

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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ (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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ from 31.6 to 47.1%, thereby decreasing the calculated temperature from 1026 to 941 °C. Various $\text{Fe}^{3+}/\Sigma\text{Fe}$ values for garnet and clinopyroxene were also tested for their effects on calculated temperatures: for clinopyroxene, T decreases with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ whereas for garnet, T increases with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$. 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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.