LETTER

Accurate determination of ferric iron in garnets

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ABSTRACT

Numerous techniques are available to determine the amount of Fe2+ and Fe3+ in minerals. Calculating Fe2+ and Fe3+ by charge-balance using electron probe microanalysis (EPMA) data is the most common method, but several studies question the usefulness and accuracy of this approach (Canil and O’Neill 1996; Dyar et al. 1993, 2012; Lalonde et al. 1998; Li et al. 2005; McGuire et al. 1989; Schingaro et al. 2016; Schmid et al. 2003; Sobolev et al. 2011). We compile and compare data for natural garnets that have been analyzed by both EPMA and Mössbauer spectroscopy. Comparison of Fe2+/ΣFe determined by charge-balance vs. Mössbauer spectroscopy shows an approximate 1:1 correlation. The EPMA data set of Dyar et al. (2012) is reexamined and it is shown that disagreement between EPMA and Mössbauer for their data is not nearly as bad as reported. Data for charge-balance vs. Mössbauer spectroscopy are compared and show that the EPMA/charge-balance approach provides a suitable alternative when other methods are not practical.

Keywords: Ferric iron, EPMA, charge-balance, Mössbauer spectroscopy

INTRODUCTION

The oxidation state of iron is important for many aspects of mineralogy and petrology including thermobarometry and determination of oxygen fugacity in rocks or melts. Several methods exist for determining the ratio of Fe3+ to Fe2+ . Most commonly, it is either directly measured by wet chemistry (Johnson and Maxwell 1981; Wilson 1960) or Mössbauer spectroscopy (Dyar et al. 2006), or calculated from electron probe microanalysis (EPMA; e.g., Valley et al. 1983; Droop 1987; Essene 1989; Grew et al. 2013). Other techniques including X-ray photoelectron spectroscopy (Raeburn et al. 1997a, 1997b), electron energy loss spectroscopy (Garvie and Buseck 1998), EPMA-based “flank method” (Höfer and Brey 2007), and synchrotron based X-ray absorption near-edge spectroscopy (Bajt et al. 1994) have been employed to explicitly measure the valence of iron. The EPMA/charge-balance technique is the most frequently employed because of widespread EPMA accessibility, small spot size (~3 µm), and speed of analysis. Furthermore, analysis is essentially non-destructive. However, the EPMA/charge-balance approach is, in some circumstances, less precise and requires accurate analysis while making some assumptions: no vacancies, no unmeasured elements (e.g., H, Li, B), and that Fe is the only element with more than one valence state. Fluorine should be measured by EPMA (Valley et al. 1983). These assumptions are not met for hydrous minerals, e.g., amphiboles, micas, chlorites, hydro-garnets, and staurolites; because H2O is not measured by EPMA (Essene 1989). It is well known that charge-balance does not yield a unique result when the assumptions fail (Droop 1987), and we will not discuss these minerals. Instead we focus on the garnet group (excluding hydrous species where H2O was unmeasured), where the authors believe charge-balance calculations to be a valuable tool after EPMA analysis.

METHOD

We calculate Fe2+/ΣFe by charge-balance for garnets (Table 1) according to the following procedure.

1. Calculate the formula from EPMA data normalized to eight cations.
2. Calculate the total charge contribution from all cations assuming all Fe is Fe2+.
3. (a) If the total cation charge is greater than 24 (cation charge of an ideal formula), then all Fe is ferrous and there is no ferric Fe. (b) If the cation charge is <24, calculate the amount of Fe3+ cations by subtracting the total cation charge from 24, i.e.,

Fe3+ = 24 − \sum C_i V_i

where \( C \) is the amount of the \( i \)th cation and \( V \) is the valence of the \( i \)th cation.

4. (a) If the amount of calculated Fe3+ is greater than ΣFe, then enter zero for Fe3+ and set Fe2+ to equal ΣFe. (b) If the amount of calculated Fe3+ is less than ΣFe, subtract the calculated Fe3+ from ΣFe to determine amount of Fe2+.

This procedure is slightly different than that of Droop (1987), but is preferred by the authors due to its simplicity. For each data set that we review, we back-calculated ΣFe as FeO from reported FeO and/or Fe2O3 and the above procedure was implemented to ensure consistency of charge-balance calculations. If data for H2O, Li2O, or other oxides that are not typically measured by EPMA are available through another method, e.g., secondary ion mass spectrometry (Schingaro et al. 2016) or Fourier transform infrared spectroscopy (Locock et al. 1995), then they can be combined with EPMA data and incorporated into charge-balance calculations according to (Grew et al. 2013).

The accuracy of charge-balance calculations depends on several factors. Counting statistics during EPMA analysis provides an assessment of instrumental precision, but not of accuracy. Choice of analytical standards can make critical differences for EPMA of garnets due to chemical peak shifts for MgKα and AlKα between non-garnet standards and sample garnets (Fournelle 2007; Fournelle and Jonnard 2011). Fournelle and Geiger (2010) examined EPMA of synthetic grossular and pyrope, using non-garnet standards (e.g., wollastonite, corundum, Fo-rich olivine) and noted a range of errors (Al = 3% low; Mg = 1% high; Si = 1% high) and different possible analytical results that were dependent upon (1) which mass absorption coefficient and (2) which matrix correction were used. These results emphasize the need for garnets as standards, ideally for all elements, obviating any chemical peak shift and minimizing error in matrix correction.

Conditions of EPMA analysis and the selected standards, mass absorption coefficients, and matrix correction are not always reported resulting in data that are...