

Electron probe microanalysis of $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios in calcic and sodic-calcic amphibole and biotite using the flank method

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We present an analytical approach to determine the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio in amphiboles and biotites using electron probe microanalysis (EPMA) [1]. The “flank method” applied in this study is based on the fact that the $\text{Fe}L$ line spectra show different peak positions and intensities for Fe^{2+} and Fe^{3+} , which is associated with a resonant process involving both X-ray absorption and emission. The flank positions for $L\alpha$ and $L\beta$, which correspond to sites with minimal $\text{Fe}^{3+} L3$ absorption and maximal $\text{Fe}^{2+} L2$ absorption, respectively, are determined based on the L -line spectra difference of two Fe-rich ferric and ferrous garnet endmembers, i.e. andradite and almandine. Spectra intensities measured at the $L\alpha$ and $L\beta$ flank positions for selected amphibole and biotite references can be quantitatively correlated with their Fe^{2+} weight contents by a linear relation: $L\beta/L\alpha = a + b \cdot \text{Fe}^{2+}$, in which a and b are constants calibrated upon reference materials. It is emphasized that the constants a and b may vary significantly for different mineral groups and analytical conditions. Thus, a calibration is necessary for each analytical session. Our tests show that the potential beam damage during EPMA, that may induce oxidation of the measured material, can be minimized by using a large beam size (e.g., 20 μm). The $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios determined using the EPMA flank method in natural calcic and sodic-calcic amphiboles ($\text{FeO}^{\text{T}} = 2.4\text{-}12.7$ wt%, $\text{Fe}^{2+}/\Sigma\text{Fe} = 0.45\text{-}0.75$) and biotites ($\text{FeO}^{\text{T}} = 4.3\text{-}28.2$ wt%, $\text{Fe}^{2+}/\Sigma\text{Fe} = 0.67\text{-}0.87$) are consistent within an error of ± 0.1 with the data obtained from the colorimetric wet chemistry method. The EPMA flank method has the potential to be widely applied for accurate in-situ determination of Fe oxidation states in a wide range of minerals, provided that references are available.

[1] Li *et al.* (2019) *Chem Geol* **509**, 152-162.