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# The iron oxidation state of garnet by electron microprobe: Its determination with the flank method combined with major-element analysis

**HEIDI E. HÖFER* AND GERHARD P. BREY**

Institut für Geowissenschaften, Facheinheit Mineralogie, Johann Wolfgang Goethe-Universität, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany

## ABSTRACT

We have established a method to determine the oxidation state of Fe using the electron microprobe—the “flank method.” This method has the possibility to analyze simultaneously the major-element chemistry on the same spot. The method is based on Fe*L* X-ray emission spectra that show a concomitant change of both the intensity and the wavelength of the soft Fe$L\alpha$ and Fe$L\beta$ emission lines. The method has been developed for garnets using well-characterized synthetic samples, and an empirical correction scheme has been established for self-absorption of the Fe*L* X-ray emission. This enables the unambiguous correlation of measured intensity ratios of Fe$L\alpha$/Fe$L\beta$ X-ray emission to the oxidation state in garnet. The flank method can be used with routine microprobe settings (e.g., 15 kV, 60 nA) and, for garnets, with minimum beam size. This way, $Fe^{3+}/\Sigma Fe$ and major and trace elements can be determined within 10 minutes on the microscale. The resulting accuracy of $Fe^{3+}/\Sigma Fe$ is then ±0.04 for garnets at 10 wt% total Fe. Application to natural garnet megacrysts with 8 wt% total Fe and $Fe^{3+}$ known from Mössbauer spectroscopy yields excellent agreement between the two methods. For practical application, the calibration can be achieved by using three natural standards and fitting the data to $Fe^{2+}$ and $Fe^{3+}$ with linear equations. Through repeated measurements on homogeneous samples, the error in $Fe^{3+}/\Sigma Fe$ becomes approximately ±0.02 ($1\sigma$). Optimization of analytical parameters such as beam current, measurement time, and repetition of analyses, will further lower the uncertainty.

**Keywords:** Iron oxidation state, flank method, self-absorption, electron microprobe, garnet