

Electronic Appendix 1

EPMA Analysis of Experimental Materials

Recovered aliquots of quenched melt (glass) were mounted in epoxy wafers and polished for petrographic examination and electron microprobe analysis. The glasses were analyzed with a Cameca SX-100 electron microprobe at the American Museum of Natural History, with a 15-kV accelerating potential and defocused beam diameter of 15 μm . To minimize alkali loss and other burn-in effects, Na, Si, and Cl were analyzed at the beginning of the analytical routine with a 2-nA beam current following the recommendations of Morgan and London (2006). The remaining elements were analyzed with a 10-nA beam current immediately after the low-current spectrometer pass. Matrix corrections utilized the PAP algorithm available in the Cameca software. The accuracy of the EPMA data was periodically monitored by analyzing andesitic glass AGV-1 as a secondary standard during each analytical session. EPMA-determined compositions of the experimental glasses are listed in Table 1 below.

Table 1

| | SiO ₂ | Al ₂ O ₃ | TiO ₂ | MgO | FeO | CaO | Na ₂ O | K ₂ O | Cl | Total | Fluid/Glass ratio loaded |
|-----------------------------|------------------|--------------------------------|------------------|------------|------------|------------|-------------------|------------------|------------|-------|-----------------------------|
| <u>Starting Glasses</u> | | | | | | | | | | | |
| SRD2-glass | 70.3 | 16.2 | 0.3 | 0.9 | 2.1 | 2.4 | 4.2 | 3.3 | 0 | 99.9 | NA |
| <u>Experimental Glasses</u> | | | | | | | | | | | |
| SRD2-2 (n=17) | 64.0 (0.47) | 16.9 (0.19) | 0.2 (0.08) | 0.8 (0.03) | 1.0 (0.10) | 2.0 (0.05) | 4.6 (0.19) | 4.7 (0.10) | 0.8 (0.04) | 95.2 | 0.58 |
| SRD2-4 (n=16) | 63.7 (0.33) | 16.2 (0.19) | 0.2 (0.11) | 0.8 (0.02) | 1.3 (0.12) | 1.9 (0.05) | 4.4 (0.22) | 4.9 (0.08) | 0.8 (0.04) | 94.4 | 0.28 |
| SRD2-9 (n=13) | 63.9 (0.34) | 16.6 (0.22) | 0.2 (0.07) | 0.8 (0.03) | 1.1 (0.10) | 1.9 (0.05) | 4.7 (0.25) | 4.6 (0.08) | 0.8 (0.04) | 94.9 | 0.55 |
| SRD2-10 (n=13) | 63.9 (0.44) | 16.8 (0.10) | 0.2 (0.04) | 0.8 (0.02) | 0.6 (0.04) | 1.7 (0.02) | 4.6 (0.20) | 5.5 (0.08) | 0.7 (0.05) | 94.8 | 0.95 |
| MagLiq5 (n=13) | 62.7 (0.3) | 16.1 (0.15) | 0.6 (0.06) | 0.6 (0.02) | 4.9 (0.13) | 2.0 (0.04) | 4.0 (0.23) | 2.9 (0.11) | 0.5 (0.02) | 94.6 | >0.1 |
| MagLiq6 (n=20) | 64.0 (0.3) | 16.2 (0.2) | 0.6 (0.07) | 0.5 (0.03) | 4.2 (0.18) | 2.1 (0.05) | 3.8 (0.21) | 2.7 (0.06) | 0 | 94.3 | >0.1 |
| MagLiq7 (n=19) | 65.8 (0.54) | 15.7 (0.37) | 0.3 (0.08) | 0.5 (0.09) | 3.5 (0.13) | 2.1 (0.10) | 3.8 (0.29) | 3.0 (0.06) | 0 | 94.6 | >0.1 |
| MagLiq8 (n=12) | 62.2 (0.37) | 15.7 (0.24) | 0.3 (0.01) | 0.5 (0.05) | 4.4 (0.19) | 2.1 (0.05) | 4.3 (0.26) | 3.4 (0.05) | 1.1 (0.04) | 94.4 | >0.1 |
| <u>XANES Std Glasses</u> | | | | | | | | | | | |
| PD2K-3 (n=16) | 61.7 (0.42) | 15.7 (0.11) | 0.5 (0.05) | 3.7 (0.05) | 2.1 (0.12) | 4.8 (0.07) | 4.3 (0.12) | 1.3 (0.07) | 0 | 94.5 | NA |
| PD2K-4 (n=13) | 62.5 (0.29) | 16.0 (0.10) | 0.5 (0.05) | 3.6 (0.04) | 2.2 (0.11) | 4.7 (0.03) | 4.5 (0.09) | 1.4 (0.07) | 0 | 95.8 | NA |

Development of Dacitic Glass Standards for XANES

Two dacitic glasses were fabricated and developed as XANES standards as a part of this study. The dacite glasses used as standards were produced from a sample of Pinatubo dacite kindly provided by Prof. Malcolm Rutherford. The dacite sample was ground under alcohol in an agate mortar and pestle and subsequently homogenized in an Al₂O₃ ball mill. This mixture was then melted in a Pt crucible in air at 1400° C for three hours. After repeating this process, the resultant material was a compositionally homogenous, crystal-free brown glass that contained no detectable volatiles.

The two PD2K synthesis experiments were loaded with appropriate quantities of distilled and de-ionized water to achieve the desired concentration of H₂O in the melt. The PD2K standard glasses were run in the AMNH IHPV at 1050 °C and 200 MPa at in 4 (OD) × 3.7 (ID) × 20 mm Ag₇₀Pd₃₀ capsules. The experiments were run simultaneously, with a Shaw membrane p_{H₂} of 3.6 bars. The water contents of the two glasses were 5.4 and 5.1 wt % for PD2K-3 and PD2K-4, respectively. Oxygen fugacity of each experiment was calculated using the *f*_{H₂O} of each charge in conjunction with the Shaw membrane imposed *f*_{H₂} and equilibrium constant from Robie and Hemmingway (1995); water fugacity values were evaluated with the Burnham (1979) model and H₂O content of the glass in each charge.

Mössbauer Spectroscopy

Approximately 50 mg of glass from PD2K-3 and PD2K-4 were gently crushed under acetone, and then mixed with a sugar-acetone solution. Grains were gently heaped in a sample holder confined by Kapton[®] tape. Mössbauer spectra were acquired at temperatures ranging from 4-295 K using a source of ca. 40-100 mCi ⁵⁷Co in Rh on a WEB Research Co. model WT302 spectrometer. Mossbauer spectra for the standard glasses are shown in Figure 1. Spectra were collected over a ±4 mm/s velocity range in 2048 channels and corrected for nonlinearity via interpolation to a linear velocity scale, which is defined by the spectrum of the 25 µm Fe foil used for calibration. Spectra were

Figure 1

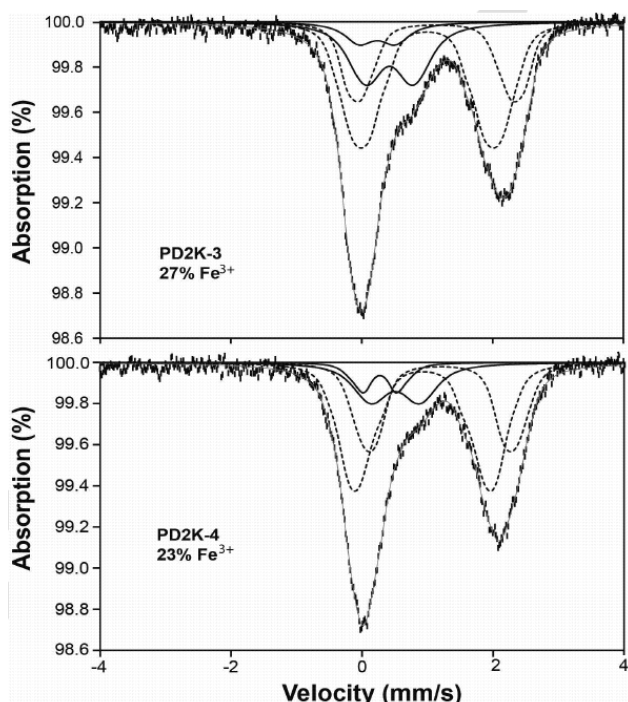


Figure 1 shows the Mossbauer spectra and the model curves fit to the spectra for each of the hydrous standard glasses.

collected in 2048 channels, folded, and corrected for nonlinearity. Data were modeled using an in-house program from the University of Ghent, in Belgium, called DIST_3E, which uses model-independent quadrupole splitting distributions for which the subspectra are constituted by Lorentzian shaped lines. Errors are appropriately ± 0.02 mm/s for center shift and quadrupole splitting. Reproducibility of Mossbauer measurements for peak areas is generally ± 1 -3% absolute on areas.

Extrapolation of the areas to abundances of Fe²⁺ and Fe³⁺ depends on knowledge of the recoil-free fraction associated with each valence state in the material and structure studied, but these are unknown and impractical to calculate for glasses. So in subsequent discussions, the recoil-free fractions for Fe²⁺ and Fe³⁺ are assumed to be equal, so that their corresponding areas relate directly to the abundances of each valence state.

X-ray Absorption Near Edge Spectroscopy (XANES)

$\text{Fe}^{3+}/\Sigma\text{Fe}$ of the experimental SRD2 and PD2K glasses was also quantified using Fe K-edge XANES with the x-ray microprobe of GSECARS beamline 13-ID at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois. The x-ray source at APS beamline 13-ID was a 72-pole, 3-mm period undulator. Beam focusing was accomplished with dynamically-figured Kirkpatrick-Baez focusing mirrors. An x-ray microprobe beam size of 5×3 microns was used on thin, doubly polished wafers of the sample and standard glasses. XANES spectra were acquired in fluorescence mode utilizing a cryogenically cooled, double layer Si(111) monochromator and a silicon drift solid state detector offset at a 45° angle from the sample. Metallic iron foil was used as an internal reference material for the energy calibration of the monochromator.

A total of three spectral sweeps were collected on each analytical point for both the unknown and reference glasses. The stepwise energy interval for these sweeps were set to 0.2 eV in the spectral region from 7102.0 eV to 7137.0 eV and 5.0 eV in the pre-edge and post-edge spectral regions from 7012 eV to 7102 eV and 7140 eV to 7490 eV, respectively. The acquisition time for each individual spectrum was approximately 13 minutes, or 40 minutes total for the three spectra that comprised a single point-analysis. The measured fluorescence intensities were dead time corrected normalized to the ionization-chamber current prior to the spectral processing and fitting. Each set of three spectral sweeps were subsequently dead time corrected, merged into a single spectrum, and edge-step normalized with the IFEFFIT software package. No corrections for Fe self-absorption effects were applied to the spectra. Plots of the stacked SRD2 spectra are shown in Figure 2.

Figure 2

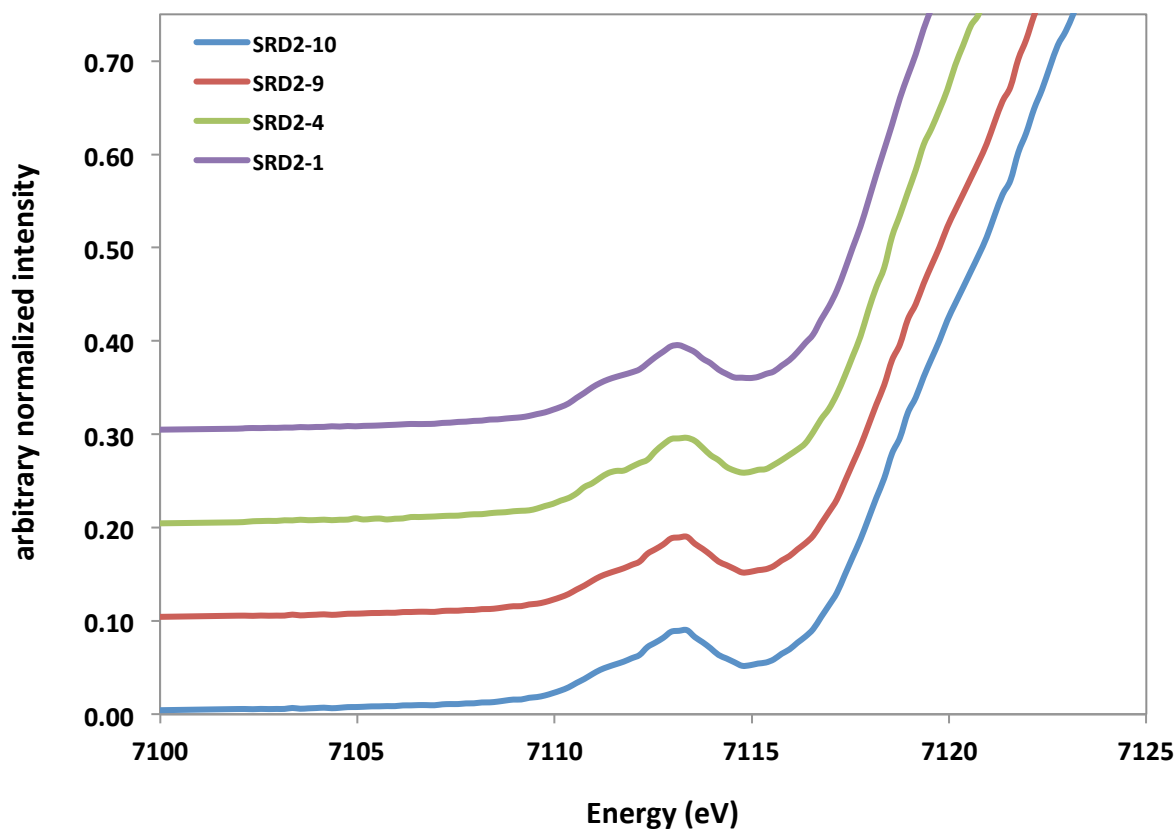


Figure 2 shows a merged and normalized XANES spectra for each of the SRD2 experimental glasses. The pre-edge doublet used to calculate the Fe valence of glasses is the spectral feature approximately centered at 7112.5 eV.

Spectral fitting for both the background and the pre-edge features was accomplished using the commercially available Fityk[®] software package. The fitting was conducted in the 7110 eV to 7120 eV region of the processed spectra. A combination of two Gaussian functions was chosen to model the background of the main Fe absorption edge following the approach of Wilke et al. (2005).

Through trial and error we determined that a background model consisting of two Gaussian functions yielded more robust and reproducible fits to the experimental spectra than any other combination of functions. The pre-edge feature was fit with a combination of two Gaussian functions. All four functions

Figure 3

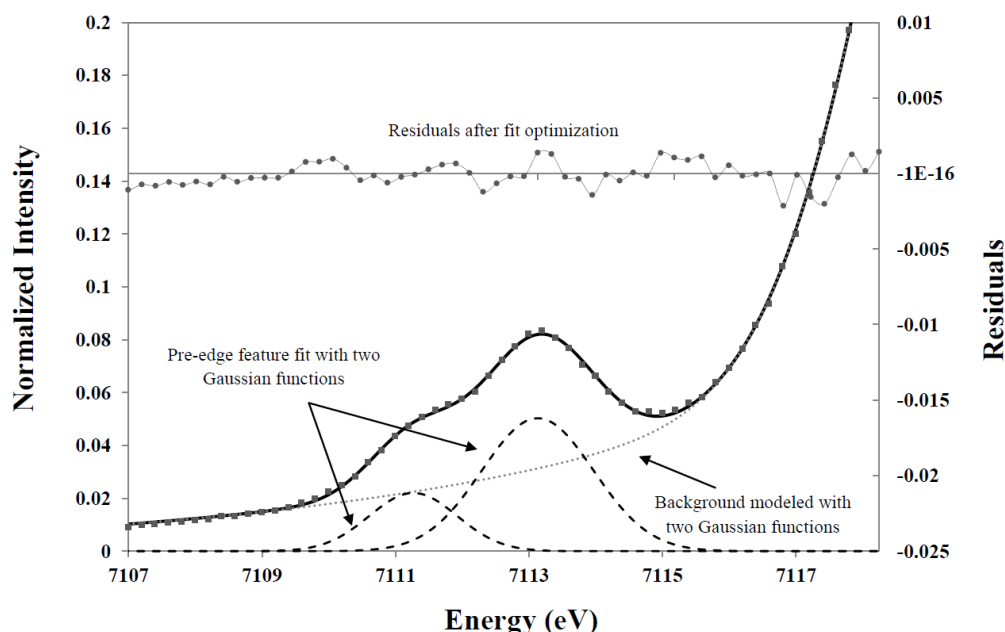


Figure 3 shows the functional components used in the fitting of the XANES spectrum of glass SRD2-2 and the residuals from the fitting procedure. The two Gaussian functions that comprise the background model have been combined into a single function in this figure.

were simultaneously fit to the experimental spectra using a non-linear Levenberg–Marquardt algorithm in the Fityk[®] software. The centroid positions of the two Gaussian functions used to fit the pre-edge feature were variable parameters during the optimization of the fit. Residuals for all of the fitted functions (both background and pre-edge) typically fall within the range of 10^{-4} to 10^{-5} , never exceeding 1.5×10^{-3} (see Figure 3). The peak-area weighted centroid of the pre-edge feature was calculated for all experimental and standard glasses, and a calibration curve was constructed with a set of reference glasses including the set of hydrous, alkaline-rhyolite glasses described in Cottrell et al. (2010) and the dacitic PD2K glasses from this study. The calibration curve is depicted in Figure 4.

Figure 4

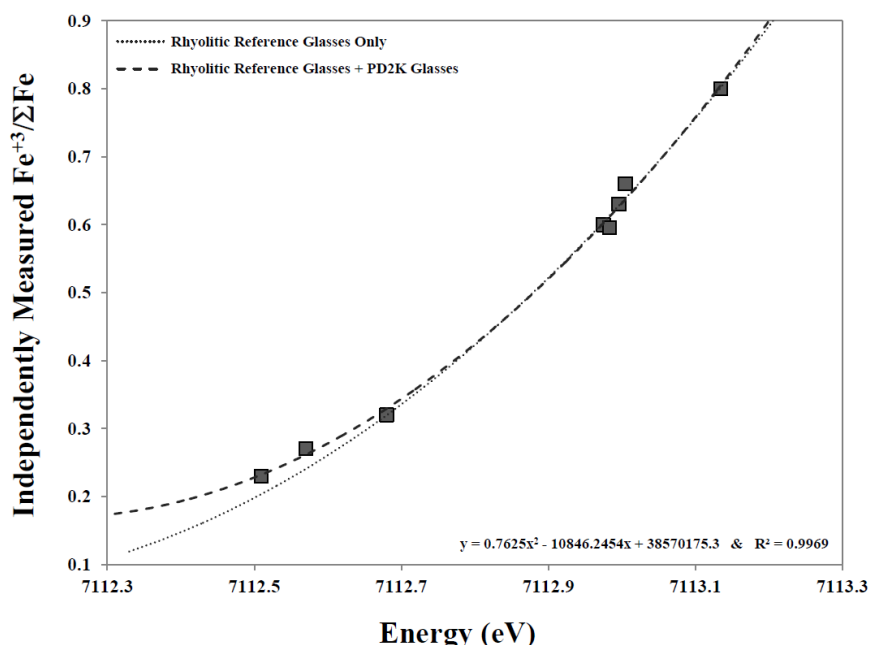


Figure 4 shows the calibration curve used to calculate the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the SRD2 experimental glasses. The heavy dashed curve is the fit for all of the reference glasses and the light dashed curve is the fit for only the alkaline rhyolite reference glasses. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the reference glasses were determined by wet chemistry for the rhyolitic glasses and Mossbauer spectroscopy for the PD2K glasses.

This calibration curve was constructed by plotting the calculated peak-area weighted centroid of the pre-edge feature against the independently measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of the standard glasses and fit by non-linear least squares regression with a quadratic polynomial (Wilke et al. 2005 and Cotrell et al. 2009). The correlation coefficient for this fit ($r^2=0.993$) indicates that the quadratic function robustly describes the trend of $\text{Fe}^{3+}/\Sigma\text{Fe}$ as a function of the peak-area weighted centroid of the reference glasses. Furthermore, the smooth variation of peak-area weighted centroid as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$ suggests that the effects of the compositional differences among the reference glasses on this relationship are minimal. The integrated intensities of the pre-edge feature peaks and the calculated pre-edge centroid position used in the construction of the calibration curve are given in Table 2.

Table 2

| <u>Experiment</u> | <u>7111.5 eV-Peak Area</u> | <u>7113.2 eV-Peak Area</u> | <u>Weighted Centroid (eV)</u> |
|-----------------------|----------------------------|----------------------------|-------------------------------|
| SRD2-2 | 0.0330 | 0.1021 | 7112.65 |
| SRD2-4 | 0.0424 | 0.1094 | 7112.73 |
| SRD2-9 | 0.0360 | 0.1217 | 7112.77 |
| SRD2-10 | 0.0552 | 0.1072 | 7112.66 |
| PD2K-3 | 0.0558 | 0.0951 | 7112.52 |
| PD2K-4 | 0.0773 | 0.1001 | 7112.46 |
| <u>Standard Glass</u> | | | |
| DT18 | 0.0727 | 0.2012 | 7112.95 |
| DT29 | 0.0371 | 0.2478 | 7113.08 |
| DT31 | 0.0434 | 0.1801 | 7112.92 |
| DT39 | 0.0727 | 0.1167 | 7112.63 |
| DT46 | 0.0556 | 0.2017 | 7112.92 |
| H2O63 | 0.0589 | 0.1916 | 7112.93 |

Table 2 displays the integrated intensities of the Fe^{3+} and the Fe^{2+} peaks of the pre-edge doublet from processed and fit XANES data. Calculation of the weighted centroid position is described in section 3.3 of the text. The centroid positions listed in the table were variable parameters during the fitting procedure, thus the actual positions associated with the “7111.5 eV” and “7113.2 eV” peaks vary by ± 0.15 eV

In order to further test the applicability of the rhyolitic glass calibration curve for the rhyodacitic compositions of SRD2 glasses in this study, the PD2K glasses have also been analyzed as blind standards using an extrapolated calibration curve comprised of the only the rhyolitic reference glasses ($r^2 = 0.993$). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated in this manner were 0.21 for PD2K-3 and 0.24 for PD2K-4. These values are in good agreement with those measured by Mossbauer spectroscopy (PD2K-3 = 0.23 and PD2K-4 = 0.27), and this result suggests that the rhyolitic calibration curve is applicable to compositions ranging from dacitic to rhyolitic. The small differences in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values calculated with the two methods likely result from the extrapolation of the parabolic rhyolitic calibration curve to lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ values (the lowest $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the calibration curve is 0.315). The extrapolated curve may under-estimate the degree of curvature in the parabolic calibration, thereby giving rise to the lower calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ values. The intrinsic uncertainty of the calculated centroid positions was assessed with a set of four

replicate point analyses (each consisting of three individual spectral sweeps that were merged into a single spectra) that were performed on a single wafer of SRD2-9 glass. The mean for the calculated pre-edge centroid and the 1σ standard deviation for these analyses were 7112.764 eV and 0.039 eV, respectively. Assuming the uncertainty associated with the calculated pre-edge centroid is the dominate source of error in the XANES measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ values, an uncertainty of 0.039 eV translates to an $\text{Fe}^{3+}/\Sigma\text{Fe}$ error of ± 0.025 . The uncertainty of the calculated centroid positions in this study is approximately a factor of two higher than the values reported for the rhyolitic glasses Cottrell et al. (2009) but is overall quite low.

References

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