Use of multivariate analysis for synchrotron micro-XANES analysis of iron valence state in amphiboles

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ABSTRACT

Microanalysis of Fe3+/ΣFe in geological samples using synchrotron-based X-ray absorption spectroscopy has become routine since the introduction of standards and model compounds. Existing calibrations commonly use least-squares linear combinations of pre-edge data from standard reference spectra with known coordination number and valence state acquired on powdered samples to avoid preferred orientation. However, application of these methods to single mineral grains is appropriate only for isometric minerals and limits their application to analysis of in situ grains in thin sections. In this work, a calibration suite developed by acquiring X-ray absorption near-edge spectroscopy (XANES) data from amphibole single crystals with the beam polarized along the major optical directions (X, Y, and Z) is employed. Seven different methods for predicting %Fe3+ were employed based on (1) area-normalized pre-edge peak centroid, (2) the energy of the main absorption edge at the location where the normalized edge intensity has the highest R2 correlation with Fe3+/ΣFe, (3) the ratio of spectral intensities at two energies determined by highest R2 correlation with Fe3+/ΣFe, (4) use of the slope (first derivative) at every channel to select the best predictor channel, (5 and 6) partial least-squares models with variable and constant numbers of components, and (7) least absolute shrinkage and selection operator models. The latter three sophisticated multivariate analysis techniques for predicting Fe3+/ΣFe show significant improvements in accuracy over the former four types of univariate models. Fe3+/ΣFe can be measured in randomly oriented amphibole single crystals with an accuracy of ±5.5–6.2% absolute. Multivariate approaches demonstrate that for amphiboles main edge and EXAFS regions contain important features for predicting valence state. This suggests that in this mineral group, local structural changes accommodating site occupancy by Fe3+ vs. Fe2+ have a pronounced (and diagnostic) effect on the XAS spectra that can be reliably used to precisely constrain Fe3+/ΣFe.

Keywords: Amphibole, X-ray absorption spectroscopy, X-ray near-edge spectroscopy, kaersutite, potassic-magnesio-hastingsite, oxo-potassic-magnesio-hastingsite, pargasite, magnesio-hornblende, actinolite, magnesio-edenite, partial least-squares analysis, Lasso, garnet

INTRODUCTION

A growing worldwide community of synchrotron users is pursuing studies of the redox state of iron at microscales within minerals and glasses using Fe K-edge X-ray absorption near-edge structure (XANES) spectroscopy. For these materials, there is a general consensus that calibrations based on the intensity and energy of the Fe K-edge pre-edge signal, which is composed of contributions from Fe cations in different valence states and coordination polyhedra, provide a fairly representative measure of Fe valence state. The area-weighted average peak centroid energy of the pre-edge multiplets has been shown to be representative of contributions from the composite transitions, as first pioneered by Bajt et al. (1994). Subsequently it was recognized that the intensity of the pre-edge signal is also a function of site distortion and coordination, so Galois et al. (2001) utilized pseudo-Voigt line shapes of minerals with known coordination geometries to deconvolute XANES pre-edge spectra into component peaks, e.g., andradite spectra are used for [6]Fe2+, augite glass for [4]Fe2+, bertrandite for [4]Fe3+, staurolite for [6]Fe3+, and siderite for [6]Fe3+. This work was generalized by Wilke et al. (2001) and Petit et al. (2001), who characterized and fit 30 minerals and synthetic compounds to correlate energy and intensity of pre-edge features with oxidation

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