Variation in XANES in biotite as a function of orientation, crystal composition, and metamorphic history

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ABSTRACT

Microscale analysis of ferrous:ferric iron ratios in silicate minerals has the potential to constrain geological processes but has proved challenging because textural information and spatial resolution are limited with bulk techniques, and in situ methods have limited spatial resolution. Synchrotron methods, such as XANES, have been hampered by the sensitivity of spectra to crystal orientation and matrix effects. In an attempt to break this nexus, biotites from Tanzania were characterized with a combination of optical microscopy, electron microprobe, Mössbauer analysis, electron backscatter diffraction (EBSD) and X-ray absorption near edge structure (XANES) spectroscopy. Pre-edge and edge characteristics of the FeKα absorption feature were compared to orientation information derived by EBSD and ferric iron content derived from Mössbauer analysis. Statistically significant correlations between measured spectral features and optic/crystallographic orientation were observed for individual samples. However, orientation corrections derived from these correlations did not reduce the uncertainty in Fe3+/Fetot. The observations are consistent with matrix- and ordering-dependency of the XANES features, and further work is necessary if a general formulation for orientation corrections is to be devised.

Keywords: Fe, oxidation, XANES, biotite, orientation

INTRODUCTION

The oxidation state of iron in minerals is a critical control on mineral properties and is a strong determinant of the oxidation state of the host rock, which in turn affects parameters such as rheology (Mackwell et al. 1990; Keefner et al. 2011), melting characteristics (Wyllie 1995; Foley 2011), and the release of elements of environmental and economic interest (e.g., S, C, Cu, Au) by melting and devolatilization (Mavrogenes and O’Neill 1999; Jugo et al. 2005; Jugo 2009).

Fe3+/Fetot in minerals can vary on a micrometer scale (Schmid et al. 2003; Delaney et al. 1998; Berry et al. 2010), and acquisition of this information could provide invaluable information on geological processes. However, measurement of Fe3+/Fetot is challenging. Wet chemical and bulk Mössbauer methods (Meyrowitz 1963; Li et al. 2005) require a bulk sample and so cannot resolve micrometer scale spatial variation of Fe3+/Fetot. In situ Mössbauer has the potential to reach 50 μm spatial resolution, but the measurements are time-consuming and impractical for detailed studies of within-grain Fe3+/Fetot variation (McCannon et al. 2004; McCammon 2005). Electron energy loss spectroscopy (EELS) also has potential (e.g., Garvie et al. 2004; Keast et al. 2001) but requires a TEM thickness sample, so textural information is often lost during sample preparation.

Synchrotron XANES-based methods provide a promising opportunity for in situ Fe3+/Fetot analysis on beamlines with micro-focus capability. Spatial resolution is typically <10 μm and potentially <1 μm on the new high-resolution beamlines. Analysis can be achieved in minutes to tens of minutes, even at iron concentrations <1 wt%. Early work provided calibrations based on the position of the centroid of the 1s to 3d Fe K pre-edge peak for iron in octahedral compounds (Bajt et al. 1994) and glasses (Berry et al. 2003, 2004). Further study revealed that the characteristics of the pre-edge peak are a complex function of site geometry, coordination, matrix composition, and mineral orientation. These functional relationships have been studied by a combination of experimental and theoretical methods (Randall et al. 1995; Arrio et al. 2000; Dyar et al. 2001, 2002a, 2002b; Petit et al. 2001; Wilke et al. 2004, 2005, 2007; Delaney et al. 2005).

Results from these studies indicate that, for minerals with a high-spin electron arrangement such as biotite, the pre-edge peak intensity is mostly a function of the extent of electric dipole coupling induced by hybridization of the 3d-4p orbitals, because the 1s to 3d transition is forbidden unless hybridization occurs. Such hybridization is facilitated by non-centrosymmetric site geometries for iron and thus peak intensities are higher for tetrahedrally coordinated than for octahedrally coordinated iron. The asymmetry of coordination polyhedra is also enhanced when...