

Natural garnet and pyroxene reference materials for determining the oxidation state of iron using the electron microprobe flank method

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Garnet and pyroxene are important carriers of ferric iron in the upper mantle. Understanding how the crystallization of garnet and pyroxene influences the oxygen fugacity of magma requires accurate determination of the oxidation state of iron, expressed as the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio. Although many techniques have been developed to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in minerals, the electron microprobe flank method [1,2] is particularly notable for its accessibility and high efficiency. However, the application of this method is limited by a shortage of suitable calibration standards. In this study, we reported ten natural garnet and nine natural pyroxene samples, following a detailed examination of their major element compositions and Mössbauer spectroscopy measurements to determine their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. For garnet, three andradite-grossular samples are highly enriched in Fe^{3+} , with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios ranging from 0.89 to 1.00. In contrast, seven almandine-pyroxene-grossular samples contain minimal Fe^{3+} , with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios ranging from 0.01 to 0.03. For pyroxene, the aegirine sample has an $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.98 ± 0.01 (1σ), whereas the hedenbergite sample contains no ferric iron. The augite and diopside samples have $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios varying from 0.21 to 0.39. One andradite sample (And1902) and one almandine sample (Ald1906) were selected to determine the flank positions for $\text{Fe}L\alpha$ and $\text{Fe}L\beta$. We measured the major elements and $\text{Fe}L\beta/L\alpha$ ratios at the flank positions for both garnet and pyroxene samples. The results demonstrate a positive linear relationship between the $\text{Fe}L\beta/L\alpha$ ratios and the Fe^{2+} content for both garnet and pyroxene. The Fe^{2+} contents and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained through a multiple linear regression equation are consistent with those determined by Mössbauer spectroscopy. This method yields Fe^{2+} content and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios with an error of ± 1 wt.% and ± 0.05 for garnet, and an error of ± 0.3 wt.% and ± 0.06 for calcic pyroxene containing 7 wt.% total FeO. Therefore, these well-characterized garnet and pyroxene samples can serve as reference materials for determining the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in unknown garnet and calcic pyroxene using the electron microprobe flank method.

[1] Höfer, Brey, Schulz-Dobrick & Oberhänsli (1994), *EJM* 6, 407-418.

[2] Höfer & Brey (2007), *American Mineralogist* 92, 873-885.