

Quantitative electron microprobe analysis of $\text{Fe}^{3+}/\Sigma\text{Fe}$: Basic concepts and experimental protocol for glasses

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ABSTRACT

The presence of an unfilled 3d electron shell in the transition metals of the first series is manifested in X-ray self-absorption effects that cause distortions in the L emission spectra. In particular, one observes peak shape changes and peak position shifts toward lower energies that are attributed to X-ray photon self-absorption in the specimen. Self-absorption corresponds to partial overlap of both L -emission and absorption transitions in the region of the Fermi level. Such an overlap is related to relaxation effects that follow the creation of the core hole in the studied ions. For Fe, the overlap between the $\text{Fe}L\alpha$ emission peak and the corresponding $\text{Fe}L_{\text{III}}$ absorption band is clearly higher for Fe^{2+} than for Fe^{3+} , leading to an enhanced self-absorption induced shift of the $\text{Fe}L\alpha$ peak for Fe^{2+} . The shift of the $L\alpha$ peak between Fe^{2+} and Fe^{3+} can be measured with the electron microprobe and hence exploited to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in silicates and glasses. For that purpose, an empirical method has been established based on working curves constructed from reference materials. A complete set of working curves is presented for glasses as well as an original experimental protocol.

Most glasses are electron beam sensitive and suffer especially from beam-induced oxidation-reduction mechanisms that are related to the implanted charge. The flux of Na^+ ions from the surface the depth in the glass (driven by the electric field induced by the electrostatic charge) tends to oxidize the surface whereas, concurrently, the counterflux of electrons produced by excitonic mechanisms and trapped at Fe^{3+} sites tends to reduce the surface. Therefore operating conditions should be set to minimize these phenomena, as they are a source of large discrepancies in $\text{Fe}^{3+}/\Sigma\text{Fe}$. The application of the current protocol gives uncertainties of about $\pm 5\%$ absolute for specimens with nominal total Fe concentrations ranging from 6 to 9 wt% (accuracy and precision on $\text{Fe}^{3+}/\Sigma\text{Fe}$ dramatically depend on the total Fe wt% concentration). Results obtained from a suite of basaltic glasses exhibit errors higher than $\pm 5\%$ absolute. Improved performances are expected for the method after the method can be used with promising new high resolution and high sensibility X-ray optics.