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

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ABSTRACT

Microanalysis of $Fe^{3+}/\Sigma Fe$ 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 $\%Fe^{3+}$ 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 R^2 correlation with $Fe^{3+}/\Sigma Fe$, (3) the ratio of spectral intensities at two energies determined by highest R^2 correlation with $Fe^{3+}/\Sigma Fe$, (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 $Fe^{3+}/\Sigma Fe$ show significant improvements in accuracy over the former four types of univariate models. $Fe^{3+}/\Sigma Fe$ 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 Fe^{3+} vs. Fe^{2+} have a pronounced (and diagnostic) effect on the XAS spectra that can be reliably used to precisely constrain $Fe^{3+}/\Sigma Fe$.

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