

The calibration of the iron oxidation state determination in synthetic and natural pyroxenes using the Flank Method

S. Baier (1), H. E. Höfer (1), G. P. Brey (1), W. O. Hibberson (2), and A. B. Woodland (1)

(1) Institut für Geowissenschaften, Johann Wolfgang Goethe-Universität, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany, (2) Research School of Earth Sciences, Australian National University

The redox state of Earth's materials is generally estimated by analyzing the Fe^{3+} content of the constituent minerals and applying well calibrated redox reactions to the appropriate parageneses. The determination of the oxidation state of minerals can be carried out by Mössbauer spectroscopy, XANES, EELS and from the L-emission lines of X-ray spectra with the electron microprobe. The latter are in-situ methods with high spatial resolution. We have previously established the "flank method" (Höfer and Brey, 2007) for the in-situ $\text{Fe}^{3+}/\Sigma\text{Fe}$ determination of individual garnets by the electron microprobe. It offers the advantage and possibility to determine the iron oxidation state simultaneously with the chemical composition of the minerals on a microscale.

The flank method is based on the concomitant change of the intensity and wave length of the iron $\text{L}\alpha$ and $\text{L}\beta$ emission spectra with iron oxidation state. However, the L emission spectra are not only sensitive to $\text{Fe}^{2+}/\text{Fe}^{3+}$, but are also affected by the electronic environment of the iron atoms. This brings with it the necessity of separate calibrations for different mineral groups. Our aim is therefore to extend the flank method to the application to clinopyroxenes. Well characterized samples with well known $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are necessary for this kind calibration work.

To obtain information on the influence of the chemical composition on the spectra (self absorption) we first synthesized "simple" end member clinopyroxenes and their solid solutions at high pressures and temperatures. We carried out experiments at 2-3 GPa and 1050-1300 °C in a piston cylinder apparatus in the system acmite-hedenbergite-diopside plus ferrosilite which gives a variation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0 to 1. Microprobe analyses established the homogeneous nature of the run products and confirmed the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios which we had aimed at from stoichiometry. Further confirmation will come from Mössbauer spectroscopy of samples for which sufficient material is available. These data for simple systems give the basis for the application to natural systems.

To calibrate for the natural system we use homogeneous clinopyroxenes obtained as mineral separates from garnet peridotites and eclogites and megacrysts from kimberlites and alkali basalts. Their total Fe contents range from 2.7 to 8.2 wt.-% and their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from 0.14 to 0.50 as determined by Mössbauer spectroscopy. The flank method results on the pyroxenes show that the systematic variations of the $\text{FeL}\alpha/\text{FeL}\beta$ ratio with $\text{Fe}^{3+}/\Sigma\text{Fe}$ and with total Fe are analogous to those found previously in garnets. Therefore, the empirical correction model for self-absorption that was established for garnets can be transferred to pyroxenes to quantitatively determine $\text{Fe}^{3+}/\Sigma\text{Fe}$.

Höfer & Brey (2007) Am. Mineral. 92, 873-885