

Fe³⁺/ΣFe vs. FeLα peak energy for minerals and glasses: Recent advances with the electron microprobe

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ABSTRACT

This paper describes a preliminary study that attempts to determine the oxidation state of Fe (Fe³⁺/ΣFe) with the electron microprobe (EMP) by measuring the self-absorption induced shift of the FeLα 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*β/*L*α ratios, caused by the large difference in the self-absorption coefficients (μ/ρ) on either sides of the *L*₃ absorption edges that are in close proximity to the *L*α peak maxima. Measurements performed on α-Fe₂O₃ and Fe_xO oxides have shown that self-absorption effects are stronger for the later oxide, leading to enhanced Fe²⁺Lα peak shift toward longer wavelengths as the beam energy increases. First measurements performed on silicates have confirmed that enhanced self-absorption of FeLα occurs on Fe²⁺ sites. The measurements consisted of plotting the FeLα peak position at a fixed beam energy (15 keV) against the total Fe concentration for two series of Fe²⁺- and Fe³⁺-bearing silicates. In a first step, these data have shown that both Fe²⁺Lα and Fe³⁺Lα peaks shift continuously toward longer wavelengths as the Fe concentration increases, with enhanced shifts for Fe²⁺Lα. For silicates containing only Fe²⁺ or Fe³⁺, no effects of the site geometry were detected on the variations of the FeLα peak position. A second set of plots has shown the variations of the peak position relative to the previous Fe²⁺-Fe³⁺ curves of step 1, as a function of the nominal Fe³⁺/ΣFe, 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 FeLα. Intervalence-charge transfer (IVCT) mechanisms between Fe²⁺ and Fe³⁺ sites may be the origin of these deviations. These crystal-structure effects limit the accuracy of the method for mixed Fe²⁺-Fe³⁺ valence silicates. Precisions achieved for further Fe³⁺/ΣFe measurements strongly depend on the total Fe concentration. For basaltic glasses containing an average of 8 wt% Fe and 10% Fe³⁺/ΣFe, the precision is about ±2% (absolute). For low Fe concentrations (below 3.5 wt%), the uncertainty in the peak position measured by the EMP spectrometers leads to error bars that are similar to with the separation of the curves fitted to the Fe²⁺ and Fe³⁺ plots, which is propagated as prohibitive lack of precision for Fe³⁺/ΣFe (>70% relative). A major 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 (in general, electron doses higher than those corresponding to 130 nA and 30 μm beam diameter should be avoided to prevent large beam induced oxidation phenomena). Additional work, in progress, concerns: (1) other beam-sensitive phases such as hydrated glasses; and (2) minerals in which FeLα is affected by large matrix effect corrections (e.g., Cr- and Ti-rich oxides where FeLα is strongly absorbed), for which the self-absorption-induced shift of FeLα is different from that of common silicates and glasses.