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Accurate XANES determination of microscale Fe redox state in clinopyroxene: A multivariate approach with polarization-dependent Fe *K*-edge XAFS

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ABSTRACT

X-ray absorption near-edge structure (XANES) spectroscopy enables in situ direct measurements of microscale Fe^{2+}/Fe^{3+} ratios in minerals and has greatly contributed to the understanding of the redox states during rock formation. Traditionally, the Fe^{2+}/Fe^{3+} has been quantified based on $1s \rightarrow 3d/4p$ pre-edge peak features. However, optically anisotropic minerals show significant differences in the absorption of polarized X-rays when measured in different crystallographic orientations, introducing considerable errors in estimates of Fe^{2+}/Fe^{3+}. Multivariate analysis (MVA) utilizing entire X-ray absorption fine structure (XAFS) spectral features combined with appropriate training data, preprocessing, and hyperparameter optimization, offers a potential solution to this issue. This study examines the X-ray absorption anisotropy of clinopyroxene for six distinct crystallographic orientations relative to X-ray propagation and polarization directions using 11 natural single crystals with a wide range of $Fe^{3+}/\Sigma Fe$ (0–0.88) and compositions (diopside, augite, aegirine). We used the full XAFS spectra of the oriented clinopyroxenes to construct MVA models that can accurately estimate $Fe^{3+}/\Sigma Fe$ in unknown orientations. Our measurements reveal that most of the XANES absorption-edge peak features display a clear dependence on the polarization direction of the incident X-ray, suggesting that their absorption anisotropy can mainly be ascribed to dipole-allowed $1s \rightarrow 4p$ transition processes. On the other hand, the pre-edge peaks exhibit a complex absorption anisotropy that depends on both the propagation and polarization directions, suggesting a complicated nature of quadrupole-allowed $1s \rightarrow 3d$ transitions enhanced by dipole transitions to mixed $3d$–$4p$ orbitals. We found that the conventional pre-edge-based determinations of $Fe^{3+}/\Sigma Fe$ involve large uncertainties of ± 13.5–$15.3\%Fe^{3+}$, mainly due to the substantial X-ray absorption anisotropy. Our optimal MVA model, using the least absolute shrinkage and selection operator (Lasso) and trained with autoscaled XANES spectra of oriented clinopyroxenes, can successfully predict $\%Fe^{3+}$ in clinopyroxenes from within the test data set without prior knowledge of the orientation, with a root-mean-squared error of $\pm 7.8\%Fe^{3+}$. In addition, our results show a good agreement between weighted energy channels of the MVA models and XANES peak features resolved by the polarization-dependent experiment. The MVA coefficients provided in this study offer an effective method for deriving reliable $Fe^{3+}/\Sigma Fe$ from XAFS measurements of clinopyroxene, regardless of orientation. This approach highlights the benefits of using features from the pre-edge, main-edge, and post-edge domains of the spectra to establish the relationships.

Keywords: Clinopyroxene, Fe^{2+}/Fe^{3+}, X-ray absorption near-edge structure, X-ray absorption anisotropy, multivariate analysis