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

MAX WILKE,[1,*] FRANÇOIS FARGES,[1,2] PIERRE-EMMANUEL PETIT,[3] GORDON E. BROWN JR.,[2,4] AND FRANÇOIS MARTIN[5]

[1]Laboratoire des géomatériaux, Université de Marne-la-Vallée, 77454 Marne la Vallée Cedex, France
[2]Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.
[3]European Synchrotron Radiation Facility BP 220, 38043 Grenoble Cedex, France
[4]Stanford Synchrotron Radiation Laboratory, SLAC, P.O. Box 4349, Stanford University, Stanford, California 94309, U.S.A.
[5]Équipe Géomarg, Université Paul Sabatier–UMR CNRS 5563 39 Allées Jules Guesde, 31000 Toulouse, France

ABSTRACT

High-resolution Fe K-edge XANES spectra of a series of crystalline Fe^{2+}- and Fe^{3+}-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 Fe^{2+}, including 5-coordinated trigonal bipyramidal Fe^{2+}, and from 4 to 6 O atoms for Fe^{3+}. 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 Fe^{2+} and Fe^{3+} 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 Fe^{2+}-Fe^{3+} compounds occurring between positions for Fe^{2+} and Fe^{3+}. 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 Fe^{2+} and Fe^{3+} 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 Fe^{2+} and Fe^{3+}, 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 Fe^{3+}/Fe^{2+} ratio in 12 minerals (magnetite, vesuvianite, franklinite, rhodonite, etc.) containing variable/unknown amounts of Fe^{2+}/Fe^{3+}.