

Determination of Fe³⁺/Fe using the electron microprobe: A calibration for amphiboles

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ABSTRACT

Iron is a common constituent in minerals from the Earth's crust and upper mantle and often occurs in minerals as mixtures of two valence states, Fe³⁺ or Fe²⁺. Quantification of the values of Fe³⁺/Fe_{Total}, where Fe_{Total} = Fe³⁺+Fe²⁺, in minerals may be necessary to accurately apply certain mineral equilibria to determine equilibrium values of important variables such as temperature (*T*), pressure (*P*), and oxygen fugacity (*f*_{O₂}). Most useful would be an analytical technique that permits determination of values of Fe³⁺/Fe_{Total} within a single mineral grain that is contained within a standard petrographic thin section, and the excellent spatial resolution and relative accessibility of the electron microprobe (EMP) have resulted in various attempts to use this instrument to determine values of Fe³⁺/Fe_{Total}. These efforts have typically involved quantifying characteristics of the FeL α and/or FeL β peaks. In this paper, we employ the method of Fialin et al. (2001), who have shown that the location of the FeL α peak changes as a function of Fe content and values of Fe³⁺/Fe_{Total}, to determine values of Fe³⁺/Fe_{Total} in amphiboles.

We have characterized the FeL α peak in several amphiboles with known values of Fe³⁺/Fe_{Total} using the electron microprobe at Texas A&M University. Initial analyses employed a beam current of 20 nA in an effort to avoid Fe-oxidation due to electron beam generated H-loss (Wagner et al. 2008). Subsequent analyses were conducted at 100 nA, and the results are consistent with the 20 nA data only when relatively short duration analytical times were used.

The position of the FeL α peak was determined for three suites of amphiboles that have been experimentally treated such that grains in any one of these mineral suites are chemically identical except for differences in the values of Fe³⁺/Fe_{Total}. A linear relation between the FeL α peak location and value of Fe³⁺/Fe_{Total} was observed for each of these three amphibole suites. These three lines differ from one another in both their slope and intercept and these differences vary as a function of Fe content. Thus, these amphiboles served as the basis for the derivation of a relation between Fe content and FeL α peak location, both measured with the EMP, and the value of Fe³⁺/Fe_{Total} as originally determined with ⁵⁷Fe Mössbauer spectroscopy. The relation between the relative peak position (RPP = hematite standard FeL α peak position – amphibole FeL α peak position), Fe content, and Fe³⁺/Fe_{Total} is

$$\begin{aligned} \text{Fe}^{3+}/\text{Fe}_{\text{Total}} &= \text{RPP} - \text{RPP}(0)/\text{RPP}(1) - \text{RPP}(0), \text{ where} \\ \text{RPP}(0) &= -1.37 \times \text{FeO}^2 + 19.59 \times \text{FeO} - 3.85, \\ \text{RPP}(1) &= -1.25 \times \text{FeO}^2 + 21.39 \times \text{FeO} + 13.05, \end{aligned}$$

and FeO refers to the wt%FeO. This relation reproduces the measured values of Fe³⁺/Fe_{Total} to within ± 0.07 and, therefore, should permit determination values of Fe³⁺/Fe_{Total} in amphiboles with Fe contents from 7 to 13 wt% FeO with similar precision. The amphiboles that were used in this study were kaersutites, Ti-bearing pargasites, and pargasitic hornblendes. The calibration presented here should, at the very least, be applicable to amphiboles with similar compositions, and although further verification is necessary, this calibration may be useful for determining values of Fe³⁺/Fe_{Total} in amphiboles with distinctly different compositions and may even be more universally applicable.

Keywords: Amphibole, ferric-ferrous, electron microprobe, Fe oxidation state