American Mineralogist, Volume 110, pages 1257–1268, 2025

Determination of the oxidation state of iron in calcic pyroxene using the electron microprobe flank method

Yonghua Cao[1,2,3,†], Chang-Ming Xing[1,2,3,*], Christina Yan Wang[1,2,3], and Xianquan Ping[4]

[1]Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[2]CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China
[3]Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou 510640, China
[4]School of Earth Sciences, China University of Geosciences, Wuhan 430074, China

Abstract

Pyroxene is an important carrier of ferric iron in basalt and the upper mantle. Understanding the influence of pyroxene crystallization on the oxygen fugacity of magma relies on accurate knowledge of the oxidation state of iron, expressed as the $Fe^{3+}/\Sigma Fe$ ratio, in pyroxene. To accurately determine the $Fe^{3+}/\Sigma Fe$ ratio in pyroxene using electron probe microanalysis, we present nine natural pyroxene samples, including one aegirine, one hedenbergite, one diopside, and six augites, for the calibration of the flank method for pyroxene. The aegirine sample is rich in the aegirine end-member with a $Fe^{3+}/\Sigma Fe$ ratio of 0.98 ± 0.01 (1σ), while the hedenbergite sample is rich in the hedenbergite end-member and free of ferric iron. The augite and diopside samples contain variable ferric iron, with the $Fe^{3+}/\Sigma Fe$ ratios varying from 0.21 to 0.39. Based on the flank positions of Fe$L\alpha$ and Fe$L\beta$ determined by natural andradite and almandine, we measured the Fe $L\beta/L\alpha$ ratios at the flank positions for the pyroxene samples. The results demonstrate a positive linear relationship between the Fe $L\beta/L\alpha$ ratios and the Fe^{2+} content of the pyroxene samples. The Fe^{2+} contents and $Fe^{3+}/\Sigma Fe$ ratios of the pyroxene samples, as determined through a multiple linear regression equation, align closely with those obtained by Mössbauer spectroscopy. This method yields the Fe^{2+} content and $Fe^{3+}/\Sigma Fe$ ratios with an error of ±0.3 wt% and ±0.06, respectively, for calcic pyroxene containing 7 wt% total FeO. These well-characterized natural pyroxene samples can serve as reference materials for determining the $Fe^{3+}/\Sigma Fe$ ratio in unknown calcic pyroxene.

Keywords: Electron probe microanalysis (EPMA), oxidation state of iron, $Fe^{3+}/\Sigma Fe$ ratio, flank method, pyroxene