1 Structural environment of iron and accurate determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
2 in andesitic glasses by XANES and Mössbauer spectroscopy

3 H.L. Zhang^{1*}, M.M. Hirschmann¹, E. Cottrell², M. Newville³ and A. Lanzirotti³

4 ¹Department of Earth Sciences, University of Minnesota, Minneapolis, MN
5 55455, USA

6 ²Smithsonian Institution, National Museum of Natural History, Washington,
7 DC 20560, USA

8 ³Center for Advanced Radiation Sources, The University of Chicago, Chicago,
9 Illinois 60637, United States.

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11 Abstract

12 Andesitic glasses equilibrated at 1350 °C over a range of oxygen fugacities
13 ($\log f\text{O}_2$ from -8.63 to -0.68) were examined with Fe K-edge X-ray absorption
14 near-edge structure (XANES) and Mössbauer spectra. XANES spectral features
15 were then calibrated as a function of Mössbauer-derived $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.
16 Additionally, both methods help characterize the local structure of iron ions in
17 andesitic glasses. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were determined from Mössbauer spectra
18 collected at room temperature but corrected with recoilless fractions obtained
19 from previously reported Mössbauer data collected on one of the glasses from
20 47-293 K. An empirical model was derived for the correlation between the pre-
21 edge centroid energy and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for andesitic glasses. This trend is
22 intermediate between those previously determined for rhyolitic and basaltic
23 glasses, but the distinction from basaltic compositions may be owing chiefly to

differences in calibrations for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, rather than to intrinsic differences in the spectra as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for mafic glasses. The ratios of intensities of pre-edge sub-peaks and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for andesitic, basaltic, and rhyolitic glasses plot along a common trend, indicating that these measures provide a XANES calibration for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio that is less dependent on silicate composition. The coordination numbers of Fe^{3+} and Fe^{2+} ions in andesitic glass can be calculated from observations of pre-edge centroid energies and total intensities, combined with independent constraints on $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio from Mössbauer spectra. The mean coordination of Fe^{2+} ions calculated this way is close to 5.5 for reduced and oxidized compositions, and this is consistent with inferences from hyperfine features of the Mössbauer spectra. The mean coordination number of Fe^{3+} inferred from XANES increases from ~4.5 to ~5 as andesitic glasses vary from reduced to oxidized; Mössbauer hyperfine parameters also suggest network-forming behavior of Fe^{3+} , but with higher coordination for more reduced glasses.

1. Introduction

The oxidation state of iron in silicate melts has an important influence on the chemical and physical properties of natural magmas (Sack et al., 1980; Virgo and Mysen, 1985; Christie et al., 1986; Dingwell et al., 1988; Kress and Carmichael, 1991; Bézous and Humler, 2005; O'Neill et al., 2006; Cottrell and Kelley, 2011, 2013). With appropriate thermodynamic calibration, the proportion of ferric and ferrous iron, expressed as $\text{Fe}^{3+}/\Sigma\text{Fe}$, can be directly related to the oxygen fugacity ($f\text{O}_2$) of magmatic source regions, and therefore is a probe of the

conditions in Earth's interior (Arculus, 1985; Christie et al., 1986; Wood et al., 1990; Carmichael, 1991; Kress and Carmichael, 1991; Lécuyer and Ricard, 1999; Jayasuriya et al., 2004; Bézos and Humler, 2005). $\text{Fe}^{3+}/\Sigma\text{Fe}$ also influences the compositions of crystallizing phases, and so affects the chemical trends produced by fractional crystallization (Osborn, 1959; Hill and Roeder, 1974).

A variety of analytical techniques are used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in minerals and glasses. Wet chemical determinations, including colorimetry, and Mössbauer spectroscopy are perhaps the best established (Wilson, 1960; Mysen et al., 1985; Virgo and Mysen, 1985; Lange and Carmichael, 1989; Kress and Carmichael, 1991; Bézos et al., 2005; Dyar et al., 2006; Rossano et al., 2008; Dyar et al., 2012), but micro X-ray absorption near edge structure (μ -XANES) spectroscopy affords high spatial resolution with comparable or superior precision (Berry et al., 2003; Wilke et al., 2005; Cottrell et al., 2009; Cottrell and Kelley, 2011; Dauphas et al., 2014), allowing analysis of glasses from complex natural samples and from experiments. Fe K-edge μ -XANES of magmatic glasses is sensitive to valence and bonding environments of the analyzed ions, but generally provides the best precision and accuracy when cross-calibrated to materials with known $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Calibrations between standards established by wet chemical or Mössbauer methods and μ -XANES have been determined for basalt (Berry et al., 2003; Botcharnikov et al., 2005; Wilke et al., 2005; Cottrell et al., 2009; Cottrell and Kelley, 2011; Dauphas et al., 2014), andesite (Dauphas et al., 2014), dacite (Dauphas et al., 2014), rhyolite (Cottrell

et al., 2009; Cottrell and Kelley, 2011; Dauphas et al., 2014), alkali-silicates (Knipping et al., 2015) and haplotonalite and haplogranite (Wilke et al., 2006). These calibrations typically are based on the area-weighted average energy of the pre-edge absorption peaks for Fe^{3+} and Fe^{2+} relative to the calibration standards of known $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Berry et al., 2003; Wilke et al., 2005; Cottrell et al., 2009). In this paper we present Mössbauer and μ -XANES data for a suite of andesitic glasses and use them to establish a new calibration curve.

Mössbauer spectroscopy and μ -XANES are also useful for investigating the local structural environments of iron ions in silicate glasses. Both Fe^{3+} and Fe^{2+} have the potential to behave as either network forming or network-modifying ions (Fox et al., 1982; Mysen et al., 1982; Virgo et al., 1982; Virgo et al., 1983; Virgo and Mysen, 1985; Rossano et al., 2000; Mysen, 2006). Characterization of the average coordination state of Fe^{2+} and Fe^{3+} in glasses provides useful insight into the effects of melt composition and pressure on the thermodynamic and transport properties of silicate liquids (Mysen and Richet, 2005). Previous studies employing a range of spectroscopic methods and molecular dynamics calculations have concluded that at low pressure Fe^{2+} and Fe^{3+} in natural and synthetic analog glasses and melts take on a variety of coordination states. In this paper we add to these observations, with new constraints on the coordination of Fe^{2+} and Fe^{3+} in andesitic glasses.

2. Methods

2.1 Starting materials

The starting material of VF Series consists of a synthetic andesite similar in

composition to that used by O'Neill et al. (2006) and Zhang et al. (2015), and was prepared from reagent oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MgO), silicates (CaSiO_3 , Na_2SiO_3) and stoichiometric sanidine glass. The Fe_2O_3 consisted of 90% normal reagent oxide and 10% $^{57}\text{Fe}_2\text{O}_3$ (Isoflex, Inc) to obtain quality Mössbauer spectra at practical total count times. Prior to weighing, the SiO_2 , Al_2O_3 , TiO_2 , and MgO were devolatilized by heating overnight in a furnace at 1000 °C, until the weight stabilized. These reagents were then weighed and mixed with the silicates and sanidine by grinding under ethanol for at least one hour, until the grinding sound diminished and then again devolatilized by firing at 1000 °C for 48 hrs. Finally, the Fe_2O_3 , which had been dried at 800 °C for 1 hour and then weighed, $^{57}\text{Fe}_2\text{O}_3$ was added and the final mixture was homogenized by grinding under ethanol.

2.2 High temperature experiments

VF series andesitic melts were equilibrated at 1 atm and 1350 °C for 24 hours in a Deltech VT28 vertical gas mixing rapid-quench furnace at the University of Minnesota, with temperature measured by a Type S ($\text{Pt}_{90}\text{Rh}_{10}/\text{Pt}_{100}$) thermocouple. Temperature uncertainties are believed to be ± 4 °C, as judged from an Au melting calibration, which was observed at 1059 °C. Oxygen fugacity ($f\text{O}_2$) was controlled with CO_2/CO , O_2/CO_2 or air gas steams and measured with a SRO₂ C700+ Solid Zirconia Electrolyte oxygen sensor. The sensor was calibrated against the Ni-NiO buffer (Huebner and Sato, 1970) and the reference gas was air.

Except for experiment VF85, which used a 0.005" diameter Re wire,

experiments used 0.005" Pt wire loops, and these were pre-equilibrated with the starting material by loading approximately 30 mg, bonded by polyvinyl acetate (PVA) on the loops and melting at the experimental temperature and fO_2 . The loops were then cleaned in HF and reloaded with starting material, with the experiment then repeated. Electron microprobe analyses on each quenched glass verified that this procedure prevented detectable Fe loss during the experiment (Table S1). Andesite glasses were equilibrated at 1350 °C in flowing CO/CO₂ for 24 h when $\log fO_2 < -3.2$ (~QFM+3.5, where QFM refers the quartz-fayalite-magnetite redox buffer), and in CO₂/O₂ or air for more oxidized conditions. This duration was judged sufficient to completely equilibrate Fe speciation with the gas mix based on previous studies (Kilinc et al., 1983; Roskosz et al., 2008; Knipping et al., 2015). All experimental conditions were listed in Table 1. Some experiments (VF30-VF59), whose oxygen fugacity were measured before experiments, were quenched by being removed from the furnace and put into cold water within seconds, and others (VF66-VF88), whose oxygen fugacity were monitored during the experiments, were rapidly drop quenched into a water bath by vaporizing the Pt hang wire.

ECA series andesitic glasses were equilibrated at 1 atm and 1350 °C in a vertical gas mixing rapid-quench furnace at the Smithsonian Institution for 24 hrs. ECA is a natural trachyandesite erupted from El Chichón volcano in 1982, unit A (Andrews, et al., 2008, Table S1). Oxygen fugacity (fO_2) was controlled with flowing CO₂/CO, and measured with an SIRO₂ C700+ Solid Zirconia Electrolyte oxygen sensor. The experimental details were described in Cottrell et al. (2009)

and are also listed in Table 1.

Although the structure of the glass likely is not identical to that of the liquid from which it was quenched, at cooling rates typical of drop quench ($<100^{\circ}\text{C}/\text{second}$) from 1 atmosphere furnaces (Dyar et al., 1987) both the $\text{Fe}^{3+}/\Sigma\text{Fe}$ and the key structural features such as Fe-O coordination characteristic of the molten liquid are likely only slightly changed from that in the glass (Wilke et al., 2007; Cottrell and Kelley, 2011). For example, previous studies show that hyperfine parameters from Mössbauer spectra show no effect of quench rate on Fe^{2+} and Fe^{3+} bonding environments, except for glasses quenched at ultra slow rates ($<0.02\text{ K/s}$) (Wilke et al., 2002; Wilke et al., 2006; Rossano et al., 2008). Similarly, varying quench rates from $>2000\text{ K/s}$ to $\sim 2\text{ K/s}$ in basaltic glass do not influence oxidation state of iron derived from XANES spectra (Cottrell and Kelley, 2011). All glasses were carefully separated from the Pt or Re loops. From each experiment, several glass chips were removed and doubly polished for optical examination, XANES, and electron microprobe analyses, while the remainder was ground to powder for Mössbauer spectroscopy.

2.3 Analytical Methods

2.3.1 Electron Microprobe

Textures of polished sections from VF Series and ECA Series experiments were examined by back-scattered electron (BSE) and secondary electron imaging (SEI) using the JEOL JXA8900R EPMA at the University of Minnesota and using the JEOL-8900 at the Smithsonian Institution respectively. Major element concentrations of quenched glasses were determined by wave-length-

dispersive EPMA, using a 15kV acceleration voltage.

A focused 5 μm diameter beam of 20 nA was employed for VF Series glasses, with counting times of 20 s for unknowns and 10 s for the standards, including synthetic Mg_2SiO_4 for Mg, anorthite for Ca, ilmenite for Ti and Fe, albite for Si and Na, and microcline for Al and K, and matrix corrections were computed with Probe for Windows software (Table S1). During microprobe analyses, MPI-DING glass ATHO-G (Jochum et al., 2006) was analyzed as a secondary standard before and after analyses of unknown samples, as well as in between each 5 or 6 unknown samples. The x-ray intensities of standards, secondary standards and unknown samples were checked for time dependent (TDI) changes and Na $\text{K}\alpha$ counts were corrected with TDI using a self-calibrated correction; no TDI effect was observed for other elements.

2.3.2 Mössbauer Spectroscopy

Mössbauer spectra were collected using a constant acceleration Ranger spectrometer at the Institute for Rock Magnetism, University of Minnesota, and the measurements were carried out with a $^{57}\text{Co/Rh}$ source and a pure Fe foil calibrant at room temperature (293 K). Data were collected over 512 channels, which were then folded to produce 256 unique channels. All spectra were collected over at least one day and until sufficient counts ($>1,200,000$ counts / channel) were accumulated. Sample mounts consisted of powdered glass mixed with powdered sugar evenly distributed in an approximately circular shape of diameter 12.7 mm. The absorber thicknesses were adjusted for an absorber density of $\sim 2 \text{ mg/cm}^2 \text{ Fe}$.

185 All Mössbauer spectra were fitted using the RECOIL software package
 186 (Lagarec and Rancourt, 1998) with a 2D distribution extended Voigt-based fitting
 187 (xVBF) method described in detail by Zhang et al. (2015). Considerations of
 188 precision and accuracy, including accounting for the effect of recoilless fraction,
 189 are introduced briefly here. Lorentzian half widths at half maximum (L HWHM)
 190 are assumed to be the same for all sub-spectra of Mössbauer spectra with the
 191 xVBF method (Lagarec and Rancourt, 1997). Each doublet was fit as a 2D
 192 distribution, for which the parameters consist of the center shift (CS), the
 193 quadrupole splitting (QS), and their respective Gaussian widths, δ_{CS} and δ_{QS} .
 194 The correlation between the CS distribution and QS distribution (ρ) was assumed
 195 to be 0 for Fe^{3+} (Alberto et al., 1996) and variable for Fe^{2+} . All hyperfine
 196 parameters and their uncertainties, in 1σ , were calculated based on a bootstrap
 197 method and are cataloged in Table S2. The quality of these fits is characterized
 198 by χ^2 values, which are also listed in Table S2. Irrespective of fitting method,
 199 resolving precise $Fe^{3+}/\Sigma Fe$ from Mössbauer spectra is challenging for samples
 200 with $Fe^{3+}/\Sigma Fe$ below $\sim 15\%$, as has also been reported previously (Dyar et al.,
 201 1987; Rossano et al., 1999; Berry et al., 2003; Botcharnikov et al., 2005; Wilke et
 202 al., 2005; Cottrell et al., 2009). This challenge is not alleviated by shape-
 203 independent distribution analysis, and the inclusion of additional doublets did not
 204 improve model fit statistics, as also found by Cottrell et al. (2009), and so all
 205 xVBF fits employ only one site each for the ferrous and ferric components.
 206 However, to aid reasonable fits for reduced glasses, we use the Gaussian width
 207 of the ferric quadrupole splitting, δ_{QS} , as a parameter marker. If fits to δ_{QS} fell

below the range of 0.4~0.6, we fixed the value to 0.4 and the Gaussian width of ferric center shift, δ_{CS} , to 0 (Table S2). This is because all fits for more oxidized spectra, which have three distinguishable peaks and so place better constraints on the Fe^{3+} doublets, have δ_{QS} between 0.4~0.6 and values of δ_{CS} near zero, as also found by Alberto et al. (1996).

Besides the shape-independent distribution analysis described above, we also constructed, for all andesite glasses, a second set of fits using the Lorentzian Multiplet Analysis (LMA) using RECOIL (Lagarec and Rancourt, 1998). One or more symmetric doublets of Lorentzian shape were used to fit the spectra. All hyperfine parameters and their uncertainties, in 1σ , were calculated based on a bootstrap method and are cataloged in Table S3. The quality of these fits is characterized by χ^2 values, which are also listed in Table S3. The $Fe^{3+}/\Sigma Fe$ ratios determined from LMA are listed in Table 1. For samples with $Fe^{3+}/\Sigma Fe$ ratios <0.15 , we use the same approach as Wilke et al. (2005), adding ferrous iron doublets and observing the change in the χ^2 statistic. Best fits incorporated 5 ferrous doublets for the reduced andesite glasses (Table S3). xVBF and LMA fitting extract $Fe^{3+}/\Sigma Fe$ ratios similar to one other (Fig. 1, Table 1).

Zhang et al. (2015), using a composition identical to that employed in the present study, demonstrated that recoilless fractions for Fe^{3+} and Fe^{2+} (f_{Fe3+} and f_{Fe2+}) in andesitic glasses are unequal at room temperature, and used low temperature analyses as well as comparison to wet chemical determinations, to establish a factor C (f_{Fe3+}/f_{Fe2+}) of 1.256 ± 0.153 . This factor should be applied to room temperature Mössbauer analyses of $Fe^{3+}/\Sigma Fe$ ratios in andesite glasses

according to the relation:

$$\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}_{\text{Corrected}} = \frac{\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}}{\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}} + C \left(1 - \frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}\right)} \quad (1).$$

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of glasses determined from xVBF and then corrected with C are listed in Table 1 and are similar to the ratios predicted from the model of Kress and Carmichael (1991) based on the temperature and $f\text{O}_2$, from which they were quenched as well as the major element composition of the andesite glasses (Fig. 2, Table 1). Fig. 2 also illustrates that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that are not corrected for recoilless fraction effects yield an inferior match to the predictions of Kress and Carmichael (1991), particularly for glasses with high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.

2.3.3 X-ray absorption near edge structure (XANES)

Fe K-edge XANES spectra were collected at station X26A (bending magnet) of the National Synchrotron Light Source (NSLS), Brookhaven National Lab (BNL) in one session, and at beamline 13-IDE at the Advanced Photon Source (APS), Argonne National Lab (ANL), in two sessions. A minimum of 3 spectra was collected on each andesitic glass, each time on a fresh spot.

NSLS operates at 2.8 GeV and 300 mA, and the spot size on sample was $9 \times 5 \mu\text{m}$. Energy selection was achieved with a silicon monochromator channel-cut along Si (311) described in Cottrell et al. (2009). All spectra were collected in fluorescence mode using both a single 4-element Vortex ME-4 silicon drift diode detector with two single element Vortex-Ex detector (Hitachi) coupled to an XMap digital spectrometer system (XIA). The monochromator energy at X26A was calibrated so that the first derivative peak for Fe K-edge spectra for Fe foil was 7112.0 eV (Ruffoni and Pettifer, 2006). Incident beam flux at X26A for these

experiments was $\sim 3 \times 10^9$ photons/sec. Spectra at X26A were recorded with four energy regions previously defined by Cottrell et al. (2009) and drifts in monochromator energy over time, correlated to decreasing current in the X-ray storage ring at NSLS through an injection cycle, and hence to the temperature of the monochromator, were corrected through repeated analysis of glass LW_0 to provide a corrected energy weighted centroid energy of 7112.3 eV using the method described in Cottrell et al. 2009. We use the same ratio to correct the center positions for Fe^{3+} and Fe^{2+} for drift. The drift-corrected NSLS centroid energies are reproducible from session to session with precision similar to that within a single session (Cottrell et al., 2009).

The APS operates at 7 GeV and 85-101 mA. The spot size on samples for these experiments was varied between $2 \times 2 \mu\text{m}$ and $25 \times 25 \mu\text{m}$ and the incident flux rate was also variably set to between $5\text{-}20 \times 10^{10}$ photons/sec to best manage detector saturation. Energy selection was achieved using a fixed exit, liquid nitrogen cooled double crystal monochromator and a Si (311) crystal set. X-ray fluorescence from the samples was detected using a Vortex ME4 silicon-drift diode array detector array coupled to a high-speed digital spectrometer system (Quantum Xpress3). APS data were corrected for detector dead time. At 13-IDE the monochromator calibration provides a first derivative for the Fe K-edge spectra on Fe foil of 7110.7 eV (Kraft et al., 1996). Spectra were recorded from 7020 to 7312 eV with four regions: 5 eV steps from 7020 to 7105 eV with 1 s dwell; 0.1 eV steps from 7106 to 7118 eV, over the pre-edge energy range with 3 s dwell; 1.0 eV steps from 7118 to 7120 eV with a 2 s dwell, 2.0 eV steps from

7120 to 7312 eV at 1 s dwell. Spectra of the LW_0 reference glass (Cottrell et al., 2009) were collected every 2~3 hours and across two sessions. The centroid energy of LW_0 was 7111.95 ± 0.02 eV ($n=86$), with no indication of instrumental drift; therefore no time-dependent energy corrections were applied to unknown spectra. Due to the difference in monochromator energy calibration at the NSLS and APS beamlines of ~ 1.3 eV, all APS spectra were corrected by a constant so that standard LW_0 $\equiv 7112.3$ eV (Cottrell et al., 2009). Center positions of pre-edge sub-peaks of Fe^{3+} and Fe^{2+} were corrected with the same ratio based on the centroid energy correction.

All XANES spectra were fit using the methods described by Cottrell et al. (2009) and are only briefly introduced here. All spectra were edge-step normalized using a region from 7200 to 7312 eV. All parameters for the pre-edge features were extracted by simultaneously fitting the baseline, which consists of a linear function with a positive slope, a damped harmonic oscillator (DHO) function, and two Gaussian functions to describe pre-edge peaks. The fit of the pre-edge region, from 7110 eV to 7118 eV was performed using Interactive Data Language (IDL) software and the MPFIT set of routines for robust least-squares minimization (Markwardt, 2008). All fit parameters with standard energy (LW_0 $\equiv 7112.3$ eV, Cottrell et al., 2009) corrected are reported in Table S4.

With fluorescence detection, self-absorption becomes a factor when the penetration depth into the sample is dominated by the absorbing atom, in this case iron. Self-absorption attenuates X-rays, modifying the intensities of pre-edge and other components of the XANES spectrum. All spectra were corrected

for self-absorption with average andesite composition from Table S1, using the FLUO algorithm (Haskel, 1999) embedded in Athena software package written by Ravel and Newville (2005). After corrections, total integrated normalized intensities of the pre-edge decreased ~ 0.014 in average, and the intensity ratios and centroid energies were the same within error, consistent with previous studies of self-absorption on Fe-XANES spectra in silicate glasses (Botcharnikov et al., 2005; Cottrell et al., 2009).

3. Results

3.1 EMPA determinations

BSE imaging of the quenched materials indicated that they consisted wholly of glass, with no observed crystallites down to the resolution of the EPMA instrument. Electron microprobe analyses of the glasses and secondary standards established FeO* in VF Series glasses (Table S1). The resulting FeO* of the unknown glasses have high precision (generally $\pm 1\%$ relative) and are believed to have high accuracy because analyses reproduced the accepted FeO* concentrations of secondary standards, with discrepancies of no more than 0.1 wt.% (Table S1). FeO* concentrations of glasses range from 8.2 to 10.2 wt.%, with average deviations compared of the nominal starting composition (9.4 wt% FeO*) of 5% relative and a maximum of 13% indicating that Fe gains or losses from/to the Pt hanging wires was minimal. Apart from FeO*, SiO₂, and Na₂O, all the glasses have the same major element chemical composition within analytical uncertainty (Table S1), indicating that melts were compositionally homogeneous.

3.2 Mössbauer Spectroscopy

Mössbauer spectra consist of two quadrupole doublets, one each originating from paramagnetic ferric and ferrous iron. No obvious sextets at 12 mm/s, as would arise from ferromagnetic Fe, are evident. All hyperfine parameters obtained from Mössbauer spectral fits (Table S2 and Table S3), are similar to those previously reported for silicate glasses (Mysen et al., 1985; Alberto et al., 1996; Jayasuriya et al., 2004; Botcharnikov et al., 2005; O'Neill et al., 2006; Zhang et al., 2015).

The Mössbauer spectra have broadened line-shapes typical of silicate glasses, with examples showed in Fig. S1, and these can be well-accommodated by distribution fitting methods (Alberto et al., 1996; Rossano et al., 1999; O'Neill et al., 2006; Rossano et al., 2008; Borisov and McCammon, 2010; Zhang et al., 2015). Wilke et al. (2002) argued that relative to conventional fitting with Lorentzian doublets, the improvement of a shape-independent distribution analysis for determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is negligible. As shown in Fig. 1, the two fit methods produce $\text{Fe}^{3+}/\Sigma\text{Fe}$ that are consistent within uncertainty, although the average ratio is displaced to slightly higher values with LMA, with the average $\text{Fe}^{3+}/\Sigma\text{Fe}$ of all measurements 0.022 ± 0.020 greater. As xVBF methods are thought to better-describe the internal structure of glass (Alberto et al., 1996; Rossano et al., 1999; Rossano et al., 2008) and produce smaller statistical errors (Table S2), for the rest of paper, we present $\text{Fe}^{3+}/\Sigma\text{Fe}$ resulting from xVBF fits.

Hyperfine parameters (CS and QS) obtained from xVBF and LMA are plotted versus $\text{Fe}^{3+}/\Sigma\text{Fe} \times 100$ resolved from xVBF in Figs. 3 and Fig. 4. For LMA methods that assume that Fe^{3+} or Fe^{2+} has more than one site, subspectra area-

weighted CS and QS are used. Overall, hyperfine parameters obtained from the two fit methods show similar values and trends with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$, but determinations from xVBF show less variability, most notably for QS (Fe^{3+}), and are therefore possibly more accurate. CS (Fe^{3+}) decreases with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 3a). However, QS (Fe^{3+}) varies little with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 4a). CS (Fe^{2+}) and QS (Fe^{2+}) change little with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 3b and Fig. 4b), indicating that the nearest neighbor environment of Fe^{2+} does not change significantly from 8.04% to 83.5% $\text{Fe}^{3+}/\Sigma\text{Fe}$.

3.3 XANES spectra

XANES spectra also provide information on the coordination and bonding of iron in the silicate glasses. In particular, the pre-edge region (position I in Fig. 5a) is attributed to the $1s \rightarrow 3d$ transition, the energy of main absorption (position II in Fig. 5a) is produced by a $1s \rightarrow 4p$ electron transition (Penner - Hahn, 2012). Smooth variations of these features are observed with changes in Fe oxidation state (Fig 5a, 5b), including shifts to higher energy of the main absorption (Fig. 5a, position II), and changes in the intensity, shape, and centroid energy of the pre-edge feature (Fig. 5a Position I, Fig. 5b). We focus our attention on the pre-edge feature, as it provides the most easily quantifiable constraints.

For the suite of andesite glasses, the pre-edge region consists of two sub-peaks, which can be attributed to Fe^{2+} ions (center near 7111.9 eV) and Fe^{3+} ions (center near 7113.5 eV), respectively. Features of the pre-edge change systematically with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the glass, as illustrated in Fig. 5c, which shows baseline-subtracted pre-edge spectra for glasses with a representative

range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. The ferrous and ferric peak height intensities grow and diminish in normalized absorbance as oxidation state changes. The ferrous center positions, $E_0(\text{Fe}^{2+})$, shift downwards by 0.2 eV as $\text{Fe}^{3+}/\Sigma\text{Fe}$ varies from 0.84 to 0.08 (Fig. 6a), whilst, the ferric center positions, $E_0(\text{Fe}^{3+})$, increase by 0.3 eV (Fig. 6b). We fit these variations to quadratic functions, which are specified in Table 2. Area-weighted center positions, also known as centroid energies, can be calculated from individual peak areas ($I(\text{Fe}^{3+})$ and $I(\text{Fe}^{2+})$), and center positions ($E_0(\text{Fe}^{3+})$ and $E_0(\text{Fe}^{2+})$) according to

$$\text{Centroid Energy} = \frac{I(\text{Fe}^{3+})E_0(\text{Fe}^{3+}) + I(\text{Fe}^{2+})E_0(\text{Fe}^{2+})}{I(\text{Fe}^{3+}) + I(\text{Fe}^{2+})} \quad (2)$$

Variations in the centroid energy with $\text{Fe}^{3+}/\Sigma\text{Fe}$ and associated errors are shown in Fig. 7.

Several features of the XANES pre-edge shape produce trends that can be empirically correlated to $\text{Fe}^{3+}/\Sigma\text{Fe}$ in andesitic glasses, as has been previously explored for other silicate glasses (Berry et al., 2003; Botcharnikov et al., 2005; Wilke et al., 2005; Métrich et al., 2006; Cottrell et al., 2009; Dauphas et al., 2014; Knipping et al., 2015). For andesitic glasses ranging from $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.06 to 0.80, area-weighted centroid energies increase from 7112.092 to 7113.404 (Fig. 7). Similarly, baseline-subtracted pre-edge integrated intensity ratios ($I(\text{Fe}^{3+})/I(\text{Fe}^{2+})$, and $I(\text{Fe}^{3+})/[I(\text{Fe}^{3+}) + I(\text{Fe}^{2+})]$) increase systematically with $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 8). Uncertainties, established by replicate analyses of at least 3 separate spots on each sample, are typically 0.014 and 0.010 eV for the area-weighted centroid energies measured at NSLS and APS, respectively. Uncertainties in area ratios vary from 0.005 to 0.67 for $I(\text{Fe}^{3+})/I(\text{Fe}^{2+})$, and 0.001

to 0.049 for $I(\text{Fe}^{3+})/[I(\text{Fe}^{3+})+I(\text{Fe}^{2+})]$, respectively, with greater values (up to 10% and 9% relative) associated with larger $I(\text{Fe}^{3+})/I(\text{Fe}^{2+})$ and $I(\text{Fe}^{3+})/[I(\text{Fe}^{3+})+I(\text{Fe}^{2+})]$ ratios. Application of these features to quantitative determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is explored further in the Discussion.

The total integrated intensities of the pre-edge peaks, normalized to those of the *K* edge (Fig. 9) provide information about the average coordination of Fe ions in the silicate structure, with larger normalized total integrated intensities associated with lower coordination states and greater $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. (e.g., Wilke et al. 2001). Among the andesite glasses, normalized pre-edge intensities range from 0.1 for the more reduced glasses up to 0.18 for those more oxidized (Table 3). Quantitative interpretations of coordination are examined in the Discussion.

4. Discussion

4.1 Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ by XANES

Variations in XANES pre-edge features with $\text{Fe}^{3+}/\Sigma\text{Fe}$ can be calibrated to produce empirical quantitative measures of the oxidation state of Fe in silicate glasses (Berry et al., 2003; Botcharnikov et al., 2005; Wilke et al., 2005; Métrich et al., 2006; Cottrell et al., 2009; Dauphas et al., 2014; Knipping et al., 2015). The most widely-used such parameterization uses the area-weighted centroid energy. For glasses in this study, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio was calculated from room temperature Mössbauer spectra, corrected for the effects of recoilless fraction (Zhang et al., 2015). Corrections for recoilless fraction diminish apparent $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios by 1.5% to 5.7% relative (Table 1).

415 Prior to comparing the present results to those from the literature, it is
416 important to consider possible systematic biases owing to different methods of
417 establishing $\text{Fe}^{3+}/\Sigma\text{Fe}$. Most of the glasses from the studies of Cottrell et al.
418 (2009) and Dauphas et al. (2014) were characterized by Mössbauer
419 measurements without correction for recoilless fraction effects, though some of
420 the rhyolites used by Cottrell et al. (2009) were characterized by wet chemical
421 analyses. The accuracy of uncorrected room temperature (RT) Mössbauer
422 measurements of $\text{Fe}^{3+}/\Sigma\text{Fe}$ has long been debated. This history was reviewed in
423 detail by Zhang et al. (2015), but theoretical arguments based on bond strength
424 (Chen and Yang, 2007) make clear that RT Mössbauer should overestimate
425 $\text{Fe}^{3+}/\Sigma\text{Fe}$, as known to be true based on measurements of recoilless fractions
426 from a wide spectrum of Fe-bearing minerals (De Grave and Van Alboom, 1991).
427 Also, most studies that are generally cited to suggest that RT Mössbauer of
428 silicate glasses yields accurate $\text{Fe}^{3+}/\Sigma\text{Fe}$ within analytical uncertainty (Mysen and
429 Virgo, 1985; Dingwell, 1991; Jayasuriya et al., 2004; Wilke et al., 2005) actually
430 show systematic biases to higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Lange and Carmichael, 1989;
431 Richter et al., 2013; Zhang et al., 2015). Partzsch et al. (2004) observed the
432 opposite trend, finding that wet chemical analyses yielded higher Fe^{3+} than
433 Mössbauer analyses of glasses quenched from similar conditions; but in their
434 study individual experiments were not analyzed by multiple methods. Dyar et al.
435 (1987) also observed that wet chemical analyses yielded higher Fe^{3+} , however,
436 their Fe^{3+} contents were not directly from the fit of Mössbauer spectra. Similarly,
437 Jayasuriya et al. (2004) showed that $\text{Fe}^{3+}/\Sigma\text{Fe}$ in synthetic basaltic glasses

calculated from RT Mössbauer gave similar results to $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated from Mössbauer spectra taken at 4.2 K, but both their RT and low temperature spectra are complicated by strong non-paramagnetic components, which introduce ambiguity to quantification of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Zhang et al., 2015). Thus, there is no consensus in the literature regarding whether Mössbauer and wet chemical methods are consistent, or even in which direction the results may be biased. The following comparisons consider the possibility that, while RT Mössbauer is accurate within normal analytical uncertainties, there is a small (~few percent relative) systematic bias toward overestimating Fe^{3+} if adjustments are not made for recoilless fraction (Zhang et al., 2015).

Previous studies have noted that the relationship between the area-weighted pre-edge centroid energy and $\text{Fe}^{3+}/\Sigma\text{Fe}$ can depend on glass composition, and most notably that trends for rhyolite are distinct from those for less silicic natural glass compositions (Cottrell et al., 2009; Dauphas et al., 2014). Consequently, the previous observations most similar to those in the present study are three andesitic glasses analysed by RT Mössbauer and XANES spectroscopy by Dauphas et al. (2014). If we compare the relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined by RT Mössbauer and centroid energies, andesites and basalts lie on the same calibration curve within error of the measurements (Dauphas et al., 2014, Table 1, Table S5, Fig. S2). Likewise, if we adjust their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined at RT for recoil-free fraction effects by the same factor as that determined for the andesites in Zhang et al. (2015) (Table S5), two of the three glasses have variations in centroid energies and $\text{Fe}^{3+}/\Sigma\text{Fe}$ that are similar to the

trend established from the present study (Fig. 7). The third, equilibrated at IW, does not have a well-resolved $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio from the Mössbauer spectrum. Combining the recoil-free fraction-corrected Mössbauer determinations with the centroid energies for the suite of andesite glasses from this study plus the two additional constraints from Dauphas et al. (2014) allows regression of a function

$$\text{Fe}^{3+}/\Sigma\text{Fe} = a + b \cdot (x - d) + c \cdot (x - d)^2 \quad (3)$$

for quantitative prediction of $\text{Fe}^{3+}/\Sigma\text{Fe}$, with coefficients listed in Table 4.

For rhyolites, the relation between centroid energy and $\text{Fe}^{3+}/\Sigma\text{Fe}$ is anchored chiefly from the XANES observations of Cottrell et al. (2009), for which Fe oxidation states were determined principally by wet chemical analyses (Moore et al., 1995). Exceptions include one glass, 568_2, from Cottrell et al. (2009) and the 3 glasses analyzed by Dauphas et al. (2014), for which only RT Mössbauer data are available. These four samples can be adjusted by a factor derived by comparison of wet chemical (Moore et al., 1995) and RT Mössbauer results (Cottrell et al., 2009) for samples DT_46 and DT_39, which indicate a factor, C , equal to 1.124 ± 0.035 . The resulting centroid versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ trend for rhyolites (Table S5, Fig. 7) remains distinct from that derived for andesite glasses, which could be owing to differences in Fe-O bond strengths in the two glass compositions, as suggested by Dauphas et al. (2014).

Centroid versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ trends for basalt are established chiefly from RT Mössbauer spectroscopy and at this time we do not have an unambiguous constraint on how these should be corrected for recoilless fraction. Fig. 7 shows the basalt trend from the measurements of Cottrell et al. (2009) in which the

original RT Mössbauer determinations were modified with values of C of 1.1, 1.2, and 1.3. With values between 1.2 and 1.3, similar to that applied here (1.256) to the andesite glasses based on Zhang et al. (2015), the basalt and andesite trends are more nearly coincident. Thus, much, or all, of the offset between basalt and andesite could be owing to the absence of a recoil-free fraction correction for the basalt Mössbauer data. Data for basalts from Wilke et al. (2005) can be corrected with a factor of C of 1.29 and eqn. (1), based on comparison between RT Mössbauer and wet chemical analyses for four samples analyzed in that study. These data show greater scatter, owing in part to much lower analytical precision for centroid determinations as compared to more recent analyses, but generally agree with the trends established for basalts by Cottrell et al. (2009) and for andesites in this study. Within the uncertainties of analytical precision and, at this time, imperfectly constrained corrections of $\text{Fe}^{3+}/\Sigma\text{Fe}$, the XANES centroid trends for basalts are not distinguishable from those of andesites.

The ratios of the intensities of the different sub-peaks of the pre-edge, $I(\text{Fe}^{3+})/I(\text{Fe}^{2+})$, and $I(\text{Fe}^{3+})/[I(\text{Fe}^{3+})+I(\text{Fe}^{2+})]$, are also potential quantitative measures of $\text{Fe}^{3+}/\Sigma\text{Fe}$. The two ratios are complementary, as the former is more sensitive to changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ for oxidized compositions and the latter for more reduced compositions (Fig. 8). The relationship between integrated pre-edge intensity ratios and $\text{Fe}^{3+}/\Sigma\text{Fe}$ from basalts, rhyolites (Cottrell et al., 2009) and andesites (this study), can be modeled with an exponential function (Table 4, Fig. 8) and can be used to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in glasses. Intensity ratios are

insensitive to energy drift, which more readily facilitates comparison of observations from studies at different beamlines than centroid observations (Cottrell et al., 2009). Perhaps more importantly, in contrast to centroids, intensity ratios for different glass compositions have essentially the same relationship to $\text{Fe}^{3+}/\Sigma\text{Fe}$, and so provide a method of $\text{Fe}^{3+}/\Sigma\text{Fe}$ determination that is less sensitive to composition. Thus, although centroid-based calibrations have greater precision, especially for reduced glasses, and are preferred in XANES analyses of glasses for which compositions can be closely matched to existing standard calibrations, peak-area ratios are more suitable for evaluation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in silicate glasses for which specific compositions have not yet been calibrated.

4.2 Bonding and coordination of Fe in andesitic glasses

Variations in XANES pre-edge integrated intensity and centroid energy can be interpreted in terms of the coordination of Fe^{2+} and Fe^{3+} in silicate glasses according to the variogram first introduced by Wilke et al. (2001) (Fig. 9). Total integrated intensities ($I(\text{Fe}^{3+}) + I(\text{Fe}^{2+})$), increase together with centroid energies along a trend consistent with average coordination of Fe^{2+} and Fe^{3+} that are approximately 5-fold (Figure 9a). This result is similar to that found by Wilke et al. (2005) for basaltic glasses. Of course a measure of the average coordination in a glass is only semi-quantitative, as the variogram is a generalization based on integrated pre-edge intensities typical of various Fe-rich minerals (Wilke et al., 2001) and cannot distinguish between absolute coordination and a mixture of a range of 4-, 5-, and 6-fold coordination (Wilke et al., 2005).

To examine the apparent coordination of Fe ions in greater detail, we can

calculate average coordination of Fe^{2+} and Fe^{3+} in each glass based on the integrated intensities of the observed glasses as well as those assumed for the 4-, 5-, and 6-fold coordination states of each ion from Wilke et al. (2001) together with values of $E_0(\text{Fe}^{2+})$ and $E_0(\text{Fe}^{3+})$ appropriate for each composition (Fig. 9b), and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined from Mössbauer data. This approach differs slightly from the variogram methodology in Fig. 9a which assumes a single value of $E_0(\text{Fe}^{2+})$ and $E_0(\text{Fe}^{3+})$ for all compositions. Fig. 10 shows average coordination calculated with both approaches, and the quantitative difference between the two is small. Calculated average coordination of Fe^{2+} is consistently near 5.5, or decreasing slightly for more oxidized glasses, whereas that for Fe^{3+} is near 4.5 for reduced glasses and closer to 5 for more oxidized glasses. Thus, these calculations suggest Fe^{2+} is more nearly a network modifying ion for both reduced and oxidized glasses, whereas Fe^{3+} is closer to a network forming ion for reduced glasses, where its abundance is low, and becomes more network-modifying as its abundance increases (or equivalently, as the availability of network-modifying Fe^{2+} diminishes).

Hyperfine parameter values obtained from Mössbauer spectra provide information on the next-nearest neighbor environment of iron in minerals (Dyar et al., 2006; Chen and Yang, 2007). The center shift is sensitive to bonding parameters such as coordination and co-valency, and quadrupole splitting is sensitive to changes in the distortion of the iron coordination environment (Dyar and Schaefer, 2004; Dyar et al., 2006; Chen and Yang, 2007). Values of CS for Fe^{2+} for the andesitic glasses are close to 1.05 (Fig. 3b), similar to values found

in previous studies of mafic glasses (Dyar, 1985; Mysen and Virgo, 1985; Botcharnikov et al., 2005) and suggesting Fe^{2+} -O coordination close to 6-fold (Dyar, 1985), consistent with results from XANES. CS values for Fe^{3+} are more variable, with values between 0.45 and 0.6 for glasses with low $\text{Fe}^{3+}/\Sigma\text{Fe}$, and 0.3 for glasses above 30% $\text{Fe}^{3+}/\Sigma\text{Fe}$. This trend of decreasing CS Fe^{3+} with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ for reduced glasses has been observed previously for a variety of natural and synthetic silicate melt compositions, and has been attributed to decreasing Fe^{3+} -O coordination in glasses quenched from more oxidized conditions (Mysen et al., 1985; Virgo and Mysen, 1985; Dingwell and Virgo, 1987; Dingwell, 1991; Jayasuriya et al., 2004; Partzsch et al., 2004; Mysen, 2006; Volovetskii et al., 2012). In contrast, XANES results for the andesitic glasses in this study suggest increased coordination of Fe^{3+} for more oxidized glasses (Fig. 10). Also, whereas some previous studies found changes in Fe^{3+} quadrupole splittings that correlate positively with observed shifts in Fe^{3+} CS (Jayasuriya et al., 2004; Volovetskii et al., 2012), others found Fe^{3+} QSs have negative correlations (Mysen et al., 1985; Virgo and Mysen, 1985; Dingwell, 1991) and still others found Fe^{3+} QS to be nearly constant (Partzsch et al. 2004; Mysen 2006; this study). This lack of consistency suggests that artifacts could affect these variations in hyperfine features of Fe^{3+} . As noted above, fitting of Fe^{3+} hyperfine parameters in reduced glasses is challenging, as the Fe^{3+} doublet is largely obscured by the Fe^{2+} doublet, and there are consequently possibly unavoidable covariances between the resolved parameters for Fe^{2+} and Fe^{3+} for these glasses.

In summary, the Mössbauer and XANES measurements on andesitic glasses show that Fe^{2+} has a higher average coordination with oxygen than Fe^{3+} , and this is broadly consistent with previous spectroscopic studies. It is also consistent with measurements of viscosities, which indicate that oxidized glasses are more polymerized than their reduced equivalents (e.g., Dingwell and Virgo, 1987). The spectroscopy suggests that Fe^{2+} is a network modifier with consistent melt structure from reduced to oxidized glasses, whereas inferences from Mössbauer and XANES conflict regarding variations in Fe^{3+} structure with $f\text{O}_2$.

5 Conclusion

The first detailed calibration for determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio for andesitic glasses by XANES has been derived from a suite of samples spanning 8 to 84% $\text{Fe}^{3+}/\Sigma\text{Fe}$, with ratios determined from recoilless fraction-corrected room temperature Mössbauer spectroscopy. Variations in the centroid energy of XANES pre-edge features produce the most precise calibration. The centroid versus $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio trend is intermediate between those previously derived for basalts and rhyolites (Cottrell et al., 2009; Dauphas et al., 2014) from facilities from which area-weighted centroid energies can be compared directly. The distinction between andesitic and basaltic glasses may derive in part from the methods used to calibrate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in the basaltic standards. Alternative calibrations for $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio based on the relative intensities of pre-edge sub-peak features show less dependence on composition.

XANES and Mössbauer spectra on andesitic glasses confirm previous spectroscopic studies indicating that Fe^{2+} is a network modifying cation in natural

silicate glasses, whereas Fe^{3+} is more similar to a network-forming ion. However, in detail, XANES and Mössbauer show conflicting trends of Fe^{3+} coordination with changing bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$; XANES indicates increasing average coordination in more oxidizing glasses, whereas Mössbauer indicates that Fe^{3+} in the most reduced glasses has higher coordination. The origin of this conflict is not known, though it may relate to the indirect basis of coordination assignments in XANES, which is based chiefly by analogy to XANES spectra in minerals.

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Figure Captions

Fig. 1: Comparison between $\text{Fe}^{3+}/\Sigma\text{Fe}$ obtained for andesitic glasses from uncorrected Mössbauer spectra collected at room temperature (RT) using the extended Voigt-based fitting (xVBF) and Lorentzian multiplet analysis (LMA) fit methods, both calculated from RECOIL software (Lagarec and Rancourt, 1998) using methods described in the text. The two methods give similar results, though the LMA fits yield on average slightly higher $\text{Fe}^{3+}/\Sigma\text{Fe}$. The results of the xVBF fits are used in the remaining portion of the text.

Fig. 2: Variations in $\text{Fe}^{3+}/\Sigma\text{Fe}$ in quenched andesitic glasses with oxygen fugacity determined by the solid zirconia electrolyte oxygen sensor in the gas mixing furnace at 1350°C. Dots represent $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained from Mössbauer spectra collected at room temperature using xVBF fit methods and

corrected for recoilless fraction with a value of $C=1.256$ (Zhang et al., 2015). Squares are $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined from the same Mössbauer spectra, but without correction for recoilless fraction. Empty and solid symbols represent VF Series and ECA Series glasses, respectively. Black line is $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated with eqn. (7) from Kress and Carmichael (1991) using the T , $f\text{O}_2$, and averaged major element glass composition.

Fig. 3: Mössbauer Center Shift (CS) of paramagnetic doublets for a) Fe^{3+} and b) Fe^{2+} from xVBF and LMA fits of spectra from andesitic glasses collected at room temperature as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$, calculated from recoilless-fraction corrected room temperature Mössbauer spectra with xVBF fits.

Fig. 4: Quadrupole splitting (QS) of paramagnetic doublets for a) Fe^{3+} and b) Fe^{2+} from xVBF and LMA fits of spectra from andesitic glasses collected at room temperature as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$, calculated from recoilless-fraction corrected room temperature Mössbauer spectra with xVBF fits.

Fig. 5: Examples of XANES spectra from 6 andesitic glasses collected at APS with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ranging from 0.08 to 0.78. a) Edge-step normalized full XANES spectra. b) A magnified view of the pre-edge. c) Iron $1s \rightarrow 3d$ pre-edge transition, baseline-subtracted and drift-corrected. Spectra are vertically offset for clarity.

Fig. 6: XANES energies (E_0) of pre-edge features attributable to Fe^{2+} (a) and Fe^{3+} (b) of andesitic glasses variations as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$ as determined from recoilless-fraction-corrected room temperature Mössbauer spectra. The

purple and yellow triangles represent VF Series glasses' XANES spectra collected at NSLS, and APS respectively, and the orange triangles represent ECA Series glasses' XANES spectra collected at NSLS. Uncertainties of XANES energies and $\text{Fe}^{3+}/\Sigma\text{Fe}$ equal 1σ standard deviation. The curves in (a) and (b) are least squares best fit curves, with coefficients listed in Table 3, and allow extrapolation of E_0 values to hypothetical compositions with pure Fe^{2+} or pure Fe^{3+} .

Fig. 7: XANES pre-edge centroid energies as a function $\text{Fe}^{3+}/\Sigma\text{Fe}$ for andesitic glasses collected at NSLS and APS. The triangles represent andesitic glasses from this study and from Dauphas et al. (2014), both of which are plotted against $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined from room temperature Mössbauer spectra corrected for recoilless fraction using the C factor of 1.256 from Zhang et al. (2015) (see text). The curve through these data is an empirical best fit to these andesite data (excluding the most reduced glass from Dauphas et al. (2014), which has a large uncertainty). The squares, and dots represent rhyolitic glasses, and basaltic glasses separately from Cottrell et al., 2009 and Dauphas et al., 2014. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of rhyolites determined with room temperature Mössbauer spectra are corrected with a C factor of 1.124, determined from comparison between RT Mössbauer and wet chemical determinations from Cottrell et al. (2009). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of basalts are plotted with values obtained from room temperature Mössbauer spectra owing to the uncertain correction value. Dashed and solid black curves represent basalt and rhyolite calibration curves respectively from Cottrell et al. (2009). A new rhyolite calibration (solid gray

curve) is applied based on all rhyolite glasses in the plot. Three more basalt calibration curves are calculated based on C factor of 1.1, 1.2 and 1.3. All uncertainties are 1 σ standard deviation. All plotted data, with corrections, are listed in Table S5; coefficients to the new curves in this plot are given in Table 4.

Fig. 8 The ratio of Gaussian component integrated XANES pre-edge intensity (a) $I(\text{Fe}^{3+})/I(\text{Fe}^{2+})$ and (b) $I(\text{Fe}^{3+})/[I(\text{Fe}^{3+}) + I(\text{Fe}^{2+})]$ as a function of $\text{Fe}^{3+}/\Sigma\text{Fe}$, after Wilke et al. (2005) and Cottrell et al. (2009). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of rhyolites, andesites are corrected as described in Fig. 7 and basalts are not corrected and listed in Table 1 and Table S5. Symbols are applied same as Fig 7. All uncertainties are 1 σ standard deviation. New calibration curves are applied for all three compositions with $\text{Fe}^{3+}/\Sigma\text{Fe}$ of basalts plotted for different C factors of 1, 1.1, 1.2 and 1.3.

Fig 9. Pre-edge parameters of **a)** all andesitic glasses and **b)** VF83 plotted in the variogram after Wilke et al. (2001). Grey fields designate pre-edge parameters for the Fe coordination and oxidation state indicated. Dashed lines between fields indicate the variation of pre-edge parameters assuming binary mixtures of **a)** respective end-members, determined from center position of Fe^{3+} and Fe^{2+} (Fig.1) and **b)** energy positions of Fe^{3+} and Fe^{2+} from VF83. Ticks on curves refer to the percentage of mixtures with **a)** the average coordination number of Fe^{2+} and Fe^{3+} for all andesitic glasses and **b)** coordination number of Fe^{2+} and Fe^{3+} for VF83.

Fig 10. Coordination number of Fe^{3+} and Fe^{2+} calculated based on the

917 XANES pre-edge intensities and $\text{Fe}^{3+}/\Sigma\text{Fe}$. $\text{CN}(\text{Fe}^{2+})$ calculated with individual
918 E_0 , = 5.53 ± 0.12 ; $\text{CN}(\text{Fe}^{3+})$ calculated with individual E_0 , = 4.79 ± 0.30 ; $\text{CN}(\text{Fe}^{2+})$
919 calculated with end member E_0 = 5.51 ± 0.14 ; $\text{CN}(\text{Fe}^{3+})$ calculated with end
920 member E_0 = 4.76 ± 0.37 .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table 1: Experimental conditions* and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined from Mössbauer spectroscopy

Sample	wire	gas flow	$\log f\text{O}_2$	$\text{Fe}^{3+}/\Sigma\text{Fe} * 100$ (xVBF) ^ψ	$\text{Fe}^{3+}/\Sigma\text{Fe} * 100$ (LMA) ^ψ	$\text{Fe}^{3+}/\Sigma\text{Fe} * 100$ (xVBF) corrected [#]	Predicted ^{&} $\text{Fe}^{3+}/\Sigma\text{Fe} * 100$
VF Series							
VF30	Pt	air	-0.68	83.50(0.60)	84.92(1.86)	80.12(0.60)	74.03
VF35	Pt	CO ₂ /CO	-8.07	8.04(0.49)	8.30(1.50)	6.51(0.49)	8.63
VF49	Pt	CO ₂ /CO	-8.63	12.94(0.47)	13.21(2.50)	10.58(0.47)	6.86
VF50	Pt	CO ₂ /CO	-6.52	13.98(0.50)	16.32(2.50)	11.45(0.50)	16.53
VF53	Pt	CO ₂ /O ₂	-1.30	73.17(0.35)	79.68(2.10)	68.47(0.35)	67.76
VF54	Pt	CO ₂ /CO	-5.15	34.38(0.39)	35.10(2.10)	29.44(0.39)	26.62
VF59	Pt	pure CO ₂	-3.18	49.25(0.27)	52.05(1.60)	43.59(0.27)	47.20
VF66	Pt	CO ₂ /CO	-4.94	35.01(0.25)	35.52(2.00)	30.02(0.25)	28.26
VF68	Pt	CO ₂ /CO	-5.72	24.83(0.43)	24.85(2.30)	20.82(0.43)	21.70
VF70	Pt	CO ₂ /CO	-6.27	21.69(0.35)	20.71(1.80)	18.07(0.35)	17.69
VF74	Pt	CO ₂ /O ₂	-2.06	65.20(0.38)	66.60(2.31)	59.87(0.38)	59.46
VF75	Pt	CO ₂ /O ₂	-2.27	62.43(0.25)	65.69(1.70)	56.95(0.25)	57.16
VF81	Pt	CO ₂ /CO	-6.98	13.00(0.70)	13.19(3.40)	10.63(0.70)	13.63
VF83	Pt	CO ₂ /CO	-3.76	39.30(0.60)	40.53(1.90)	34.01(0.60)	40.42
VF85	Re	CO ₂ /CO	-8.24	9.10(1.40)	6.87(1.60)	7.38(1.40)	8.07
VF87	Pt	air	-0.68	78.41(0.21)	77.53(2.36)	74.30(0.21)	73.25
VF88	Pt	CO ₂ /CO	-6.26	19.40(0.24)	17.67(2.10)	16.08(0.24)	17.52
ECA Series							
ECA_0	Pt	CO ₂ /CO	-6.68	13.80(1.25)	15.1(2.9)	11.31(1.25)	15.52
ECA_05	Pt	CO ₂ /CO	-6.32	17.70(1.25)	14.7(2.5)	14.62(1.25)	17.86

Uncertainties are in 1 σ .

^ψMössbauer spectra collected at room temperature were fitted with Extended Voigt-based Fitting (xVBF) and Lorentzian Multiplet Analysis (LMA).

*All experiments were performed at 1350 °C

[#]equals $(\text{Fe}^{3+}/\Sigma\text{Fe}) / [(\text{Fe}^{3+}/\Sigma\text{Fe}) + C * (1 - \text{Fe}^{3+}/\Sigma\text{Fe})]$, where $\text{Fe}^{3+}/\Sigma\text{Fe}$ is the ratio inferred from the relative areas of doublets from Mössbauer spectra collected from room temperature and C is the correction (1.256) for recoilless fraction for andesite glass quenched at ambient pressure (Zhang et al. 2015).

[&]Predicted from the model of Kress and Carmichael, 1991, using the observed composition of each glass (Table S1).

Table 2: Regression coefficients for least-squares fits with error estimates for the centroid energies (E_0) of the pre-edge XANES attributable to Fe^{2+} and Fe^{3+}

	Coefficients		
	a	b	c
$E_0(\text{Fe}^{3+})^*$	7113.625±0.015	-0.4939±0.0329	0.0494±0.0007
$E_0(\text{Fe}^{2+})^\#$	7111.771±0.038	0.00017±0.00217	2.04E-05±2.47E-05

$^* : E_0(\text{Fe}^{3+}) = \mathbf{a} + \mathbf{b} * (\text{Fe}^{3+} / \Sigma \text{Fe}) + \mathbf{c} * (\text{Fe}^{3+} / \Sigma \text{Fe})^2$

$^\# : E_0(\text{Fe}^{2+}) = \mathbf{a} + \mathbf{b} * \exp(-\mathbf{c} * (\text{Fe}^{3+} / \Sigma \text{Fe}))$

Table 3: Parameters from step edge normalized XANES spectra

Sample	Corrected ^{&} Centroid (eV)	$I(\text{Fe}^{3+}) + I(\text{Fe}^{2+})^*$	$I(\text{Fe}^{3+})/I(\text{Fe}^{2+})^*$	$I(\text{Fe}^{3+})/[I(\text{Fe}^{2+}) + I(\text{Fe}^{3+})]^*$
APS				
VF3	7113.265(0.007)	0.172(0.004)	4.064(0.236)	0.802(0.009)
VF30	7113.369(0.019)	0.181(0.003)	6.579(0.670)	0.867(0.012)
VF54	7112.749(0.035)	0.156(0.010)	1.193(0.277)	0.539(0.049)
VF59	7112.999(0.009)	0.165(0.012)	1.930(0.092)	0.658(0.011)
VF66	7112.782(0.016)	0.140(0.001)	1.294(0.068)	0.564(0.013)
VF68	7112.568(0.010)	0.131(0.004)	0.830(0.024)	0.454(0.007)
VF70	7112.393(0.002)	0.114(0.001)	0.599(0.005)	0.375(0.002)
VF74	7113.226(0.013)	0.179(0.001)	3.259(0.097)	0.765(0.005)
VF75	7113.175(0.001)	0.179(0.001)	2.974(0.023)	0.748(0.001)
VF81	7112.218(0.001)	0.111(0.001)	0.387(0.007)	0.279(0.003)
VF83	7112.833(0.007)	0.154(0.017)	1.423(0.011)	0.587(0.002)
VF85	7112.174(0.008)	0.113(0.001)	0.326(0.009)	0.246(0.005)
VF87	7113.386(0.003)	0.187(0.002)	5.341(0.103)	0.842(0.003)
VF88	7112.350(0.006)	0.120(0.002)	0.539(0.008)	0.350(0.003)
NSLS				
VF3	7113.241(0.007)	0.179(0.003)	3.904(0.121)	0.796(0.005)
VF30	7113.404(0.018)	0.164(0.007)	6.204(0.623)	0.861(0.012)
VF35	7112.146(0.005)	0.096(0.001)	0.247(0.017)	0.198(0.011)
VF49	7112.092(0.015)	0.102(0.001)	0.187(0.012)	0.158(0.009)
VF53	7113.308(0.021)	0.148(0.004)	4.321(0.352)	0.812(0.012)
VF54	7112.736(0.011)	0.132(0.003)	0.968(0.041)	0.492(0.011)
ECA_0	7112.301(0.019)	0.111(0.002)	0.404(0.044)	0.287(0.022)
ECA_05	7112.362(0.016)	0.110(0.002)	0.467(0.023)	0.318(0.011)

[&]Centroid position corrected for drift based on LW_0=7112.3 eV (Cottrell et al. 2009).

^{*}I: Integrated pre-edge intensity

APS: Advanced Photon Source

NSLS: National Synchrotron Light Source

Table 4: Regression coefficients for least-squares fits with error estimates for $\text{Fe}^{3+}/\Sigma\text{Fe}$ calibration curves from XANES pre-edge features.

x^*		Coefficients			
		a	b	c	d
Centroid Energy [#]	Rhyolite	17.8188±3.1682	-2.6657±7.7448	51.0927±4.6651	7112.33
	Andesite	6.2605±0.2635	23.2568±1.4136	22.8245±1.1375	7112.092
	Basalt with C=1 [§]	9.4221±0.2839	34.0051±1.4332	14.4706±1.2569	7112.112
	Basalt with C=1.1 [§]	8.6990±0.2839	30.6326±1.4332	16.2446±1.2569	7112.112
	Basalt with C=1.2 [§]	8.0910±0.2839	27.6918±1.4332	17.6539±0.1.2569	7112.112
	Basalt with C=1.3 [§]	7.5721±0.2839	25.1161±1.4332	18.7700±0.1.2569	7112.112
$\frac{I(\text{Fe}^{3+})}{I(\text{Fe}^{3+})+I(\text{Fe}^{2+})}$ ^{&}	Basalt with C=1 [§]	10.8672±0.7300	-25.6301±2.9937	121.4639±2.7077	
	Basalt with C=1.1 [§]	12.1671±0.7300	-35.9602±2.9937	131.2931±2.7077	
	Basalt with C=1.2 [§]	13.4327±0.7300	-45.4702±2.9937	140.2293±2.7077	
	Basalt with C=1.3 [§]	14.6509±0.7300	-54.2374±2.9937	148.3810±2.7077	
$\frac{I(\text{Fe}^{3+})}{I(\text{Fe}^{2+})}$ [♦]	Basalt with C=1 [§]	54.1468±2.8530	4.5087±0.4355	-54.1188±2.5431	-0.6053±0.0399
	Basalt with C=1.1 [§]	49.7235±2.7311	5.2482±0.4209	-50.1688±2.4214	-0.6169±0.0469
	Basalt with C=1.2 [§]	45.4579±2.5786	5.9589±0.4023	-46.2841±2.2694	-0.6327±0.0458
	Basalt with C=1.3 [§]	41.3553±2.3979	6.6408±0.3801	-42.5014±2.0895	-0.6536±0.0492

All data used for fitting are listed in Table S5.

* : x is the quantity measured from XANES.

: $\text{Fe}^{3+}/\Sigma\text{Fe} = a + b \cdot (x - d) + c \cdot (x - d)^2$

& : $\text{Fe}^{3+}/\Sigma\text{Fe} = a + b \cdot x + c \cdot x^2$

♦ : $\text{Fe}^{3+}/\Sigma\text{Fe} = a + b \cdot x + c \cdot \exp(d \cdot x)$

§ : $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of basalt are adjusted for recoilless fraction with the specified values of C based on Eqn. 1 in the text.