Investigating nanoscale mineral compositions: Iron $L_{2,3}$-edge spectroscopic evaluation of iron oxide and oxy-hydroxide coordination

BJORN P. VON DER HEYDEN$^1$,*, ALAKENDRA N. ROYCHOUDHURY$^1$, TOLEK TYLISZCZAK$^3$, AND SATISH C.B. MYNENI$^3$

$^1$Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa
$^2$Department of Geosciences, Princeton University, Princeton, New Jersey 08544, U.S.A.
$^3$Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, U.S.A.

**ABSTRACT**

The iron (Fe) $L_{2,3}$-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 $L_{2,3}$-edge are parameterized according to the difference in the energy position ($\Delta E$), and the quotient (intensity ratio) of the two peaks' maxima. Variations in the $\Delta E$ 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 $\Delta E$ 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-less phase-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 $L_{2,3}$-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; Mikhlín 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. 1992; 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; Cressy 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 $2p$ and $2p$ 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., Dynes et al. 2006; Bluhm et al. 2006). The foremost reason for this is that XAS allows for the