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# Precise Mössbauer milliprobe determination of ferric iron in rock-forming minerals and limitations of electron microprobe analysis

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## Abstract

For estimations of *P-T* conditions of igneous and metamorphic rocks, $Fe^{3+}$ in coexisting minerals is either assumed to be zero or is calculated from electron microprobe analyses (EMPA) based upon stoichiometry and charge balance. Geothermobarometers that involve $Fe^{2+}$-$Mg^{2+}$ exchange can be significantly affected by either neglecting $Fe^{3+}$ or using incorrect values. Ratios of $Fe^{3+}/\Sigma Fe$ in garnet and clinopyroxene measured by a Mössbauer milliprobe were compared to those calculated from EMPA of garnet and clinopyroxene from eclogite xenoliths from the Udachnaya kimberlite in Yakutia. The effects of $Fe^{3+}$ contents in garnet and clinopyroxene on temperature estimations were evaluated.

The following $Fe^{3+}/\Sigma Fe$ (in at%) values were obtained (EMPA/Mössbauer): Gt = 9.4/6.0; 11.5/7.0; 19.4/16.0; and 24.7/15.0; Cpx = 22.0/22.9; 34.2/22.0. The effects of $Fe^{3+}$ in clinopyroxenes on calculated temperatures are illustrated by taking eclogitic clinopyroxene compositions and changing contents of certain elements within the range of standard deviations for EMPA of those particular elements. Increasing $Na_2O$ contents from 5.67 to 5.74 wt% (<2.0% relative error) would lead to increasing $Fe^{3+}/\Sigma Fe$ from 31.6 to 47.1%, thereby decreasing the calculated temperature from 1026 to 941 °C. Various $Fe^{3+}/\Sigma Fe$ values for garnet and clinopyroxene were also tested for their effects on calculated temperatures: for clinopyroxene, *T* decreases with increasing $Fe^{3+}/\Sigma Fe$ whereas for garnet, *T* increases with increasing $Fe^{3+}/\Sigma Fe$. This compensation effect between garnet and clinopyroxene moderates the variation in temperature estimations of eclogites based on $Fe^{3+}$ corrected vs. uncorrected microprobe analyses.

Little correlation exists between EMPA-calculated and Mössbauer-measured $Fe^{3+}/\Sigma Fe$ values for these mantle-derived garnets and clinopyroxenes. Even a small relative error in $Fe^{3+}$ may significantly change calculated temperatures of equilibration, seriously affecting petrologic interpretations. In particular, uncertainty in $Fe^{3+}$ calculated from EMPA of silicate minerals leads to serious questions with regard to $K_D$ values obtained from natural assemblages.