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, Fe3+ 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 Fe2+-Mg2+ exchange can be significantly affected by either neglecting Fe3+ or using incorrect values. Ratios of Fe3+/ΣFe 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 Fe3+ contents in garnet and clinopyroxene on temperature estimations were evaluated.

The following Fe3+/ΣFe (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 Fe3+ 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 Na2O contents from 5.67 to 5.74 wt% (<2.0% relative error) would lead to increasing Fe3+/ΣFe from 31.6 to 47.1%, thereby decreasing the calculated temperature from 1026 to 941 °C. Various Fe3+/ΣFe values for garnet and clinopyroxene were also tested for their effects on calculated temperatures: for clinopyroxene, T decreases with increasing Fe3+/ΣFe whereas for garnet, T increases with increasing Fe3+/ΣFe. This compensation effect between garnet and clinopyroxene moderates the variation in temperature estimations of eclogites based on Fe3+ corrected vs. uncorrected microprobe analyses.

Little correlation exists between EMPA-calculated and Mössbauer-measured Fe3+/ΣFe values for these mantle-derived garnets and clinopyroxenes. Even a small relative error in Fe3+ may significantly change calculated temperatures of equilibration, seriously affecting petrologic interpretations. In particular, uncertainty in Fe3+ calculated from EMPA of silicate minerals leads to serious questions with regard to K0 values obtained from natural assemblages.

INTRODUCTION

Several chemical elements can occur in multiple oxidation states in both terrestrial and extraterrestrial minerals. Iron is one example of a multivalent element that is a common constituent of silicate minerals in igneous and metamorphic rocks. The significance of variation of Fe3+/ΣFe is difficult to overestimate. Many petrogenetic and thermodynamic parameters of Fe-bearing minerals involve Fe3+, such as Xmg = (Mg/[(Mg + Fe3+)]) and K0, the Fe2+-Mg distribution coefficient. These values are a direct function of Fe2+ and Fe3+ contents. However, in most cases, modern analytical techniques are incapable of measuring oxidation state, resulting in various assumptions (e.g., that all Fe present in a sample has the same valence).

Previously, there were only two analytical methods commonly used to determine Fe3+/ΣFe and Fe2O3, content directly, Mössbauer spectroscopy, and wet chemistry. These methods permit distinction between Fe2+ and Fe3+, which is crucial to any estimation of redox and P-T conditions during mineral formation. However, both techniques require relatively large amounts of sample (>50 mg for Mössbauer spectroscopy for a sample containing 10 wt% FeO, and >0.5 g for wet chemistry). These mass requirements have made it impossible to analyze single mineral grains or minerals in thin section (i.e., in situ). Recently, another technique for Fe3+/ΣFe measurement has become available, X-ray absorption near-edge struc-