Incorporating previously neglected excess oxygen associated with ferric iron in matrix corrections of microprobe data from cubic and rhombohedral Fe-Ti oxides

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Abstract

Estimates of the oxidation states of magmas are important to current investigations of the geochemical characteristics of their source regions and of evolved magmatic series created during differentiation. One means of achieving such estimates is to capitalize on compositions of coexisting cubic and rhombohedral Fe-Ti oxides determined by electron microprobe. A combination of experimental calibration points and thermodynamic modeling provides a basis for translating such compositions into $T$-$f_{O_2}$ values. This has been done until recently by estimating Fe*/ΣFe on the basis of charge balance and stoichiometry by the method of Droop (1987), after matrix corrections of X-ray intensity data have been performed, as EPMA cannot be used routinely to distinguish different elemental valence states, much less accurately quantify abundances of Fe⁺ and Fe⁵⁺. The traditional approach of undertaking post-data-reduction calculations falls short of attaining the best possible quantitative results. The tactical choice of not accounting for light elements that have not been explicitly analyzed prior to matrix corrections of X-ray intensity data leads to systematic errors in reported oxide abundances for measured elements. This article addresses one such issue, the oxygen associated with Fe³⁺ (hereafter “excess oxygen”), on the basis of coexisting Fe-Ti oxides from Andean lavas. A new software routine in probe for EPMA (PFE) uses an iterative calculation scheme to calculate amounts of excess oxygen that would not be considered if all iron were assumed to be ferrous and then applies this excess oxygen during matrix corrections. The PFE approach reveals that Fe-concentrations have been underestimated, universally, in these minerals because O atoms absorb FeKα radiation: discrepancies increase as total Fe and Fe³⁺/Fe²⁺, hence excess oxygen, increase. Analyses of the most Fe-rich cubic oxide compositions in this data set have ~6 wt% excess oxygen and ~1 wt% more FeO+Fe₂O₃ than would be reported without incorporating the impact of excess oxygen in matrix corrections. Minor to negligible differences in other elements are also observed. These effects are not because excess oxygen is directly attributed to these elements, although some may be present in multiple valence states, as matrix corrections are undertaken on the basis of the conventional assumptions that they occur as Cr³⁺, V³⁺, Mn²⁺, Mg²⁺, Ca²⁺, and Si⁴⁺. Rather, variably small increases in total Fe propagate through the matrix corrections for other elements, and these differences may be recorded as minor increases or decreases in some concentrations, depending on the particular element and the amount of change in Fe-concentration. Fe*/ΣFe in analyses produced with the PFE routine are essentially identical to those determined in the traditional mode, as cation proportions calculated on the basis of charge balance and stoichiometry, with the method of Droop (1987), is a necessary step. The new method: (1) provides more accurate concentrations, mainly for Fe and Ti; (2) is applicable to any mineral containing ferric iron (subject to stoichiometric constraints); (3) provides more accurate analytical totals, which can be advantageous for evaluating analytical quality; and (4) does not impact estimates of oxidation state. Oxygen fugacities and temperatures determined with the model of Ghiorso and Evans (2008) are essentially unchanged.

Keywords: Fe-Ti oxides, $T$-$f_{O_2}$, electron microprobe, analytical methods, matrix corrections

Introduction

Magmatic oxygen fugacity is an important intensive parameter because, to a large extent, it reflects Fe*/ΣFe, which: (1) in some sense, is a proxy for key geochemical aspects of magmatic source regions; (2) plays a role in determining the stabilities of ferromagnesian silicate and oxide phases; and (3) is, therefore, a factor that influences liquid lines of descent. Several different laboratory methods are used, ideally in combination, to assess the oxidation-states of erupted mafic to silicic magmas, but exploitation of coexisting Fe-Ti oxides is a frequently applied approach. If coexisting grains of the cubic phase (Fe₂TiO₄ – Fe₃O₄; hereafter spinel) and the rhombohedral phase (FeTiO₃ – Fe₂O₃) can be shown to be in equilibrium for Mg and Mn (Bacon and Hirschmann 1988), the compositions of such pairs are commonly used to calculate temperature and $f_{O_2}$ (Ghiorso and Evans 2008). These results are often interpreted/presented as being equivalent to, or at least highly indicative of the oxidation-states of host magmas.