

## 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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , 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  $\text{Fe}^{2+}$  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  $\mu\text{m}$ ). 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  $\pm 0.1$  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.