

## Direct Determination of Ferrous - Ferric Concentrations with the Electron Microprobe

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This presentation describes a preliminary study for determining the oxidation state of iron ( $\text{Fe}^{3+}/\text{sum Fe}$ ) with the electron microprobe (EMP) by measuring the self-absorption induced shift of the Fe  $L\alpha$  peak emitted from minerals and glasses. In transition metals of the first row, the L spectra exhibit common distortions, namely peak position shifts, peak shape alterations and changes in the  $L\beta$  to  $L\alpha$  ratios, caused by the large difference in the self-absorption coefficients ( $\mu/\rho$ ) on either sides of the  $L_3$  absorption edges that are in close proximity of the  $L\alpha$  peak maxima. Measurements performed on  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{1-x}\text{O}$  oxides have shown that self-absorption effects are stronger for the latter oxide, leading to enhanced  $\text{Fe}^{2+}$   $L\alpha$  peak shift towards larger wavelength as the beam energy increases. First measurements performed on silicates have confirmed that enhanced self-absorption of Fe  $L\alpha$  occurs on  $\text{Fe}^{2+}$  sites. These measurements consisted of plotting the Fe  $L\alpha$  peak position at a fixed beam energy (15keV) against the total Fe wt% concentration for two series of  $\text{Fe}^{2+}$ - and  $\text{Fe}^{3+}$ - bearing silicates. The latter data have shown that both  $\text{Fe}^{2+}$   $L\alpha$  and  $\text{Fe}^{3+}$   $L\alpha$  peaks shift continuously towards larger wavelength as the Fe wt% concentration increases, with enhanced shifts for  $\text{Fe}^{2+}$   $L\alpha$ . Plots of both end-member silicate series can be adjusted by Ln curves. No effects of the site geometry were detected on the variations of the Fe  $L\alpha$  peak position. Precisions achieved for further  $\text{Fe}^{3+}/\text{sum Fe}$  measurements strongly depend on the total Fe wt% concentration. For low Fe concentrations (below 3.5wt%), the

uncertainty in the peak position measured by the EMP spectrometers leads to error bars that are not little compared with the distance between both above  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  curves, which should be reflected as prohibitive lack of precision on  $\text{Fe}^{3+}/\text{sum Fe}$ . A second set of plots has shown the variations of the peak position relative to the previous  $\text{Fe}^{2+}$ -  $\text{Fe}^{3+}$  curves, as a function of the nominal  $\text{Fe}^{3+}/\text{sum Fe}$ , for a series of reference minerals (hydrated and non-hydrated) and basaltic glasses. Data from chain and sheet silicates (e.g., pyroxenes, amphiboles, micas) exhibited strong deviations compared to other phases (e.g. garnets, Al-rich spinels, glasses), due to reduced self-absorption of Fe  $L\alpha$ . Intervalence charge transfer (IVCT) mechanisms between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites may be at the origin of these deviations. The main limitation of microbeam methods in general deals with beam damage. This aspect has been carefully studied for basaltic glasses and optimal beam conditions have been established (typically electron doses higher than those corresponding to 130nA and 30 $\mu\text{m}$  beam diameter should be avoided to prevent large beam induced oxidation-reduction phenomena). Next developments in progress concern (i) other beam sensitive phases such as hydrated glasses and (ii) minerals in which Fe  $L\alpha$  is affected with large matrix effect corrections (e.g. Cr- and Ti-rich oxides where Fe  $L\alpha$  is strongly absorbed), for which the self-absorption-induced shift of Fe  $L\alpha$  is different from that of common silicates and glasses.