Methods for Determination of $Fe^{3+}/\sum Fe$ in Microscopic Samples

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Introduction

Analytical methods have evolved such that determination of chemical composition in microscopic samples can be carried out with high precision and spatial resolution. However, none of the analytical methods are able to distinguish between different valence states, e.g. Fe^{2+} and Fe^{3+}, which is crucial to determination of important parameters such as oxygen fugacity. Methods such as wet chemistry can be used to measure $Fe^{3+}/\sum Fe$ values, but cannot be applied to small samples. To address this problem, methods have been evolving in recent years to measure $Fe^{3+}/\sum Fe$ with higher spatial resolution. This paper will critically examine these methods and describe some recent applications.

Electron microprobe

The possiblity to calculate the stoichiometric formula of a mineral from its chemical analysis is often applied to determine $Fe^{3+}/\sum Fe$ values from electron microprobe analyses. It is important, however, to propagate the uncertainties through the calculation in order to evaluate the significance of the results. For example, Canil and O'Neill (1996) calculate uncertainties in $Fe^{3+}/\sum Fe$ for representative mantle samples of spinel, garnet and clinopyroxene to be 2.5%, 12% and 51%, respectively. Additional errors are introduced if the phase is not stoichiometric, or if there are other cations present with multiple valence.

Another possibility to determine $Fe^{3+}/\sum Fe$ using the electron microprobe is through analysis of oxygen (e.g. Bastin and Heijligers, 1989). Sample preparation is critical, however, since emission is restricted to shallow depths (of the order 1000 Å). Effects such as surface contamination and roughness are disastrous, and it is crucial to use correct procedures in collecting and analysing the data. As above, calculation of $Fe^{3+}/\sum Fe$ assumes that phases are stoichiometric and that iron is the only cation with multiple valence.

A more direct method for calculating $Fe^{3+}/\sum Fe$ using the electron microprobe has been recently developed by Höfer et al. (1994) through analysis of the Fe L_α and L_β X-ray emission spectra. Calibration curves between $Fe^{3+}/\sum Fe$ and the intensity ratio L_β/L_α are structure dependent, but can be determined with an accuracy of $\pm 5\%$ in $Fe^{3+}/\sum Fe$ as shown by Enders et al. (1997) for alkali- andcalcic-amphiboles.

X-ray Photoelectron Spectroscopy (XPS)

Photoelectron energy spectra obtained by bombarding a sample with X-rays can be analysed to provide information about the elemental and chemical state of the atoms. In particular, Fe^{2+} and Fe^{3+} have photopeaks at different energies, so the oxidation state of Fe can be determined with reasonable accuracy (e.g. McIntyre and Zetaruk, 1977). A recent study by Raeburn et al. (1997a,b) applied the method to biotite samples with a spot size of 2×0.25 mm and an accuracy of 5-15% in $Fe^{3+}/\sum Fe$. One advantage of the method is the wide availability of XPS instruments, while a large disadvantage is the strong surface sensitvity (typically only the top 5 nm are sampled).

X-ray Absorption Near-Edge Spectroscopy (XANES)

The X-ray K- and L-absorption edges of iron have features which are sensitive to the valence electrons, and can be used to estimate $Fe^{3+}/\sum Fe$. The L edge is dominated by dipole transitions which are sensitive to oxidation state, site symmetry, spin state and crystal field splitting, and has been used to characterise valence states for a number of different 3d transition metals (e.g. Cressey et al., 1993). The pre-edge region of the K-absorption edge is sensitive primarily to oxidation state, and has been used in numerous studies to determine $Fe^{3+}/\sum Fe$. For example, a recent study by Delaney et al. (1996) determined $Fe^{3+}/\sum Fe$ values in amphibole with a spot size of 30×50 μm. Advantages of the method include the potentially high spatial resolution (to ~ 1 μm), while a disadvantage is the need for a synchrotron source of X-rays.

Electron Energy Loss Spectroscopy (ELNES)

ELNES is the electron equivalent of XANES. The energy spectrum can be measured using a high-resolution spectrometer attached to a standard transmission electron microscope. The energy difference in maxima arising from Fe^{2+} and Fe^{3+} in the spectrum is sufficiently large to enable quantitative determination of Fe^{2+}/Fe^{3+} ratios. Fe $L_{2,3}$ edge spectra were used by van Aken et al. (1998) on a large suite of synthetic and natural minerals to calibrate $Fe^{3+}/\sum Fe$ values determined by Mössbauer spectroscopy with values determined from the intergal intensity ratio L_3/L_2. Absolute errors for the quantitative determination were estimated to be approximately $\pm$ 0.05 for $Fe^{3+}/\sum Fe <$ 0.4 and $\pm$ 0.03 for $Fe^{3+}/\sum Fe >$ 0.6. A large advantage of the method is the extremely high spatial resolution possible (down to ~ 10 nm), while one disadvantage is the destructive nature of sample preparation.

Mössbauer spectroscopy

Mössbauer spectroscopy is a reliable method for determination of $Fe^{3+}/\sum Fe$, and provides additional crystal chemical information about the environment of iron in the sample. Traditionally it has required samples with diameter ~ 1 cm, but a method developed by McCammon et al. (1991) enables experiments to be carried out on samples of diameters as small as 50 μm (see also McCammon, 1994). Advantages of the method include the wide availability of Mössbauer spectrometers and the non-destructive nature of the technique, while disadvantages are the limited spatial resolution (not less than 50 μm) and the relatively long time required to collect spectra (> 12 hr).

Applications

Applications of techniques to determine $Fe^{3+}/\sum Fe$ in microscopic samples are numerous. The Mössbauer method has been applied to a number of mantle problems:

(1) Oxygen fugacity conditions during formation of diamonds from George Creek, Colorado as measured from $Fe^{3+}/\sum Fe$ of garnet and clinopyroxene inclusions (McCammon et al., 1998)

(2) Fe^{3+} content of inclusions in diamond from the lower mantle with implications for lower mantle oxidation state (McCammon et al., 1997)

(3) Distribution of Fe^{3+} in garnets from the Wesselton kimberlite with implications for oxygen fugacity (McCammon et al., in preparation)

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