

## 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)  $L_{2,3}$ -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  $L_3$ -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  $\Delta E$  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 Fe<sup>2+</sup> and Fe<sup>3+</sup> minerals. The effects of polyhedral distortion on the magnitudes of  $\Delta E$  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  $\Delta E$  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  $\Delta E$  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