

The oxidation state of Fe in clinopyroxenes – the determination with the “flank-method” by EPMA

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The most common method to determine the oxidation state of Fe in Earth materials is the Mössbauer spectroscopy, but other methods like XANES, EELS and the “flank method” for the in situ determination with high spatial resolution have been developed meanwhile. The “flank-method” by electron microprobe (EMP) is based on the concomitant change of the intensity and of the wave length of the iron $L\alpha$ and $L\beta$ emission lines with the iron oxidation state and is well calibrated for garnets [1]. Our aim is to extend such a calibration to clinopyroxenes. Well characterized samples with known $Fe^{3+}/\Sigma Fe$ are necessary for this approach. One kind of calibration materials were clinopyroxene members of acmite-hedenbergite-diopside-ferrosilite solid solutions that were synthesized at high pressures and temperatures. The other kind were homogeneous clinopyroxenes that were handpicked from garnet peridotite and eclogite xenoliths and megacrysts from kimberlites and alkalibasalts. Their total iron contents ranged from 2.7 to 7.0 wt%. The $Fe^{3+}/\Sigma Fe$ ratios were determined by Mössbauer spectroscopy and range from 0.14 to 0.5. These samples serve as standards to develop the flank-method for clinopyroxenes. The $cpsL\beta/cpsL\alpha$ ratios as measured by EPMA vary with the cpx composition in an analogous way as for garnets. Our first tests show that the error for $Fe^{3+}/\Sigma Fe$ is around ± 0.05 (1σ) at present.

[1] Höfer and Brey (2007) *Am. Min.* **92**, 873-885