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XANES calibrations for the oxidation state of iron in a silicate glass

**ANDREW J. BERRY,[1,*] HUGH ST.C. O'NEILL,[1] KASTHURI D. JAYASURIYA,[2,†]
STEWART J. CAMPBELL,[2] AND GARRY J. FORAN[3,4]**

[1]Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia
[2]School of Physics, University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia
[3]Australian Synchrotron Research Program, Australian Nuclear Science and Technology Organization, PMB 1, Menai, NSW 2234, Australia
[4]Australian National Beamline Facility, KEK, Photon Factory, Oho 1-1, Tsukuba-shi, Ibaraki-ken 305-0801, Japan

ABSTRACT

Fe *K*-edge X-ray absorption near edge structure (XANES) spectra were recorded for a series of anorthite-diopside eutectic glasses containing 1 wt% $^{57}Fe_2O_3$ quenched from melts equilibrated over a range of oxygen fugacities at 1409 °C. The $Fe^{3+}/\Sigma Fe$ ratios were determined previously by ^{57}Fe Mössbauer spectroscopy and vary between 0 (fully reduced) and 1 (fully oxidized). Using the Mössbauer results as a reference, various methods for extracting $Fe^{3+}/\Sigma Fe$ ratios from XANES spectra were investigated. The energy of the $1s \rightarrow 3d$ pre-edge transition centroid was found to correlate linearly with the oxidation state. Correlations also exist with the energy of the *K* absorption edge and the area of peaks in the derivative spectrum associated with the $1s \rightarrow 4s$ and crest ($1s \rightarrow 4p$) transitions. The $Fe^{3+}/\Sigma Fe$ ratios determined from linear combinations of end-member spectra ($Fe^{3+}/\Sigma Fe$ ~0 and ~1) were found to deviate significantly from the Mössbauer values. This may indicate the susceptibility of this method either to errors arising from the treatment of the background or to changes in Fe^{2+} or Fe^{3+} coordination with the $Fe^{3+}/\Sigma Fe$ ratio. The general applicability of any XANES calibration for determining oxidation states is limited by variations in the Fe coordination environment, which affects both the intensity and energy of spectral features. Thus previous calibrations based on mineral spectra are not applicable to silicate glasses. Nevertheless, systematic trends in spectral features suggest that $Fe^{3+}/\Sigma Fe$ values may be obtained from XANES spectra, with an accuracy comparable to Mössbauer spectroscopy, by reference to empirical calibration curves derived from compositionally similar standards.