Investigating nanoscale mineral compositions: Iron L₂-edge spectroscopic evaluation of iron oxide and oxy-hydroxide coordination

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ABSTRACT

The iron (Fe) L₂,₃-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-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 are strongly linked to factors that impact on the strength of the ligand field (e.g., Fe valence state, coordination number, and the nature of ligand bonding). The intensity ratio is affected by the strength of the ligand field and by the composition of the resultant molecular orbitals. The Fe valence state also strongly affects the intensity ratio, and an intensity ratio equal to one can be used to distinguish between Fe²⁺ and Fe³⁺ minerals. The effects of polyhedral distortion on the magnitudes of ΔE and intensity ratio values were tested by considering the Fe oxide and -oxy-hydroxide mineral system, in which ligand effects are limited to the differences between the oxygen and hydroxyl ligands. In this system, the distribution of Fe oxide and -oxy-hydroxide minerals on a ΔE vs. intensity ratio 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-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 L₂,₃-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. 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; 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 2s 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