American Mineralogist, Volume 103, pages 1445–1454, 2018

Electron microprobe technique for the determination of iron oxidation state in silicate glasses

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Abstract

We present a new calibration for the determination of the iron oxidation state in silicate glasses by electron probe microanalysis (EPMA) with the "flank method." This method is based on the changes in both intensity and wavelength of the Fe$L\alpha$ and Fe$L\beta$ X-ray emission lines with iron oxidation state. The flank method utilizes the maximum difference for the Fe$L\alpha$ and Fe$L\beta$ spectra observed at the peak flanks between different standard materials, which quantitatively correlates with the Fe^{2+} content. Provided that this correlation is calibrated on reference materials, the $Fe^{2+}/\Sigma Fe$ ratio can be determined for samples with known total Fe content. Two synthetic Fe-rich ferric and ferrous garnet end-members, i.e., andradite and almandine, were used to identify the Fe$L\alpha$ and Fe$L\beta$ flank method measuring positions that were then applied to the measurement of a variety of silicate glasses with known $Fe^{2+}/\Sigma Fe$ ratio (ranging from 0.2 to 1.0). The measured intensity ratio of Fe$L\beta$ over Fe$L\alpha$ at these flank positions ($L\beta/L\alpha$) is a linear function of the Fe^{2+}content (in wt%). A single linear trend can be established for both garnets and silicate glasses with 4–18 wt% FeO_T (total iron expressed as FeO). In glasses with up to 18 wt% FeO_T and 15 wt% TiO_2, no systematic compositional (matrix) effects were observed. A possible influence of Ti on the Fe^{2+} determination has only been observed in one high-Ti glass with ~25 wt% TiO_2, a content that is not typical for natural terrestrial silicate melts. The accuracy of the $Fe^{2+}/\Sigma Fe$ determination, which depends on both the Fe^{2+} content determined with the flank method and on the total Fe content, is estimated to be within ±0.1 for silicate glasses with $FeO_T > 5$ wt% and within ±0.3 for silicate glasses with low $FeO_T \leq 5$ wt%. The application of the flank method on silicate glasses requires minimization of the EPMA beam damage that can be successfully achieved by continuous movement of the sample stage under the electron beam during analysis, e.g., with a speed of 2 μm/s.

Keywords: Microprobe, ferric-ferrous ratio, silicate glasses, redox state, flank method, pillow glasses