

Calibration of Fe XANES for high-precision determination of Fe oxidation state in glasses: Comparison of new and existing results obtained at different synchrotron radiation sources

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ABSTRACT

Micro-X-ray absorption near-edge structure (μ -XANES) spectroscopy has been used by several recent studies to determine the oxidation state and coordination of iron in silicate glasses. Here, we present new results from Fe μ -XANES analyses on a set of 19 Fe-bearing felsic glasses and 9 basaltic glasses with known, independently determined, iron oxidation state. Some of these glasses were measured previously via Fe XANES (7 rhyolitic, 9 basaltic glasses; Cottrell et al. 2009), while most felsic reference glasses (12) were analyzed for the first time. The main purpose of this study was to understand how small changes in glass composition, especially at the evolved end of silicate melt compositions occurring in nature, may affect a calibration of the Fe μ -XANES method.

We performed Fe μ -XANES analyses at different synchrotron radiation sources [Advanced Photon Source (APS), Argonne, U.S.A., and Angströmquelle Karlsruhe (ANKA), Germany] and compared our results to existing calibrations obtained at other synchrotron radiation sources worldwide. The compiled results revealed that changes in instrumentation have a negligible effect on the correlation between the centroid energy of the Fe pre-edge peak and the Fe oxidation state in the glasses. Oxidation of the glasses during extended exposure (up to 50 min) to the X-ray beam was not observed.

Based on the new results and literature data we determined a set of equations for different glass compositions, which can be applied for the calculation of the iron valence ratio ($\text{Fe}^{3+}/\Sigma\text{Fe}$) in glasses by using XANES spectra collected at different synchrotron beamlines. For instance, the compiled felsic reference material data demonstrated that the correlation between the centroid energy of the Fe pre-edge peak C_{Fe} (eV) and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of felsic glasses containing 60.9 to 77.5 wt% SiO_2 and 1.3 to 5.7 wt% FeO_{tot} can be accurately described by a single linear trend, if the spectra were collected at 13-ID-E beamline at APS and for $0.3 \leq \text{Fe}^{3+}/\Sigma\text{Fe} \leq 0.85$:

$$C_{\text{Fe}} [\text{eV}] = 0.012395 (\pm 0.00026217) \times \text{Fe}^{3+}/\Sigma\text{Fe} + 7112.1 (\pm 0.014525); R^2 = 0.987.$$

Based on this equation, the Fe oxidation state of felsic glasses can be estimated at an absolute uncertainty of $\pm 2.4\%$ $\text{Fe}^{3+}/\Sigma\text{Fe}$.

In general, the differences between the calibrations for felsic and mafic glasses were small and the compiled data set (i.e., results collected at four different beamlines on 79 reference glass materials) is well described by a single second-order polynomial equation.

Keywords: Fe micro-XANES, synchrotron radiation sources/beamlines, Fe oxidation state, Fe coordination, silicate glasses, rhyolite, dacite, basalt