Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study

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ABSTRACT

High-resolution Fe K-edge XANES spectra of a series of crystalline Fe2+–Fe3+-bearing model compounds were measured in an effort to correlate characteristics of the pre-edge feature with oxidation state and local coordination environment of Fe atoms. The model compounds comprise 30 natural minerals and synthetic compounds, with Fe coordination environments ranging from 4 to 12 O atoms for Fe2+, including 5-coordinated trigonal bipyramidal Fe2+, and from 4 to 6 O atoms for Fe3+. Most pre-edge spectra show two components (due to crystal-field splitting) that are located just above the Fermi level.

The most useful characteristics of the Fe-K pre-edge for determining Fe oxidation state and coordination number are the position of its centroid and its integrated intensity. The separation between the average pre-edge centroid positions for Fe2+ and Fe3+ is 1.4 ± 0.1 eV. Thus, the position of the pre-edge feature can be used as a measure of the average Fe-redox state, with the average pre-edge position for mixed Fe2+-Fe3+ compounds occurring between positions for Fe2+ and Fe3+. The lowest pre-edge normalized heights and integrated intensities are observed for the most centrosymmetric sites of Fe, in agreement with previous studies (see Waychunas et al. 1983). Examination of the pre-edge features of mechanical mixtures of phases containing different proportions of Fe2+ and Fe3+ suggests that the pre-edge position and intensity for these mixtures can vary quite non-linearly with the average redox state of Fe. However, distinctly different trends of pre-edge position vs. pre-edge intensity can be observed, depending on the coordination environment of Fe2+ and Fe3+, with an accuracy in redox determination of ±10 mol% provided that the site geometry for each redox state is known. These methods have been used to estimate the Fe3+/Fe2+ ratio in 12 minerals (magnetite, vesuvianite, franklinite, rhodonite, etc.) containing variable/unknown amounts of Fe2+/Fe3+.

INTRODUCTION

Iron is the most important transition element in minerals and silicate melts. However, depending on redox conditions during the formation, Fe3+/Fe2+ ratios can vary significantly. Quantitative determination of the redox state of Fe is essential for constraining the thermodynamic conditions under which rocks and magma formed (see, e.g., Wood and Virgo 1989; Parkinson and Arculus 1997). Mössbauer spectroscopy has been widely used to measure these redox states in mineralogically and geochemically relevant phases (e.g., Dyar 1985; Mysen 1991; McCammon 1997; Dunlap et al. 1998; Wilke et al. 1999; Rossano et al. 1999 among others). However, this method is challenging in the case of small samples (e.g., micrometer sized: see Sobolev et al. 1999) or in natural samples with dilute levels of Fe (i.e., below 1 wt%, due to the relatively low natural abundance (2.1 isotopic%) of 57Fe). In addition, there have been several electron energy loss spectroscopy (EELS) studies at the L-, M-edges of iron in model compounds in order to derive Fe-oxidation state information (Garvie and Busek 1998; van Aken et al. 1998, 1999). However, this method requires high vacuum conditions, which prohibits in-situ experiments at high temperature and/or high pressure.

X-ray absorption fine structure (XAFS) spectroscopy is sensitive to Fe redox states, especially the pre-edge feature, which is located ~15–20 eV before the main K-edge crest of Fe (see Waychunas et al. 1983). Pre-edges are related to 1s → 3d (quadrupolar) and/or to 1s → 4p (dipolar) metal electronic transitions (Dräger et al. 1988; Westre et al. 1997; Heumann et al. 1997). The pre-edge position shifts towards higher energy with increasing oxidation state (White and McKinstry 1966; Srivastava and Nigam 1973). During the past few years, the Fe pre-K-edge position has been used to determine the redox state of Fe in a number of earth materials, including weathered magnetites (Bajt et al. 1994), biotite (Heald et al. 1998), amphiboles (Delaney et al. 1996b), and glasses (Delaney et al. 1996a; Galoisy et al. 2001). In addition, Delaney et al. (1998) demonstrated that this method may...