>[Fe(cat)3]3–</td>
<td>0.39</td>
<td>2.017</td>
<td>65</td>
</tr>
</tbody>
</table>

Note: All data after Hocking et al. (2010).

Figure 5. (a) Goodness of fit plot obtained from r² values derived from comparisons between spectral parameters and various structural and distortion parameters. Plus and minus symbols refer to positive and negative correlations, respectively. (b) Volume distortion percentage vs. ΔE and, (c) volume distortion percentage vs. intensity ratio plots for polyhedra from the Fe oxide and oxy-hydroxide system. Trend lines reflect the degree of correlation between the respective parameters.
to $\Delta D$ and the highest volume distortion percentage (+ correlation to $\Delta D$). The average lepidocrocite intensity ratio value (0.48) is very similar to that of akaganeite and its dissimilarity to the goethite value can only be attributed to the differences in volume distortion percentage and the percentage of corner sharing polyhedra.

The Fe oxide side of the plot (intensity ratio > 0.55) consists of the polymorphs of the Fe$_2$O$_3$ system and the mixed valence phase magnetite. The magnetite point is plotted from data collected from only one spectrum and the associated error bars are estimated from the average of the standard deviations found in the other six data points. The magnetite spectral shape and position of this field on the plot matches well with other published data (Kendelevicz et al. 2000; Regan et al. 2001; de Smit et al. 2009; Zhu et al. 2015). Magnetite has a low $\Delta D$ value, largely attributable to the presence of tetrahedral Fe$^{3+}$, which has a low degree of crystal field splitting relative to octahedral Fe$^{3+}$ (Fig. 1c). The low volume distortion in the polyhedra can further lower the observed $\Delta D$ value, as can the large percentage of corner-sharing linkages (Figs. 4i and 4j). Magnetite has the highest intensity ratio due to structural Fe$^{3+}$, the absence of hydroxyl ligands, a high number adjacent polyhedra and a large proportion of the polyhedral linkages connecting via corner-shared oxygen atoms.

Maghemite and hematite are both polymorphs of Fe$_3$O$_4$ with the former having a cubic crystal structure and the latter belonging to the trigonal crystal system. Spectral interpretation of the maghemite data points may be complicated by the presence of three different types of Fe sites (Figs. 4k–4m), which can lead to additional multiplicity in the number and energies of the transitions to valence orbitals. Despite being structurally similar to magnetite, the maghemite point plots away from the magnetite point on the $\Delta D$ vs. intensity ratio plot (Fig. 3b). Although both phases have low $\Delta D$ values due to the presence of tetrahedral Fe, the maghemite $\Delta D$ value (1.13) is lower than the magnetite $\Delta D$ value (1.43). Hematite has a larger $\Delta D$ value than the other two Fe oxide minerals, and this may be partially attributed to the prevalence of face-sharing linkages between adjacent polyhedra (i.e., lower percent of corner-sharing linkages). Additional support for the positioning of hematite above maghemite on the $\Delta D$ scale is given by hematite’s higher angle variance, lower quadratic elongation and higher percentage volume distortion. Aside from the absence of hydroxyl groups, the major factors increasing the intensity ratio of the oxide phases relative to the oxy-hydroxides, is the higher total number of polyhedral linkages associated with each Fe polyhedron and the enhanced proportion of these being corner-sharing linkages.

Amorphous iron oxy-hydroxide, or ferrihydrite, plots with a $\Delta D$ value of 0.51 ± 0.02 and an intensity ratio value of 1.50 ± 0.02. The position of this field on the $\Delta D$ vs. intensity ratio plot may render some insights into the controversy that currently ensues over the structure of ferrihydrite (Jambor and Dutrizac 1998; Janney et al. 2001; Michel et al. 2007; Peak and Regier 2012; Manseau 2012; Gilbert et al. 2013). Amorphous Fe oxy-hydroxide has an intensity ratio that is less than 0.55, suggesting that a proportion of the ligands present in the local coordination environment are hydroxyl groups. The amorphous Fe oxy-hydroxide field plots closest to goethite suggesting a degree of structural similarity between the two phases, particularly that amorphous Fe oxy-hydroxide is likely to have a more contained structure relative to the layered lepidocrocite. Because of its greater intensity ratio compared to lepidocrocite and akaganeite, amorphous Fe oxy-hydroxide is likely to have a lower degree of average percentage volume distortion than these two minerals. The $\Delta D$ value for amorphous Fe oxy-hydroxide plots in the lower range of $\Delta D$ values; and low $\Delta D$ values are more strongly associated with the Fe oxide phases (e.g., maghemite, magnetite) than with Fe oxy-hydroxide phases. This suggests that other structural properties are responsible for the decreased $\Delta D$ value. Plausible structural explanations for the lowered $\Delta D$ value include the presence of tetrahedral Fe, a lower proportion of hydroxyls than is found in oxy-hydroxide structure, or that there is a lower average volume distortion in each polyhedron (e.g., characterized by more variable bond lengths but less variable bond angles).

Comparing these theorized characteristics to the reported structure for ferrihydrite proposed by the Michel model (Figs. 4e–4g); we find a good agreement. Their model reports a presence of 10–20% structural Fe$^{3+}$ in tetrahedral coordination, although subsequent Fe L-edge work has suggested that the amount of tetrahedral Fe$^{3+}$ could be as high as 40% (Peak and Regier 2012). Because our amorphous Fe oxy-hydroxide $\Delta D$ value is larger than the maghemite $\Delta D$ value, an explanation based solely on the presence of tetrahedral Fe$^{3+}$ would then argue for a lower percentage contribution of Fe$^{3+}$ in tetrahedral coordination, in agreement with data from Michel et al. (2007). The Michel model, which is based on the structure of the mineral akdalaite [Al$_9$O$_{16}$OH$_2$], suggests that the ferrihydrite chemical formula is Fe$_8$O$_{16}$OH$_2$. This presence of hydroxyl ligands can explain the low (<0.55) intensity ratio observed in our results, and a low proportion of hydroxyl ligands relative to oxygen ligands (e.g., less than the 50:50 ratio associated with goethite) may also be (partially) causative for the lower $\Delta D$ value (Fig. 1c). This is in agreement with recent work conducted by Gilbert et al. (2013) who have suggested a “hybrid” structural model for ferrihydrite characterized by a significantly lower proportion of structural hydroxyls than is found in goethite. Distortion effects can cause third-order variations to the $\Delta D$ values; particularly, an increase in vol% distortion favors higher $\Delta D$ values (Fig. 5a). However, the average percentage volume distortion for ferrihydrite (2.21%), predicted by the Michel model, is higher than for the goethite and akaganeite distortion values (Figs. 4a and 4c–4g). This indicates that this distortion effect cannot be responsible for the observed low $\Delta D$ value, thereby highlighting the importance of the other chemical factors (e.g., tetrahedral Fe and the presence of hydroxyls) in explaining our observed results.

**Implications**

Our work reveals a new means to assess nanoscale mineral compositions. The high spectral and spatial resolution associated with Fe L$_{3}$-edge spectroscopy provides an ideal probe for investigating mineralogical and chemical variations in small (sub-micrometer-sized) particles. The technique is particularly well suited to natural samples because the analytical conditions (soft X-ray probe; 1 atm $P$; ambient $T$) ensure that the sample integrity is maintained. Because the Fe L$_{3}$-edge can be parameterized into the $\Delta D$ (reflecting the energy difference between...
the valence orbital sets) and the intensity ratio value (reflecting the chemical composition of the valence orbital sets), the discrete fields occupied by Fe minerals on the ΔE vs. intensity ratio plot reflect important molecular-level chemical variations characteristic of the coordination polyhedra of different Fe mineral phases. The plot is thus a useful tool for investigating the chemistry and mineralogy of sub-micrometer-sized particles in a diverse array of environments (e.g., aerosols, fluvial and marine colloids, soil systems).

Our previous work has applied this tool to study Fe particle speciation in the South Atlantic and Southern Oceans (Von der Heyden et al., 2012), where Fe biogeochemistry is an important driver of primary productivity (i.e., representing the biological conversion of the greenhouse gas CO₂ to phytoplankton biomass). We have also used the ΔE vs. intensity ratio plot to show that ferrous colloids are stable in oxygenated fluvial, lacustrine, and marine surface waters; and that these Fe²⁺ colloids have a meaningful association with carboxamide functional groups present in organic matter (Von der Heyden et al., 2014). These examples showcase the applicability of the plot toward understanding Fe mineral speciation; and it is foreseen that the plot will continue to render invaluable insights into Fe mineralogy in diverse environments, particularly as scientists increasingly probe the role of Fe phases in the sub-micrometer-size domain [e.g., Fe nanoparticle research (Wigginton et al. 2007)].

ACKNOWLEDGMENTS

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