Iron K-edge X-ray absorption near-edge structure spectroscopy of aerodynamically levitated silicate melts and glasses

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Abstract

The local structure about Fe(II) and Fe(III) in silicate melts was investigated *in-situ* using iron K-edge X-ray absorption near-edge structure (XANES) spectroscopy. An aerodynamic levitation and laser heating system was used to allow access to high temperatures without contamination, and was combined with a chamber and gas mixing system to allow the iron oxidation state, $\text{Fe}^{3+}/\Sigma\text{Fe}$, to be varied by systematic control of the atmospheric oxygen fugacity. Eleven alkali-free, mostly iron-rich and depolymerized base compositions were chosen for the experiments, including pure oxide FeO, olivines $(\text{Fe,Mg})_2\text{SiO}_4$, pyroxenes $(\text{Fe,Mg})\text{SiO}_3$, calcic FeO-CaSiO₃, and a calcium aluminosilicate composition, where total iron content is denoted by FeO for convenience. Melt temperatures varied between 1410 and 2160 K and oxygen fugacities between FMQ – 2.3(3) to FMQ + 9.1(3) log units (uncertainties in parentheses) relative to the fayalite-magnetite- β -quartz (FMQ) buffer. Remarkably, XANES pre-edge peak areas imply mean Fe-O coordination numbers (n_{FeO}) close to 5 in all cases, with only a slight tendency toward higher values in the most iron rich melts, suggesting an intermediate role for both Fe(II) and Fe(III) in terms of network formation. End member coordination numbers for Fe(II)-O and Fe(III)-O are estimated to be similar, having means (and standard deviations) of 5.0(2) and 4.9(1), respectively. As such, the preference for ferric iron to occupy lower coordination sites than ferrous is weak, in contrast to published behavior in

some alkali-rich systems, which may explain the larger published viscosity variations with $\text{Fe}^{3+}/\Sigma\text{Fe}$ in alkali-, compared to alkaline earth-iron silicates. Temperature effects on n_{FeO} are inferred to be small based on the melt data, as well as by comparison to glasses formed on quenching. Positive shifts of the pre-edge peak centroids observed in many cases on quenching are attributed to rapid oxidation enabled by the stirring of the melt droplets by the levitation gas jet. $\text{Fe}^{3+}/\Sigma\text{Fe}$ values were estimated from XANES pre-edge peaks using published calibrations and compared to semi-empirical thermodynamic model calculations and Mössbauer measurements on quench products. Whilst showing positive correlation, the comparisons highlight the limitations involved in applying XANES calibrations and models for $\text{Fe}^{3+}/\Sigma\text{Fe}$ derived from measurements on glasses, to high temperature basic melts. $\text{Fe}^{3+}/\Sigma\text{Fe}$ varies from approximately zero up to about 65% in the high temperature melts and 75% in the glasses.

1. Introduction

Measuring the atomic scale structure of molten materials constitutes a key step toward understanding their properties, and allows validation, or provides constraints, for any models based on the atomic scale interactions. Iron-bearing silicate melts are of particular relevance to geological processes including magma transport (Wilke, 2005), volcanism (Tuff et al., 2013), planetary (Wade and Wood, 2005; Wood et al., 2006) and chondrule (Connolly and Love, 1998; Hewins, 1997) formation, as well as to industrial smelting (Gorai et al., 2003) and glass-making processes. Being the only major component of silicate melts in terrestrial systems which coexists in multiple oxidation states, the study of the local structure of iron is complicated since the spectroscopic, as well as diffraction, signatures of Fe^{2+} and Fe^{3+} often overlap, and their relative abundance, $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = \text{Fe}^{3+}/\Sigma\text{Fe}$, ideally needs to be determined. The structural behavior of iron in silicate melts is often inferred from the study of isocompositional glasses, assuming that both melt structure and oxidation state are frozen in upon melt-quenching (Jayasuriya et al., 2004; Kilinc et al., 1983; Kress and Carmichael, 1988; Moore et al., 1995; Mysen et al., 1980; Mysen et al., 1985; Mysen et al., 1984; Sack et al., 1980; Thornber et al., 1980). *In-situ* studies of melts not only obviate the need for such assumptions, but allow access to non-glass-forming compositions (ultramafic, ultrabasic, iron-rich etc. (Alderman et al., 2017)) and to the temperature dependence of melt structure (Alderman et al., 2016a; Alderman et al., 2016b). These advantages come at the cost of dealing with reactive molten materials which may interact with container materials, which themselves limit the process atmospheres and temperature ranges accessible.

Here, we use a containerless methodology – aerodynamic levitation – combined with laser heating, to obtain silicate melts free from interactions with any solid container. We further exploit the method by varying the atmospheric gas composition to control the oxygen fugacity, $f(\text{O}_2)$, and thereby the average iron oxidation state, $\text{Fe}^{3+}/\Sigma\text{Fe}$, in the melt. Containerless methods also minimize extrinsic nucleation, enabling access to supercooled liquids and glasses that cannot be obtained in crucibles. Combined with X-ray absorption spectroscopic (XAS) measurements at the iron K-edge, our experiments provide a powerful *in-situ* probe sensitive to both the oxidation state and local structure about iron in molten oxide and silicate systems. Very few XAS studies have been reported on levitated melts, e.g. the Zr K-edge (17.998 keV) of molten ZrO_2 (Landron et al., 2001; Landron et al., 2003), Sr K-edge (16.105 keV) of $\text{SrO-Al}_2\text{O}_3$ melts (Capron et al., 2001) and Fe K-edge (7.112 keV) of molten iron oxide (Hennet et al.,

1999), although only the relative main edge position and white-line intensity were reported in the latter. Recently we have exploited the technique at the Fe K-edge of fayalitic melts (Alderman et al., 2017) and the Ti K-edge of a barium titanate melt (Alderman et al., 2016a). Here, we demonstrate that accurate information on the average oxidation state and local structure of iron can be obtained from levitated melts, from the X-ray absorption near-edge structure (XANES) region of the Fe K-edge XAS spectra, as has been demonstrated in numerous studies on minerals, glasses and occasionally contained melts (Berry et al., 2003; Botcharnikov et al., 2005; Calas and Petiau, 1983; Cicconi et al., 2015; Cottrell and Kelley, 2011; Cottrell et al., 2009; Farges et al., 2004; Galois et al., 2001; Giuli et al., 2012; Giuli et al., 2013; Giuli et al., 2014; Giuli et al., 2008; Giuli et al., 2005; Giuli et al., 2011; Giuli et al., 2003; Giuli et al., 2002; Jackson et al., 1993; Jackson et al., 2005; Knipping et al., 2015; Métrich et al., 2006; Waychunas et al., 1988; Wilke et al., 2002; Wilke et al., 2007a; Wilke et al., 2001; Wilke et al., 2005; Wilke et al., 2006; Zhang et al., 2016).

Comparison of spectra obtained from the melts and their glassy or ceramic quench products allows us to explore the question of the temperature dependence of local structure about iron, as well as possible changes in the average oxidation state and coordination of iron during cooling.

The existing literature on structure and properties of molten and glassy silicates is somewhat biased towards alkali-rich compositions (Henderson et al., 2006; Jackson et al., 2005; Mcmillan, 1984; Waychunas et al., 1988), since these often have lower liquidus temperatures and are more conducive to conventional *in-situ* studies, as well as furnace melting and quenching to obtain glasses. The bulk compositions chosen in the present study include pure iron oxide FeO, olivines $(\text{Fe}_{1-z}\text{Mg}_z)_2\text{SiO}_4$ with $z = \text{Mg}/(\text{Fe} + \text{Mg}) = 0, 0.5$, pyroxenes $(\text{Fe}_{1-z}\text{Mg}_z)\text{SiO}_3$ with $z = 0, 0.5, 0.75$, calcic $(\text{FeO})_y \cdot (\text{CaSiO}_3)_{50-y/2}$ with $y = 10, 30, 50$, and a calcium aluminosilicate composition $9\text{FeO} \cdot 17\text{CaO} \cdot 13\text{Al}_2\text{O}_3 \cdot 61\text{SiO}_2$, where total iron content is denoted by FeO for convenience. These are atypical in that they are alkali-free, mostly poor glass formers, are Fe-rich and relatively refractory compared to alkali bearing analogues. Nonetheless, such melt compositions, especially olivines and pyroxenes, are incredibly pertinent to processes such as planetary accretion and core-separation (Wade and Wood, 2005; Wood et al., 2006), transport in the Earth's mantle (Wilke, 2005) and chondrule formation in the solar nebula (Connolly and Love, 1998; Hewins, 1997).

2. Methods

2.1 Materials

Samples suitable for levitation were obtained by laser hearth melting < 100 mg quantities of SiO_2 (Materion 99.9%), Fe_2O_3 (Aldrich 99.999%), MgO (Cerac 99.95%), CaCO_3 (Cerac 99.95%), Al_2O_3 (Cerac 99.99%), and Bi_2O_3 (Aldrich 99.999%) powders, taken from pre-mixed 2 g batches with the desired molar ratios. MgO was baked at 873 K for 1 hr prior to weighing to remove absorbed volatiles (H_2O , CO_2) and homogenization of the powder mixtures was obtained by tumble mixing in HDPE bottles containing a single alumina mixing bead. The hearth melting procedure was performed in a water-cooled copper hearth, open to the air, using a 100 W CO_2 laser. Sample contamination has been shown to be negligible

by this method (Weber et al., 1996). Sample compositions are listed in Table 1 written with iron content as FeO, except in the case of the low-melting compound BiFeO₃ where Fe₂O₃ is more appropriate.

2.2 Fe K-edge XANES spectroscopy

XANES spectra were collected at the Fe K-edge on beamline 20-BM-B of the Advanced Photon Source (Argonne, IL, USA) with an unfocussed beam cross-section of 2.5 mm wide by 0.8 mm high. Experimental details and results for the fayalitic melts have been previously reported (Alderman et al., 2017). An environmental chamber was used which included a large X-ray outlet window with its normal perpendicular to the incident X-ray beam and facing a 13-element Ge detector (Canberra Lege with XIA Xmap electronics) for measuring the fluorescence signal from the sample. The chamber, with ~1L internal volume, was water-cooled and designed with additional ports, two angled at 45° above horizontal for viewing the sample with a pyrometer and video camera (silica windows, o-rings), and four laterally for (2x) sample port (silica window or steel blank, o-rings), X-ray inlet (kapton window, o-ring) and outlet (kapton window, glued). Inserts were used on both X-ray inlet and outlet ports to reduce the X-ray path length through the chamber gas to *circa* 1 cm prior to absorption by the sample and *circa* 1 cm for the fluorescence (Alderman et al., 2017). This was done to reduce absorption by Ar bearing gas mixtures (Helium is not suitable for aerodynamic levitation), with the remaining paths outside of the thin (9 µm) Kapton windows allowed to fill with air. The two thin Kapton windows located only about 1 cm from the hot melts throughout the measurements were checked for damage periodically. They were found to withstand the measurement conditions well, and only to incur damage (and therefore leak) in the unusual event of a macroscopic portion of hot sample impinging upon them, necessitating their replacement. Samples were levitated on gas flowing through the nozzle at typical metered rates of 0.2 to 0.5 L/min. The gas composition was used to vary the oxygen fugacity, $f(\text{O}_2)$, either by using a single supply of high purity O₂, Ar, or premixes of Ar:0.1vol.%O₂, Ar:5vol.%CO₂, Ar:5vol.%CO or by using a gas mixing system to mix a desired ratio of any two of these gases. The reported oxygen fugacities (Table 1) were calculated based on the measured sample temperature and published Gibbs energies of formation for CO and CO₂ gases (Barin et al., 1993), and are also reported relative to the fayalite-magnetite-β-quartz (FMQ) buffer (Frost et al., 1988). Samples were heated from above with a CO₂ laser beam. The laser beam passed through an opening in the top of the chamber which also served as outlet for the levitation gas supplied through the nozzle. This was the only opening in the chamber and tapered conically in order to prevent ingestion of air back into the chamber. Incident laser heating power was adjusted to control the sample temperature, which was measured with a single color pyrometer (Chino model IRCS) sighted onto the top of the sample where it was also being heated. The apparent temperature was corrected using a Wien's displacement law approximation (Weber et al., 1995) with a spectral emissivity value of 0.92 at the pyrometer wavelength of 0.9 µm. Pyrometer temperature was also corrected for reflection losses from a silica window and a pyrometer lens that were in the optical path.

The measurement procedure included purging the chamber with the chosen levitation gas for at least 5 minutes once the sample had been located on the nozzle. Following this the sample was heated until fully molten, which usually involved reaching temperatures 200 K in excess of the liquidus to overcome initial temperature gradients across the partially solid sample. Recovered quenched solids were

typically measured with gas flow switched off to prevent their motion affecting the fluorescence XANES spectra, and in some cases were ground to powder, mounted on tape and measured in transmission mode.

Ionization chambers, one prior and two downstream of the sample position were used to measure transmission through an Fe metal foil for energy calibration (first inflection point of the edge set to 7111.08 eV (Wilke et al., 2001)), as well as for measurements on finely powdered recovered samples mounted on tape. A Si(111) double-crystal monochromator was used, with energy resolution $\Delta E/E = 1.4 \times 10^{-4}$ or 1.00 eV at the Fe K-edge. This is to be compared to the intrinsic width due to the core-hole lifetime of 1.25 eV (Krause and Oliver, 1979), which yields a total expected width after convolution of about 1.8 eV. XANES spectra were collected from 150 eV below to 380 eV above the Fe K-edge. Fine, 0.2 eV, steps in the range 20 eV below to 40 eV above the edge were used. Total measurement time was about 8 minutes per spectrum.

2.3 XANES data treatment

XANES spectra were corrected and normalized using the IFEFFIT software (Newville, 2001) *via* the Athena interface (Ravel and Newville, 2005). Normalization involved fitting two linear functions, one below and one above the edge region, although in some cases (including all transmission measurements) a 2nd order polynomial was required for the post edge range. The edge step was then normalized to unity after subtracting the pre- and post-edge backgrounds and divided by their difference at the edge position. Given the large thickness of the samples relative to the absorption length, $\mu(E)$, the fluorescence intensities required correction due to the effects of self-absorption. For example, the absorption length, $\mu(E)$, in molten Fe_2SiO_4 is about 57 μm at 7100 eV and decreases to about 12 μm above the edge, at 7200 eV, necessitating a large self-absorption correction (Fig. 1). In $10\text{FeO} \cdot 45\text{CaO} \cdot 45\text{SiO}_2$ melt the same quantities are more similar to each other, $\mu(7100\text{eV}) = 32 \mu\text{m}$ and $\mu(7200\text{eV}) = 25 \mu\text{m}$ resulting in a smaller self-absorption effect, see Fig. 1. This effect arises due to modulation of $\mu(E)$, and thereby the probed volume, of the sample as the X-ray energy is stepped through the edge of interest, and results in a suppression of the spectral features above the edge and an enhancement of the pre-edge region. The larger the contribution of the element of interest to the total absorption coefficient, the larger the effect (Fig. 1). Here we have used the Fluo algorithm (Haskel, 1999) available within Athena. This correction algorithm is applicable to flat-plate sample geometry, and therefore not necessarily suited to the liquid and solid spheroids of the present study (approx. 1.5 mm radii of curvature). Whilst efforts have been made in the direction of self-absorption corrections (SACs) for spherical samples (Larsen et al., 2012), we have used here an empirically verified approach based on the existing Fluo algorithm. A pure iron sphere was placed within the levitator nozzle and used to represent the sample geometry of a levitated molten droplet. The strongly distorted fluorescence mode XANES spectrum of the iron sphere was then compared to the undistorted spectrum obtained by transmission measurement through a reference Fe foil (see supplemental material, Fig. S1). The magnitude of the SAC is a function of the ratio $\sin\varphi_i/\sin\varphi_f$, where φ_i and φ_f are angles between the sample surface and incident and detected fluorescence X-rays respectively. The value of $\sin\varphi_i/\sin\varphi_f$ was adjusted within the SAC until the corrected spectrum for the iron sphere agreed with that of the iron foil. It was found that the value $\sin\varphi_i/\sin\varphi_f = 2.067$ (or e.g. $\varphi_i/\varphi_f = 45^\circ/20^\circ$) gave a suitable correction, at

least up to about 10 eV above the edge, beyond which the intensities are overcorrected, presumably due to the curved sample geometry (Fig. S1). A reduced correction using $\sin\varphi_i/\sin\varphi_f = 4.072$ (or e.g. $\varphi_i/\varphi_f = 45^\circ/10^\circ$) gave a good correction in the post-edge and EXAFS region (Fig. S1). Since our analysis is focused on the pre-edge peaks, we have used the larger correction ($\sin\varphi_i/\sin\varphi_f = 2.067$) throughout, and the post edge region is used solely for normalization purposes (prior to SAC). Subsequent comparisons of iron oxide standards measured in transmission to measurements on iron oxide beads obtained by quenching melts within the levitation furnace (by cutting the laser power) suggested a range of SAC magnitudes, most likely arising from the less spherical and rougher polycrystalline bead geometries (as opposed to the smooth spherical liquids or iron sphere) resulting in an uncertainty $\sin\varphi_i/\sin\varphi_f = 2.067^{+2.005}_{-0.653}$, or $\varphi_i = 45^\circ$, $\varphi_f = 20^\circ \pm 10^\circ$. To put the size of the SAC correction in perspective, in the two exemplary cases illustrated in Fig. 1, the correction results in a $7^{+2}_{-3}\%$ (10FeO.45CaO.45SiO₂) and $49^{+10}_{-16}\%$ (Fe₂SiO₄) *reduction* of the as-measured (isolated) pre-edge peak intensity. The effect of the SAC on the pre-edge centroid energy ranged from negligible to ± 0.1 eV. Note that in cases in which Fe is more dilute, or the absorption is dominated by heavier elements, the correction becomes smaller or even negligible.

In order to isolate the pre-edge peaks, two Lorentzian peaks were fitted to the main edge, with the energy range containing the pre-edge peaks excluded (Fig. 2). Typically the fitting range extended down to 7100 eV and up to no more than 0.5 normalized intensity units up the main edge. The choice of isolation function can strongly affect the isolated pre-edge intensity (Boubnov et al., 2015; Farges et al., 2004) and a bi-Lorentzian function was chosen on the basis that it gave results from standard materials in reasonable accord with literature values (Alderman et al., 2017). Even within our chosen (bi-Lorentzian) background model, significant uncertainty arises from the existence of multiple local minima in the sum-of-squares. We estimate the uncertainty arising from this effect to be up to $\pm 10\%$ on the isolated pre-edge peak areas, and about ± 0.1 eV on the centroid energies. The isolated pre-edge peak was fitted with two Gaussian contributions, which were sufficient for simulating the spectra of molten and glassy samples (Fig. 2). In the case of crystallized oxidized samples an additional contribution to the pre-edge was usually observed at slightly higher energy (Boubnov et al., 2015; Wilke et al., 2001) and was fitted with an additional Gaussian component. This feature has non-local origin (Glatzel et al., 2009) and is a signature of the presence of neighboring pairs of Fe³⁺. The partitioning of pre-edge spectra into local and non-local contributions introduces an additional element of uncertainty into the parameters of the local contributions used to extract information on iron oxidation state and coordination, but is only apparent in the oxidized quenched crystalline solids studied here.

When making XAS measurements on levitated samples, the stability of the sample is important because any motion can alter the amount of fluorescence reaching the detector and thereby modulate the spectrum. It was found that certain conditions were favorable when measuring molten samples due to the existence of distinct levitation modes, illustrated in Fig. 3. Fig. 3a shows a molten sample at relatively low temperature and low levitation gas flow rate which holds a close to spherical shape due to the surface tension. Fig. 3b on the other hand shows a snapshot of the same melt at higher temperature and levitation gas flow rate. The melt has deformed to form an ellipsoid and rotates about a vertical axis (see videos in online material). This effect appears to be driven by the levitation gas flow,

and occurs preferentially at higher temperature, presumably due to the decreased surface tension. The behavior shown in Fig. 3b is highly undesirable for XAS measurements because the period of rotation is typically larger than the measurement timestep such that the oscillating projection observed by the detector causes periodic modulation of the signal, as shown in Fig. 3c. Hence it was necessary during the measurements to avoid the rotating ellipsoid mode, and obtain closely spherical melts, which were both sufficiently stable, and for which sample rotation did not affect the signal intensity.

2.4 Mössbauer spectroscopy

Room temperature Mössbauer spectra from $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glasses were obtained using a Rh^{57}Co source. The velocity calibration was carried out with a 25 μm absorber of metallic iron and isomer shifts are quoted with respect to the center of the spectrum of iron at room temperature. Additional low temperature measurements on oxidized $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glass at 200, 100 and 6 K were used to obtain a correction for the recoil-free fraction, leading to smaller ferric fractions than obtained from room temperature measurements alone. Mössbauer measurements on the quench products from fayalitic melts have been previously reported (Alderman et al., 2017).

2.5 Electronprobe Microanalysis

The compositions of the majority of recovered samples were measured using electronprobe microanalysis (EPMA), using a Cameca SX100 FEG electronprobe microanalyser at the University of Bristol, UK. The samples were mounted in epoxy and polished to expose a plane close to the centre of the beads. Traverses from the rims of the samples, toward their centres, were performed using a 12 μm electron beam in order to average over the quenched textures, an accelerating voltage of 20 kV and beam current of 20 nA. Synthetic MgO, albite and wollastonite were used to calibrate the analyses and the calibrations were verified using diopside.

3. Results

3.1 EPMA

Results of EPMA are reported in Table S1. For the most part the measured compositions are within a single standard deviation of the expected, nominal, compositions, although in some cases the standard deviation is relatively large owing to limited averaging over heterogeneous quench textures. In the case of $\text{Fe}_{0.25}\text{Mg}_{0.75}\text{SiO}_3$, larger deviation of the recovered composition from nominal was observed, consistent with the larger observed mass loss during the course of measurement. The resulting compositions are silica rich (56 to 61 mol% SiO_2) and magnesium deficient (~ 28 mol% MgO) compared to nominal. The FeO- CaSiO_3 series were observed to have Ca:Si ratios as high as 1.25:1, slightly larger than the nominal 1:1 ratio.

3.2 XANES spectra

Figs. 4-7 show normalized XANES spectra, with the isolated pre-edge spectra inset, and Tables 1 and 2 give the extracted pre-edge peak parameters. The pre-edge features show clear changes with the $f(\text{O}_2)$ and T dependent iron oxidation state ($\text{Fe}^{3+}/\Sigma\text{Fe}$), with the centroid energy shifting to higher energies

with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$, consistent with previous studies (Berry et al., 2003; Berry et al., 2010; Boubnov et al., 2015; Calas and Petiau, 1983; Cicconi et al., 2015; Cottrell and Kelley, 2011; Cottrell et al., 2009; Dauphas et al., 2014; Farges et al., 2004; Fiege et al., 2017; Galois et al., 2001; Giuli et al., 2012; Giuli et al., 2013; Giuli et al., 2014; Giuli et al., 2008; Giuli et al., 2005; Giuli et al., 2011; Giuli et al., 2003; Giuli et al., 2002; Jackson et al., 2005; Knipping et al., 2015; Magnien et al., 2008; Métrich et al., 2006; Wilke et al., 2007a; Wilke et al., 2001; Wilke et al., 2005; Zhang et al., 2016). However, the pre-edge peak areas, which are sensitive to iron site symmetry and coordination, do not vary greatly with bulk melt or glass composition (i.e. at fixed centroid energy, or $\text{Fe}^{3+}/\Sigma\text{Fe}$). This information is summarized in Fig. 8 by plotting the pre-edge area-centroid (A,C) coordinates within the variogram determined from measurements on Fe-bearing minerals of known structure (Wilke et al., 2001; Wilke et al., 2004, 2005). The broad conclusion is that, for the wide range of alkali-free, depolymerized compositions studied, average Fe-O coordination numbers are $n_{\text{FeO}} \approx 5$ in all cases, and for all temperatures and $\text{Fe}^{3+}/\Sigma\text{Fe}$ accessed. This is similar to existing results on basaltic glasses (Fiege et al., 2017; Wilke et al., 2004, 2005).

Comparisons between melts and their corresponding glasses in Fig. 6, 7 and 8c reveal that pre-edge peak areas change little on quenching, implying the Fe-O coordination is only weakly temperature dependent, if at all. Changes in pre-edge centroid position are observed on quenching, in particular for aluminosilicate and $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ series, whilst such shifts are small for $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$ and $\text{Fe}_{0.25}\text{Mg}_{0.75}\text{SiO}_3$ melt-glass pairs, Fig. 8c. These shifts in centroid position are attributed to oxidation during quenching, see discussion section 4.3.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ can be extracted from the pre-edge peak position if a suitable calibration exists. Most of the melt compositions studied herein do not form glasses, neither by conventional means, nor within the aerodynamic levitator. In lieu of a set of glasses of the same (or more similar) composition, we have chosen to use the calibration curves developed by Wilke et al. (2004) (Tables 1 and 2), based on basaltic glasses, which are relatively close (low silica) compositionally to our melts. Two different calibrations (Wilke et al., 2004, 2005) are based either on the centroid position C , or ratio $F = I(\text{Fe}^{3+})/[I(\text{Fe}^{2+}) + I(\text{Fe}^{3+})]$ where $I(\text{Fe}^{3+})$ represents integration of the isolated pre-edge feature over the interval $7113.0 \leq E \leq 7114.0$ eV and $I(\text{Fe}^{2+})$ over $7111.2 \leq E \leq 7112.2$ eV. These regions are represented in the insets to Figs. 4 to 7 by the vertical lines. During our analysis we noticed that the coefficients for the quadratic calibration curves given by Wilke et al. (2004) did not exactly match their graphical data. Therefore we have made our own fits to the basaltic glass data digitized from Wilke et al. (2004), yielding slightly modified coefficients: $C [\text{eV}] = 7111.976 + (2.876 \times 10^{-2})r - (1.48 \times 10^{-4})r^2$ and $F = 0.21988 + (1.06 \times 10^{-2})r - (4.09 \times 10^{-5})r^2$, where $r = 100\text{Fe}^{3+}/\Sigma\text{Fe}$ denotes the *percentage* of ferric iron. Over the range of C and F explored by our measurements, our modified coefficients lead to slightly larger values of r compared to values obtained using the reported coefficients, though the differences do not exceed 5 percentage points (at the highest $\text{Fe}^{3+}/\Sigma\text{Fe}$ encountered). The original and modified curves relating to the centroid energy vs. $\text{Fe}^{3+}/\Sigma\text{Fe}$ calibration are compared in Fig. S2. Knipping et al. (2015) have pointed out that the Mössbauer based calibrations of Wilke et al. (2004) tend to underestimate $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to wet chemical analyses. We have therefore also calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ using the Knipping et al. (2015) calibration based on wet chemical analyses of alkali trisilicate glasses (Tables 1 and 2), given by $\text{Fe}^{3+}/\Sigma\text{Fe}$

= $0.5879(C [\text{eV}] - 7111.9)^{1.2527}$. This calibration is distinct from that derived from basaltic glasses, presumably due to the distinct local structure about ferrous and ferric iron ions in alkali silicate glasses. We have included the calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ from both calibrations in order to illustrate the range in results obtained arising from the choice of calibration and large bulk compositional changes. Various literature calibrations (Berry et al., 2003; Cottrell et al., 2009; Knipping et al., 2015; Wilke et al., 2004, 2005) are compared in Fig. S2.

3.3 Mössbauer spectra

Fig. 9 shows the room temperature Mössbauer spectra obtained from the powdered $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glasses quenched from levitated melts at different $f(\text{O}_2)$ (see Tables 1 and 2). The Mössbauer derived $\text{Fe}^{3+}/\Sigma\text{Fe}$ can be most directly compared to the XANES transmission measurements through glass powder obtained from the same glass beads (Table 2, Fig. S2). The Mössbauer $\text{Fe}^{3+}/\Sigma\text{Fe}$ agree well with the values obtained using the modified Wilke et al. (2004) calibrations, at least for the two more reduced cases (for both transmission and fluorescence). In the most oxidized case, the Wilke et al. (2004) XANES calibrations appear to underestimate $\text{Fe}^{3+}/\Sigma\text{Fe}$. This is in part due to the lower sensitivity of the XANES calibration at higher $\text{Fe}^{3+}/\Sigma\text{Fe}$, i.e. the gradient $\partial C/\partial(\text{Fe}^{3+}/\Sigma\text{Fe})$ becomes smaller with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. S2). These results serve to validate our reliance on the existing calibration, although we note the large uncertainties in highly oxidized cases. An analogous comparison using the results from fayalitic melt quench products (Table 2, (Alderman et al., 2017)) is less informative owing to the multiphase crystalline nature of the fayalite-magnetite-quartz materials.

Table 3 shows the Mössbauer hyperfine parameters obtained from fitting $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glass spectra. The values are consistent with the intermediate $n_{\text{FeO}} \approx 5$ implied by Fe K-edge XANES pre-edge peak areas, by comparison to values measured in iron-bearing minerals (Burns, 1994).

4. Discussion

4.1 Local structure about Fe^{2+} and Fe^{3+} in silicate melts and glasses

4.1.1 Comparison to previous studies

The finding that $n_{\text{FeO}} \approx 5$ over a range of bulk compositions and iron oxidation states is similar to published results on related melts and glasses, examples of which are given in the following paragraph.

High-energy X-ray diffraction measurements on fayalitic melts yielded $4.4(2) < n_{\text{FeO}} < 4.7(1)$ at various $f(\text{O}_2)$ (Alderman et al., 2017) (Fig. 8b). While these n_{FeO} are smaller than is suggested by XANES, Alderman et al. (2017) discussed the possibility of underestimation of n_{FeO} by the diffraction technique used, which goes towards explaining the apparent discrepancy with XANES data in Fig. 8b, along with the large uncertainties arising from self-absorption for this melt composition. Note that the diffraction results strongly support the interpretation of the enhanced (*cf.* crystalline fayalite, hematite) XANES pre-peak areas in the melts in terms of lower-than-octahedral iron coordination, as opposed to thermally distorted octahedral environments. X-ray diffraction derived values of $n_{\text{FeO}} = 4.8(2)$ for molten Fe_2SiO_4 and $n_{\text{FeO}} = 5.1(2)$ for FeSiO_3 have also been reported (Drewitt et al., 2013). Liu and Lange (2006), using

an empirical partial molar volume model, estimated Fe(III)-O coordination numbers to be close to 5, and independent of T and composition in a range of alkali iron silicate melts. Similarly intermediate iron K-edge pre-edge peak areas, and thereby n_{FeO} , for both oxidized and reduced cases, have been observed in basaltic glasses (Fiege et al., 2017; Jackson et al., 2005; Métrich et al., 2006; Wilke et al., 2004, 2005), alkali silicate glasses and melts (Knipping et al., 2015; Wilke et al., 2007a; Wilke et al., 2004, 2005), haplogranitic glasses and melts (Wilke et al., 2007a), soda-lime silicate glasses (Jackson et al., 2005), an anorthite-diopside eutectic glass (Berry et al., 2003), a wide range of ternary silicate glasses (Farges et al., 2004) as well as natural tektites and impact glasses (Giuli et al., 2008; Giuli et al., 2005; Giuli et al., 2002). Higher areas (lower n_{FeO} , closer to 4) have been observed in a pantelleritic glass (Métrich et al., 2006), in oxidized $\text{Rb}_2\text{Si}_3\text{O}_7$ glass (Knipping et al., 2015), some alkali-iron silicate glasses (Jackson et al., 2005), and various oxidized phonolitic (Cicconi et al., 2015; Giuli et al., 2011) and rhyolitic (Fiege et al., 2017; Giuli et al., 2012) glasses. Slightly lower areas (higher n_{FeO}) have been reported recently in andesitic glasses (Zhang et al., 2016). Neutron diffraction measurements (Weigel et al., 2008a, b; Weigel et al., 2006; Wright et al., 2014) also reveal a tendency for Fe(III) to be present in lower (closer to tetrahedral) coordination in alkali-rich silicate glasses, and for Fe(II) to occupy mostly 5-fold sites.

The structural studies cited above, along with the results of the present study, tend to point toward a stronger dependence of n_{FeO} on $\text{Fe}^{3+}/\Sigma\text{Fe}$ in alkali-rich silicate glasses and melts, as compared to alkali-poor, alkaline-earth-rich compositions. In particular the alkali cations tend to stabilize 4-fold Fe(III), and more so for the larger, lower field strength cations. This observation may go toward explaining the dependence of melt viscosities on iron oxidation state (Dingwell, 1991; Dingwell and Virgo, 1987), where a stronger dependence is found for alkali, as opposed to alkaline earth, iron silicate melts.

Mean coordination numbers of $n_{\text{FeO}} \approx 5$ (intermediate between 4 and 6) imply that both Fe^{2+} and Fe^{3+} play intermediate roles in terms of network formation, similar to, for example Mg^{2+} in ultramafic glasses (Kohara et al., 2004) and Al^{3+} in peraluminous glasses (Neuville et al., 2004; Neuville et al., 2006). As such, both ferric and ferrous iron represent exceptions to the over-simplifying network former/modifier dichotomy. Given that 5-fold Fe has been shown to be present in numerous molecular dynamics (Farges et al., 2004; Guillot and Sator, 2007; Muñoz Ramo and Stixrude, 2014; Rossano et al., 2000a; Rossano et al., 2000b) and other atomistic models (Weigel et al., 2008a, b; Weigel et al., 2006) of iron-bearing melts and glasses, we expect it to be an abundant species in the melts and glasses of the present study, and that therefore the abundance of 6-fold iron is low in most cases. However, the distribution of 4-, 5- and 6-fold coordination states cannot be determined directly from XANES, nor diffraction data, without simplifying assumptions (e.g. one of the three species absent).

In detail there appear to be some subtle trends with bulk composition as well as with $\text{Fe}^{3+}/\Sigma\text{Fe}$ (or centroid energy). For example, in Fig. 8a the melt data tend to indicate a slightly smaller mean n_{FeO} as $\text{Fe}^{3+}/\Sigma\text{Fe}$ increases, implying an increasing abundance of tetrahedral Fe(III). In Fig. 8c, the aluminosilicate melts and glasses can be seen to have lower mean n_{FeO} than the $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ melts and glasses, implying a composition (or temperature) induced effect. These trends are discussed in the following sections.

4.1.2 Structural changes about iron with $\text{Fe}^{3+}/\Sigma\text{Fe}$

Farges et al. (2004) have shown that, at least where Fe(II) and Fe(III) endmembers have similar n_{FeO} , as appears to be the case for the present datasets, linear fits to individual series of A,C coordinates within the variogram, covering a range of $\text{Fe}^{3+}/\Sigma\text{Fe}$, can be used to give an estimate of the end-member coordination numbers. The results derived from such linear fits to the present data are recorded in Table 4. We note that within the variogram itself (Fig. 8) binary mixtures of Fe(II) and Fe(III) mineral endmembers generate non-linear curves, with gradients increasing with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$. This is true, although to a lesser extent, even for combinations of end-members with the same n_{FeO} , and therefore linear fits likely tend to slightly underestimate end-member areas, and overestimate n_{FeO} .

The results (Table 4) indicate that iron in both oxidation states has similar $n_{\text{FeO}} \approx 5$, but with a tendency toward slightly lower n_{FeO} for ferric cations. Error weighted averaging over all data for all of the compositions measured yields $n_{\text{Fe(II)O}} = 5.0(2)$ and $n_{\text{Fe(III)O}} = 4.9(1)$. The largest variation with $\text{Fe}^{3+}/\Sigma\text{Fe}$ is seen for $\text{CaSiO}_3\text{-FeO}$ melts, with a decrease in n_{FeO} of up to 0.6(1) (11%) upon complete oxidation from Fe(II) to Fe(III). The derived endmember coordination numbers for $(\text{FeO})_{10}\cdot(\text{CaSiO}_3)_{45}$ glasses of $n_{\text{Fe(II)O}} = 5.4(5)$ and $n_{\text{Fe(III)O}} = 5.0(2)$ are consistent with the Mössbauer hyperfine parameters, Table 3, by comparison to values measured in iron-bearing minerals (Burns, 1994). The aluminosilicate and ultramafic MgO-FeO-SiO_2 compositions show insignificant changes in n_{FeO} between ferrous and ferric end-members of only 0.1(1) and 0.0(1) respectively. The FeO-SiO_2 melts hint at an opposite trend of *increasing* n_{FeO} with $\text{Fe}^{3+}/\Sigma\text{Fe}$, qualitatively consistent with high-energy X-ray diffraction measurements on fayalitic melts (Alderman et al., 2017), Fig. 8b. The result for pure iron oxide melts is indicative of a decrease in n_{FeO} with $\text{Fe}^{3+}/\Sigma\text{Fe}$, although this may be an artefact arising from the limited data ($N = 4$) with limited range of $\text{Fe}^{3+}/\Sigma\text{Fe}$.

The smallest extrapolated endmember n_{FeO} are for the ferric cations in the aluminosilicate melts and glasses, with $n_{\text{Fe(III)O}} = 4.7(1)$, implying at least 30% of the ferric ions to be 4-fold coordinated (assuming 70% 5-fold), and up to 65% 4-fold Fe(III) (assuming 35% 6-fold).

Farges et al. (2004) studied more polymerized ternary silicate glass compositions doped with 0.2 to 2.0 at.% Fe. Those authors found mostly small variations in n_{FeO} upon oxidation from Fe(II) to Fe(III), an outlier being for a $\text{MgO-Na}_2\text{O-SiO}_2$ composition where n_{FeO} falls with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ from 4.9 to 4.4 (Table 4).

Zhang et al. (2016) recently studied a series of andesitic glasses (approx. 10 wt.% Fe_2O_3) by high-resolution iron K-edge XANES spectroscopy. They derived end-member n_{FeO} of about 5.5(1) and 4.8(3) for Fe(II) and Fe(III) respectively. These values are similar to those found here for the compositions shown in Table 4, again showing a higher oxygen coordination of ferrous iron. The change in n_{FeO} between andesitic glass ferrous and ferric end-members is slightly larger than any series studied herein, but is comparable to that for the $10\text{FeO}.45\text{CaO}.45\text{SiO}_2$ melts. Zhang et al. (2016) went a step further than estimating only the end-member n_{FeO} , and used a method based on independent knowledge of $\text{Fe}^{3+}/\Sigma\text{Fe}$, measured pre-edge intensity and centroid and individual peak positions observed under high-resolution conditions, to derive average Fe(II)-O and Fe(III)-O coordination for each individual glass. This method revealed approximately constant Fe(II)-O coordination of 5.5(1), and a gradual increase in

Fe(III)-O coordination with $\text{Fe}^{3+}/\Sigma\text{Fe}$ increasing, from about 4.5 up to 5.0, although the latter is in conflict with evidence from Mössbauer spectroscopy.

4.1.3 Structural changes about iron with bulk composition

There are differences in Fe-O coordination numbers between the compositional series considered in Table 4 and Fig. 8, and the n_{FeO} are smallest in the most polymerized, aluminosilicate composition. The question arises as to which compositional variables are most important in governing n_{FeO} , and if any simple trends can be identified at all, given the possibility of non-linear (non-additive) interactions between components. In this section we discuss what can be concluded from our data concerning the effect of bulk composition on Fe coordination, as well as by comparison to some of the relevant literature.

The series of measurements on $(\text{FeO})_y \cdot (\text{CaSiO}_3)_{50-y/2}$ melts and glasses show no clear dependence on y ($= 10, 30, 50$). As such, any dependence of n_{FeO} on total iron content is very weak in this range, as is any dependence on network polymerization ($\text{NBO}/\text{T} \geq 2.4$, see Table 4 for definition).

Over a wider range of network polymerization, this parameter (NBO/T) may begin to have an effect. For example, the smallest n_{FeO} are found for the most polymerized, aluminosilicate, composition of the present study, and a similar trend is apparent in the data of Farges et al. (2004) whose most depolymerized (diopside, $\text{NBO}/\text{T} = 2$) glasses yielded the highest n_{FeO} values, and most polymerized (albite, $\text{NBO}/\text{T} = 0$) yielded some of the lowest (Table 4). The data of Farges et al. (2004) also indicate smaller n_{FeO} than those of the present study, in most cases. This difference is qualitatively consistent with the changes with NBO/T discussed above, but could also arise from either the much lower iron concentrations, or from the presence of alkalis.

Alkali oxides, particularly those of the larger, lower field strength alkali cations, tend to stabilize tetrahedral Fe(III) (Cicconi et al., 2015; Giuli et al., 2012; Giuli et al., 2011; Jackson et al., 2005; Métrich et al., 2006; Mysen, 2006; Mysen et al., 1980; Weigel et al., 2008a, b; Weigel et al., 2006), and this could also explain the lower average n_{FeO} obtained by Farges et al. (2004), at least for the oxidized glasses which constituted the vast majority in that study.

Since all compositions of the present study are alkali free, the comparison between the aluminosilicate and $(\text{FeO})_{10} \cdot (\text{CaSiO}_3)_{45}$ melts and glasses eliminates this variable, and essentially indicates that the effect of replacing CaO with SiO_2 and Al_2O_3 is to lower n_{FeO} in both reduced and oxidized cases. However, the difference could arise as a result of the temperature difference alone (section 4.1.4).

Data from Wilke et al. (2004) are shown in Fig. 8, for basaltic glasses containing ~ 5 wt.% alkali oxide (mostly Na_2O), ~ 4 wt.% TiO_2 , and ~ 3 wt.% MgO . The alkali-free aluminosilicate melts and glasses herein have smaller n_{FeO} than the Wilke et al. (2004) glasses, which goes against the expected trend for alkali addition. This points to the importance of non-additive interactions in complex compositions, and suggests that the preferential association of Fe cations with particular species is occurring.

4.1.4 Structural changes about iron with temperature

The preceding discussion is based on the implicit assumption that variations observed in Fe-O coordination numbers between different compositional series arise directly as a result of the compositional changes. This ignores any influence on n_{FeO} of melt temperature, T , which varies over a 750 K range in our data (Table 1), owing partly to the widely varying liquidus temperatures. If one takes the other extreme view and supposes that the Fe-O coordination depends not on bulk composition, but only on T and $f(\text{O}_2)$ (or $\text{Fe}^{3+}/\Sigma\text{Fe}$) then the measured XANES pre-edge peak areas (A_{meas}) might be modelled by simple empirical relationships such as

$$A_{\text{calc}} = A_0 + \frac{B}{T} + D \log_{10} f(\text{O}_2), \quad (1)$$

$$A_{\text{calc}} = A_0 + \frac{B}{T} + D \frac{\text{Fe}^{3+}}{\Sigma\text{Fe}}. \quad (2)$$

The three fitting parameters (A_0, B, D) in each of equations 1 and 2 have been determined by non-linear least squares refinement against A_{meas} , which are compared to the calculated areas, A_{calc} , in Fig. 10. Equation 1 gives marginally better agreement, but in both cases the average deviations between A_{calc} and A_{meas} , σ_{calc} , are smaller than the average experimental uncertainty, $\langle\sigma_{\text{meas}}\rangle$, which implies that variations due to bulk composition changes are below the detection limit (within the assumptions of the model). Nonetheless, there is still weak evidence that FeO, FeSiO₃, Fe₂SiO₄ (below dashed lines, Fig. 10) tend to have higher Fe-O coordination numbers, for a given $\text{Fe}^{3+}/\Sigma\text{Fe}$ (or T and $f(\text{O}_2)$), than the Mg-rich compositions (above line). In equation 2, Fig. 10b, the influence of $\text{Fe}^{3+}/\Sigma\text{Fe}$ on A is explicitly accounted for, such that the coefficient B yields an upper-bound estimate of the direct influence of T on $n_{\text{FeO}}(A)$. Note that B is positive, meaning that $n_{\text{FeO}}(A)$ increases with T increasing. The upper-bound is defined by $10^0 < B < 10^2$ K/eV, where a range of values is given owing to the significant uncertainty arising from the fit to our dataset. Over the entire range of temperatures studied ($1400 < T < 2160$ K) this would give changes in n_{FeO} of at most 0.2 to 0.3 (Fe(III) and Fe(II) respectively), or approximately 2.6 to 3.9×10^{-4} atoms K⁻¹. However, the changes in $n_{\text{FeO}}(A)$ observed between melts and glasses ($T_g \approx 1020$ K), (Fig. 8c, Table 4), are very small (discussed further in section 4.3). For this reason we consider the difference in n_{FeO} between aluminosilicate and (FeO)₁₀·(CaSiO₃)₄₅ melts to arise from the compositional difference, as opposed to the ~500K temperature difference.

A weak dependence of n_{FeO} on temperature is consistent with the analysis of (Liu and Lange, 2006) of the partial molar volume of Fe₂O₃ in alkali iron silicate melts. Wilke et al. (2007a) found that n_{FeO} was only slightly smaller in some alkali silicate and haplogranitic melts than in corresponding glasses, and Waychunas et al. (1988) reported little change in the iron K-edge pre-edge intensities upon quenching to glass melts of composition A₂FeSi₃O₈ (A = Na, K).

4.2 Determination of iron oxidation state

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ values for the melts and glasses of the present study were estimated in several ways (Tables 1 and 2). $\text{Fe}^{3+}/\Sigma\text{Fe}$ was calculated from the measured T , calculated $f(\text{O}_2)$ and bulk composition using a semi-empirical thermodynamic model given by Jayasuriya et al. (2004) (their equation 12) which

is an update of the non-ideal exponent model of Sack et al. (1980) and has been shown to be consistent (Alderman et al., 2017) with experiments on quenched iron oxide melts (Darken and Gurry, 1946). $\text{Fe}^{3+}/\Sigma\text{Fe}$ was estimated directly from the iron K-edge XANES pre-edge peaks using the calibrations of Wilke et al. (2004), both by centroid energy, C and area ratio, F . Comparisons of the XANES based determinations to the model predictions are made in Fig. 11 for the melt data only. The measurements generally correlate with the predictions, but in both cases tend to yield lower $\text{Fe}^{3+}/\Sigma\text{Fe}$, and more so under more oxidizing conditions. Linear regressions to the data (Fig. 11) yield $r_{\text{calc}} = 2(2) + 1.50(4)r_{\text{ratio}}$, adjusted $R^2 = 0.97$, and $r_{\text{calc}} = 9(2) + 1.39(4)r_{\text{centroid}}$, $R^2 = 0.97$, where $r = 100\text{Fe}^{3+}/\Sigma\text{Fe}$ denotes the percentage of ferric iron. There are therefore systematic differences (slopes differing from unity) as well as statistical differences (scatter about the linear regression). The systematic differences may arise from a number of sources.

Firstly, measuring $\text{Fe}^{3+}/\Sigma\text{Fe}$ using XANES spectroscopy is not a direct method, but rather relies upon calibrations in which spectra are measured from materials (usually glasses) with known $\text{Fe}^{3+}/\Sigma\text{Fe}$, which are usually determined by wet chemical analysis or Mössbauer spectroscopy. Such calibrations tend to vary between studies (Berry et al., 2003; Cottrell et al., 2009; Knipping et al., 2015; Wilke et al., 2004, 2005; Zhang et al., 2016) depending on the analytical procedures (background removal etc.) applied, and also on bulk composition (see Fig. S2). Resolution has been shown to have only a small effect on centroid energies (Fiege et al., 2017). Knipping et al. (2015) have pointed out that the Mössbauer based calibrations of Wilke et al. (2004) used here tend to underestimate $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to wet chemical analyses. A similar effect is observed in the present study (Fig. 11) where indeed $\text{Fe}^{3+}/\Sigma\text{Fe}$ is underestimated by the Wilke et al. (2004) calibrations, as compared to the model calculations (and compared to the Mössbauer measurement on the most oxidized $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glass, Table 2, Fig. S2). Using the Knipping et al. (2015) calibration based on wet chemical analyses of alkali trisilicate glasses, much of the systematic discrepancy disappears, Fig. 11c. Linear fits to the data in Fig. 11c yield similar $R^2 = 0.96$, but improved slope of $1.18(4)$ (intercept of $0(3)$). This suggests that much of the systematic differences may be attributed to the choice of calibration.

Secondly, the model (Jayasuriya et al., 2004) is being used outside of the context within which it was derived – from wet-chemical analyses of $\text{Fe}^{3+}/\Sigma\text{Fe}$ on room temperature glasses obtained from melts equilibrated at various T and $f(\text{O}_2)$. Here we have studied the melts *in-situ* which would introduce a systematic difference *if* any changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ occurred during glass-formation in the literature studies used in model derivation (Jayasuriya et al., 2004; Kilinc et al., 1983; Kress and Carmichael, 1988; Kress and Carmichael, 1991; Moore et al., 1995; Sack et al., 1980; Thornber et al., 1980). Overall, such quench effects on Fe oxidation state are expected to be suppressed in the literature studies cited (wire loops quenched into water, or on furnace base in one case (Thornber et al., 1980)), as compared to our containerless aerodynamic levitation method. Furthermore such quench effects are observed to be small in our data set (sections 4.1.4, and 4.3). More importantly, we have studied mostly non-glass-forming compositions which are well outside of the bulk compositional ranges used in the model derivation. In particular, the present study includes much more iron-rich compositions, right up to the pure iron oxides, as well as MgO-rich ultra-mafic and other highly depolymerized melts which do not readily form glasses. The coefficients for MgO and FeO_t content corrections in the model may be subject

to large uncertainties owing to the limited ranges over which these components vary within the matrix of input compositions (Jayasuriya et al., 2004). Nonetheless, comparisons (Alderman et al., 2017) of the model (Jayasuriya et al., 2004) predictions to experiments on quenched iron oxide melts (Darken and Gurry, 1946) suggest that the FeO_t coefficient is applicable over a very wide range of compositions, right up to pure iron oxide. This is in contrast to other models (Kress and Carmichael, 1991; Sack et al., 1980) similarly tested.

Whatever the choice of calibration curve for extracting $\text{Fe}^{3+}/\Sigma\text{Fe}$ from XANES pre-edge information, it is evident in Fig. 11 that there is a lot of scatter in the data. Some such scatter is expected, particularly since the models used to predict $\text{Fe}^{3+}/\Sigma\text{Fe}$ do not tend to fit all input data within their quoted uncertainties (Jayasuriya et al., 2004). In addition, any disequilibrium between the melt and the gas phase atmosphere will contribute to scatter in Fig. 11. However, a further limitation of the XANES technique is that calibrations can vary with the bulk composition. For example, similar calibration curves have been reported for basaltic (Cottrell et al., 2009) and andesitic (Zhang et al., 2016) compositions, whilst for rhyolitic compositions, the further enrichment in silica leads to a distinct calibration curve (Cottrell et al., 2009; Zhang et al., 2016). As such, a given measured centroid energy covers a range of experimental $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 10% to > 30% $\text{Fe}^{3+}/\Sigma\text{Fe}$ absolute, based solely on compositional variation ((Fiege et al., 2017) and references therein). Therefore, use of a single calibration curve for the widely varying compositions of the present study may well be invalid. One of the underlying reasons for differing calibration curves between different compositional series is that the pre-edge centroid energy depends not only on the iron oxidation state. In fact, differential changes in the local site symmetry or coordination number of Fe(II) and Fe(III) will lead to shifts in centroid energy as the intensities of their respective transitions vary independently (Métrich et al., 2006), and centroid-area coordinates cannot be mapped uniquely onto oxidation state-coordination number.

4.3 Changes in Fe oxidation state and local structure on melt-quenching

Comparing pre-edge peaks of melts to their quench products (Tables 2 and 3, Figs. 6, 7, 8c and 12) reveals clear differences associated with structural and/or oxidation state changes. Structural changes on quenching are to be expected for the non-glass-forming compositions which crystallize on cooling, and which comprise the majority in the present study. This is because of the much greater degree of order present in the crystalline state, as well as the fact that average coordination numbers are typically higher in the crystalline solids, compared to the melts (Alderman et al., 2017; Alderman et al., 2014; Skinner et al., 2014). However, in 11 cases the melts were quenched to obtain glasses of the aluminosilicate, $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$, $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$ and $\text{Fe}_{0.25}\text{Mg}_{0.75}\text{SiO}_3$ compositions, Fig. 8c. In the case of glass-formation, structural changes about iron on quenching are expected to be smaller than those occurring during crystallization (Liu and Lange, 2006; Tangeman and Lange, 1998; Wang et al., 1995; Wilke et al., 2007a), and this is supported by the small changes in n_{FeO} inferred from the pre-edge peak areas, Fig. 8c and 12b.

Fig. 12a shows that in almost all cases the pre-edge peak centroid shifts to higher energy upon quenching, both in the case of crystallization, and glass-formation. Two effects could contribute to the observed positive centroid shifts: i) oxidation; ii) differential local structural changes about ferric and

ferrous iron. For melt-glass pairs, we favor the former explanation, that oxidation is occurring during quenching, for the reasons outlined below. For melts which crystallize, both mechanisms, oxidation and differential structural changes can contribute to the observed centroid shifts on quenching.

Firstly, the small changes in mean n_{FeO} evident upon glass formation (Fig. 8c and 12b) would require that any differential changes in $n_{\text{Fe(II)O}}$ and $n_{\text{Fe(III)O}}$ would have to be of the opposite sense, in order to approximately cancel and yield the same n_{FeO} . Furthermore, the $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{SiO}_3$ and $\text{Fe}_{0.25}\text{Mg}_{0.75}\text{SiO}_3$ compositions formed glass only under highly reduced conditions where ferrous Fe dominates. The data for these melt-glass pairs indicate that $n_{\text{Fe(II)O}}$ itself is not strongly temperature dependent.

Secondly, oxidation on cooling appears to be supported to some extent by the Mössbauer measurements (Table 2, Fig. 9) on the recovered solids which show average $\text{Fe}^{3+}/\Sigma\text{Fe}$ larger than those derived for the melts from XANES spectroscopy, but similar to the transmission XANES measurements on powdered glassy quench products. For example, the most reduced $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ melt (4:1 $\text{CO}_2:\text{CO}$ mixture) has $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 6 and 10% as estimated from the XANES spectrum (Table 1), whilst the glass has 19 to 30% Fe^{3+} from XANES, 26% Fe^{3+} from Mössbauer (Table 2).

The apparent oxidation during cooling supports our supposition that iron redox equilibria are obtained rapidly in the high temperature melts, such that they can change appreciably during the few seconds taken to quench to the glass transition or recalescence temperatures, Fig. 13. This rapid (not diffusion limited) equilibration is driven by the stirring arising due to shear forces between the levitation gas jet and the melt surface, as well as convective and Marangoni flows arising due to temperature gradients. Such effects are absent or greatly reduced in other experimental setups, such as those using the wire loop methodology (Jayasuriya et al., 2004; Kilinc et al., 1983; Kress and Carmichael, 1988; Kress and Carmichael, 1991; Moore et al., 1995; Sack et al., 1980; Thornber et al., 1980). Gas jet velocity through the nozzle orifice is of the order 10 m s^{-1} , whilst preliminary computational fluid dynamics modelling indicates melt flow rates of mm s^{-1} to cm s^{-1} , similar to those calculated for electromagnetically and electrostatically levitated droplets (Hyers, 2005; Hyers et al., 2004). These flow rates are significant given the mm scale radii of our melts, and cooling rates ranging from -10^3 K/s at high temperatures down to -10^2 K/s at the glass transition or recalescence temperatures, Fig. 13. It remains to be explained why oxidation on cooling is observed in $\text{CO}-\text{CO}_2$ mixtures which should buffer the Fe redox equilibrium. This could imply a lack of gas phase equilibrium at the melt surface during the quench.

There is a significant caveat on the above discussion. Each XANES spectrum was obtained over an 8 min period, with the pre-edge peaks being recorded over a 32s period completed after about 70s from the start of measurement. This leaves almost 7 minutes at high temperature between the melt measurement (of the pre-edge) and the quench to solid. Were the iron oxidizing toward equilibrium during this period, i.e. on a timescale of minutes, it would lead to the observed positive centroid energy shift 'on quenching'. Such behavior is consistent with the applied temperature-time profile in some cases, such as the fayalitic melt in $\text{Ar}:0.1\%\text{O}_2$. In that case the melt was heated to a much higher temperature prior to measurement, where it could presumably reduce rapidly, before being cooled by 720 K and the spectrum collected (see Alderman et al. (2017) for further discussion). It is noteworthy that the points for this spectrum in Fig. 11 are some of the furthest outliers. It is also worth noting that

the powder transmission pre-edge spectra, Fig. 6a-c, tend to lie intermediate between the fluorescence spectra of the melts and glass beads. Given that the fluorescence measurement is sensitive only to the surface ($\mu(7100\text{eV}) = 32\mu\text{m}$ in $(\text{FeO})_{10}\cdot(\text{CaSiO}_3)_{45}$ glass), whilst the transmission measurement should represent an average over the sample volume, this implies an iron oxidation state gradient throughout the glass beads, with the core being more reduced than the surface. This is consistent with the interpretation of the centroid energy shifts, ΔE , as arising from oxidation (from the surface).

Unfortunately this observation does not allow one to differentiate between the faster (changes occur during quench) and slower (changes occur throughout measurement on melt) scenarios for the redox kinetics. Roskosz et al. (2008) did not observe any redox gradients in their 8 wt.% Fe_2O_3 diopside glass, which they attributed to rapid electron transfer processes. The apparent existence of redox gradients in our $(\text{FeO})_{10}\cdot(\text{CaSiO}_3)_{45}$ glasses may therefore imply their generation on very rapid timescales, i.e. during quenching.

Ultimately, time-resolved techniques (Ginder-Vogel et al., 2009) should be used to characterize the redox kinetics in the context of aerodynamic levitation, and modelling of fluid flow within aerodynamically levitated droplets would also be beneficial. Despite the scatter and systematic deviations from unity slope in Fig. 11, there is nonetheless a positive correlation between XANES pre-edge peak position and predicted $\text{Fe}^{3+}/\Sigma\text{Fe}$, and from this we infer that redox equilibration timescales in our experiments are more rapid than those observed in experiments lacking forced stirring (Cochain et al., 2009; Magnien et al., 2008; Roskosz et al., 2008; Wilke et al., 2007b), and are on the order of seconds to minutes.

The above discussion focusses on the centroid energy shifts, ΔE , between melt and recovered solid. However, pre-edge peak intensity changes also occur, Figs. 11b and 8c. Intensity changes imply changes in the average local structure (centrosymmetry) about iron. It is important to note that Fe-O coordination numbers measured by diffraction from fayalitic melts (Alderman et al., 2017) support the interpretation of the XANES pre-edge peak intensities increasing (upon melting of the crystalline solid) due to decreasing coordination, and not simply due to increased distortion of more highly coordinated polyhedra at high temperature. Fig. 8c and 11b show that intensity changes upon glass formation are between $\pm 20\%$ of the value in the melt, a smaller range than observed for crystallizing compositions, implying smaller structural changes. The uncertainty on the peak area changes $\Delta I/I$ is relatively large at $\pm 20\%$ implying that the changes observed for melt-glass pairs are not significant. Fig. 8c also reveals a marked difference between the reduced MgO-FeO-SiO_2 melts, whose pre-edge centroids and areas change little upon glass formation, and the aluminosilicate and $(\text{FeO})_{10}\cdot(\text{CaSiO}_3)_{45}$ melts which show larger positive centroid shifts and area increases upon glass formation. As can be seen from the variogram (Fig. 8), centroid and area parameters are not orthogonal, such that even for fixed Fe-O coordination, changes in centroid result in changes in area, such that a portion of the observed intensity changes are attributable to oxidation. Nonetheless, we estimate from the largest observed area changes in our data an upper-bound for Fe-O coordination changes between glass and melt of $\pm 0.3(2)$. This estimate coincides with those in section 4.1.3 made based on the melt temperature dependence of pre-edge area. The finding of weak dependence of n_{FeO} on T is also consistent with studies of the partial

molar volume of Fe_2O_3 in silicate melts (Liu and Lange, 2006), Fe K-edge XANES (Wilke et al., 2007a) and Raman spectroscopic (Wang et al., 1995) studies.

4.4 Implications for natural glasses, tektites and chondrules

The observed lack of changes in either ferric or ferrous Fe-O coordination on melt quenching to form glasses implies that, at least as far as the local structure of iron is concerned, natural glasses should represent the structure of parent melts. A lack of melt temperature dependence of Fe-O coordination is also inferred, which rules out any contribution of this mechanism to thermophysical property (e.g. viscosity, density) variation with temperature.

The inferred timescales for redox equilibria in our experiments, under the forced stirring conditions of aerodynamic levitation, are on the order of minutes to seconds. Since tektites and microtektites form under potentially similar aerodynamic high-temperature conditions (Macris et al., 2014), this qualitative result implies that their iron oxidation states may be capable of relatively rapid change and could be related to the observed high Fe^{3+} contents of North American microtektites (Giuli et al., 2013). Hot ultramafic (komatiitic) eruptions dominant during the Archean (Berry et al., 2008; Huppert and Sparks, 1985) are also likely subject to the rapid re-equilibration evident in aerodynamic levitation experiments. On the other hand, evidence suggests that oxidation state is frozen-in in lower temperature basaltic (or more silicic) melts e.g. mid-ocean ridge basalt glasses (Cottrell and Kelley, 2011) and in melt inclusions trapped within early crystallizing phases (Berry et al., 2008). Further studies of both the redox kinetics in the context of aerodynamic levitation and of more polymerized, silica-rich melt compositions would be instructive.

Aerodynamic levitation also provides a platform for studying chondrule formation (Nagashima et al., 2007; Nagashima et al., 2006; Pack et al., 2010) and meteoritic fusion crusts (Hezel et al., 2015). Although chondrules form in the solar nebula which has an estimated gas pressure of 0.1 to 100 Pa, there is evidence that chondrule formation occurs at higher, non-canonical pressures, closer to 1 bar (Galy et al., 2000). Fusion crusts on the other hand form at high dynamic pressures of 2 – 5 MPa (Hezel et al., 2015). There is therefore sufficient motivation to explore the possibilities of aerodynamic levitation under pressures of at least several tens of atmospheres. Working at slightly reduced pressures is also a possibility, although other levitation techniques, such as electromagnetic and electrostatic, are more naturally suited to this (Price, 2010).

5. Conclusions

In-situ measurements of the iron K-edge XANES spectra of levitated molten silicates were made under a range of oxygen fugacities, as well as on their glassy and ceramic quench products. At least over the range of alkali-free, iron-rich compositions studied, the XANES pre-edge peak areas imply mean Fe-O coordination numbers (n_{FeO}) close to 5 in all cases. In detail, the results reveal that Fe-O coordination is i) not strongly dependent upon temperature, ii) not strongly dependent on bulk composition and iii) decreases upon complete oxidation from Fe(II) to Fe(III) by, at most, 0.6(1) (11%) for $\text{CaSiO}_3\text{-FeO}$ melts. End member coordination numbers for Fe(II)-O and Fe(III)-O are estimated to be similar on average, having means (and standard deviations) of 5.0(2) and 4.9(1) respectively, averaged over all compositions

studied. As such, both Fe(II) and Fe(III) are inferred to play intermediate roles in terms of network formation. The preference for ferric iron to occupy lower coordination sites than ferrous is therefore relatively weak, in contrast to published behavior in some alkali-rich systems, which may explain the larger published viscosity variations with $\text{Fe}^{3+}/\Sigma\text{Fe}$ in alkali-, compared to alkaline earth-iron silicates (Dingwell, 1991; Dingwell and Virgo, 1987).

$\text{Fe}^{3+}/\Sigma\text{Fe}$ values were estimated from XANES pre-edge peaks using published calibrations and compared to semi-empirical thermodynamic model calculations and Mössbauer measurements on quench products. Whilst showing positive correlation, the comparisons highlight the sensitivity to the choice of calibration curve, and indicate that existing calibrations, as well as semi-empirical thermodynamic models for $\text{Fe}^{3+}/\Sigma\text{Fe}$, may both be inadequate for high temperature basic melts.

The work demonstrates that precise information can be obtained from X-ray absorption spectroscopy of levitated melts, even at relatively low energy absorption edges, provided care is taken to ensure the stability and symmetry of the sample and self-absorption effects are accounted for when necessary. The aerodynamic levitation and laser heating methodology therefore provides a powerful tool for characterizing the local structure and oxidation state in molten materials, potentially over a very wide temperature range encompassing deeply supercooled (since heterogeneous nucleation is minimized) liquids up to extremes in excess of 3500 K, as well as wide oxygen fugacity ranges, without the typical problems encountered when using solid containers. Future work should involve the characterization of redox kinetics in the context of forced convection under aerodynamic levitation, broader exploration of melt composition and temperature space, measurement of multiple absorption edges, the study of molten tektites and chondrules and the use of *in-situ* measurements on melts to constrain both structural models (molecular dynamics) and thermodynamic models of iron oxidation state.

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963 Zhang, H.L., Hirschmann, M.M., Cottrell, E., Newville, M. and Lanzirotti, A. (2016) Structural environment
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966

967 Table 1: Experimental details and results for iron-bearing melts, extracted from iron K-edge XANES pre-edge peak parameters. σ_{FeO} gives an
968 estimate of the uncertainty in iron content based on measured mass losses during experimental runs, and assuming FeO is the most volatile
969 oxide component. Calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ are based on Jayasuriya et al. (2004) (their equation 12).

Material	σ_{FeO} (mol%)	Gas mix ^a	T (K)	$\log f(\text{O}_2)$	ΔFMQ	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%)	Centroid (eV) ± 0.1	Intensity (eV)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^c (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio ^c (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^d (%)
FeO	0	50Ar:50O ₂	1971(29)	-0.3	+3.7(2)	77(1)	7113.0	0.16(3)	45(6)	43(2)	64(7)
FeO	0	Ar:0.1%O ₂	1954(29)	-3.0	+1.1(2)	50(2)	7112.8	0.13(2)	34(5)	27(1)	50(7)
FeO	0	Ar:0.1%O ₂	1982(32)	-3.0	+0.9(2)	48(2)	7113.0	0.16(3)	47(7)	48(2)	66(8)
FeO	0	77CO ₂ :23CO	1955(29)	-6.3(2)	-2.2(3)	18(2)	7112.4	0.12(2)	17(4)	17(1)	26(6)
Fe ₂ SiO ₄	0	50Ar:50O ₂	1994(29)	-0.3	+3.5(2)	66(3)	7112.9	0.18(4)	40(6)	40(2)	59(7)
Fe ₂ SiO ₄	0.07	Ar:0.1%O ₂	1557(25)	-3.0	+4.4(3)	76(3)	7112.5	0.16(4)	20(4)	23(1)	31(6)
Fe ₂ SiO ₄	0.58	88CO ₂ :12CO	1560(34)	-9.4(2)	-2.1(3)	15(2)	7112.4	0.12(3)	15(4)	15(1)	24(6)
FeSiO ₃	4.6	50Ar:50O ₂	2159(25)	-0.3	+2.6(2)	49(3)	7112.5	0.15(3)	18(4)	25(1)	28(6)
FeSiO ₃	0.87	Ar:0.1%O ₂	2016(21)	-3.0	+0.7(3)	30(3)	7112.0	0.13(3)	0(3)	2(1)	2(4)
FeSiO ₃	1.6	77CO ₂ :23CO	1960(22)	-6.3(2)	-2.2(3)	10(1)	7112.0	0.15(3)	1(4)	7(1)	3(4)
MgFeSiO ₄	0.07	50Ar:50O ₂	1990(25)	-0.3	+3.6(3)	47(4)	7113.0	0.18(3)	45(6)	45(2)	64(7)
MgFeSiO ₄	0	50Ar:50O ₂	1996(27)	-0.3	+3.5(2)	47(2)	7112.9	0.22(4)	43(6)	44(2)	61(7)
MgFeSiO ₄	0.45	Ar:0.1%O ₂	1950(30)	-3.0	+1.1(2)	23(2)	7112.4	0.16(3)	18(4)	19(2)	27(6)
MgFeSiO ₄	0.71	77CO ₂ :23CO	1954(29)	-6.3(2)	-2.2(3)	6(1)	7112.2	0.16(3)	9(4)	12(1)	14(6)
Fe _{0.5} Mg _{0.5} SiO ₃	0.16	50Ar:50O ₂	1804(27)	-0.3	+4.9(2)	65(2)	7112.9	0.21(3)	39(6)	46(2)	57(7)
Fe _{0.5} Mg _{0.5} SiO ₃	0.23	Ar:0.1%O ₂	1808(29)	-3.0	+2.1(2)	35(2)	7112.3	0.18(2)	12(4)	17(1)	19(6)
Fe _{0.5} Mg _{0.5} SiO ₃	0.5	79CO ₂ :21CO	1805(26)	-7.5(2)	-2.3(3)	8(1)	7112.1	0.15(2)	4(4)	10(1)	7(5)
Fe _{0.25} Mg _{0.75} SiO ₃	2	O ₂	2094(26)	-0.3	+2.9(2)	36(2)	7112.5	0.15(2)	19(4)	28(1)	29(6)
Fe _{0.25} Mg _{0.75} SiO ₃	3.4	Ar:0.1%O ₂	2140(28)	-3.0	+0.0(2)	13(1)	7111.9	0.15(2)	-3(3)	1.0(4)	-
Fe _{0.25} Mg _{0.75} SiO ₃	2.4	77CO ₂ :23CO	2096(32)	-5.3(2)	-2.1(3)	5(1)	7111.8	0.13(2)	-6(3)	-1.4(4)	-
Fe _{0.25} Mg _{0.75} SiO ₃	2.9	77CO ₂ :23CO	2140(29)	-5.0(2)	-2.0(2)	5(1)	7111.8	0.14(2)	-5(3)	-0.3(4)	-
Fe _{0.25} Mg _{0.75} SiO ₃	3.2	77CO ₂ :23CO	2142(34)	-5.0(2)	-2.0(2)	5(1)	7111.9	0.15(2)	-4(3)	1.6(5)	-
Aluminosilicate ^a	0.07	O ₂	1558(29)	0.0	+7.4(3)	82(2)	7113.1	0.23(2)	56(8)	63(3)	76(8)
Aluminosilicate ^a	0.35	O ₂	1533(29)	0.0	+7.6(4)	84(2)	7113.0	0.22(2)	48(7)	62(3)	68(8)
Aluminosilicate ^a	1.3	Ar:0.1%O ₂	1566(32)	-3.0	+4.3(3)	53(3)	7112.2	0.16(2)	9(4)	17(1)	14(5)
Aluminosilicate ^a	0.83	88CO ₂ :12CO	1558(29)	-9.5(2)	-2.1(3)	6(1)	7112.0	0.16(2)	1(4)	6(1)	3(4)
BiFeO ₃	-	O ₂	1408(29)	0.0	+9.1(3)	98(1) ^f	7113.2	0.22(2)	63(10)	63(3)	82(8)
BiFeO ₃	-	Ar	1412(25)	-6.0(3)	+3.0(3)	75(5) ^f	7113.2	0.22(2)	68(12)	64(3)	86(8)
(FeO) ₁₀ ·(CaSiO ₃) ₄₅	0.14	O ₂	2074(34)	0.0	+3.4(2)	68(2)	7112.9	0.19(2)	39(6)	50(2)	57(7)
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^e	0.09	O ₂	2090(25)	0.0	+3.3(2)	67(2)	7112.9	0.18(2)	42(6)	50(2)	60(7)

(FeO) ₁₀ ·(CaSiO ₃) ₄₅	0.15	Ar:0.1%O ₂	2070(21)	-3.0	+0.4(2)	36(2)	7112.3	0.14(1)	13(4)	18(1)	20(6)
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^b	-	80CO ₂ :20CO	1899(22)	-6.6(2)	-2.1(3)	16(2)	7112.4	0.12(1)	15(4)	19(1)	23(6)
(FeO) ₁₀ ·(CaSiO ₃) ₄₅	0.17	80CO ₂ :20CO	2048(25)	-5.5(2)	-2.0(3)	16(2)	7112.1	0.12(1)	6(4)	9(1)	10(5)
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	0.49	50Ar:50O ₂	1997(27)	-0.3	+3.5(2)	71(2)	7113.0	0.20(3)	45(6)	51(2)	64(7)
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	0.44	Ar:0.1%O ₂	2000(30)	-3.0	+0.8(2)	42(2)	7112.6	0.16(2)	25(5)	27(1)	37(7)
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	0.51	80CO ₂ :20CO	1989(29)	-5.9(2)	-2.0(3)	17(2)	7112.3	0.15(2)	12(4)	17(3)	19(6)
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	0.06	50Ar:50O ₂	1914(27)	-0.3	+4.1(2)	77(2)	7113.1	0.21(2)	52(8)	53(2)	72(8)
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	0.54	Ar:0.1%O ₂	1899(29)	-3.0	+1.5(2)	52(2)	7112.7	0.17(2)	30(5)	37(2)	44(7)
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	1.1	80CO ₂ :20CO	1893(26)	-6.7(3)	-2.1(4)	17(3)	7112.4	0.14(2)	16(4)	15(1)	24(6)

970 a. 9FeO·17CaO·13Al₂O₃·61SiO₂, see ESI. b. Partially crystallized on quenching and not considered in Table 2. c. Wilke et al. (2004) calibration. d.
971 Knipping et al. (2015) calibration. e. Repeat measurement on fresh sample. f. No correction term for Bi₂O₃ content available, calculated as for
972 pure iron oxide.

973

974 Table 2: Results for solid quench products of the iron-bearing melts of Table 1, extracted from iron K-edge XANES pre-edge peak parameters
975 and Mössbauer spectroscopy. Calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ are based on Jayasuriya et al. (2004) (their equation 12) and use the estimated glass
976 transition or recalescence (crystallization) temperatures in the 2nd column.

Material	$T_{\text{recalescence}}$ or T_g (K)	Glass/ ceramic product	$\log$ $f(\text{O}_2)$	ΔFMQ	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%)	Centroid (eV) ± 0.1	Intensity (eV)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^c (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio ^c (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^d (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Mössbauer (%) ± 1
FeO	1772(22)	Ceramic	-0.3	+5.1(2)	87(1)	7113.4	0.15(2)	100(30)	63(3)	97(8)	
FeO ^b	1772(22)	Ceramic	-0.3	+5.1(2)	87(1)	7113.2	0.16(2)	63(10)	58(5)	82(8)	
FeO	1566(18)	Ceramic	-3.0	+4.3(2)	83(1)	7113.2	0.15(2)	65(11)	64(5)	84(8)	
FeO	1474(17)	Ceramic	-11.2(2)	-2.9(3)	16(2)	7112.8	0.12(2)	34(5)	37(1)	50(7)	
Fe ₂ SiO ₄	1660(20)	Ceramic	-0.3	+6.1(2)	87(1)	7113.1	0.10(2)	54(8)	56(2)	73(8)	70
Fe ₂ SiO ₄ ^b	1660(20)	Ceramic	-0.3	+6.1(2)	87(1)	7113.1	0.14(1)	55(8)	62(5)	75(8)	70
Fe ₂ SiO ₄	1264(14)	Ceramic	-3.0	+8.1(2)	95(1)	7112.6	0.09(2)	26(5)	38(3)	39(7)	50
Fe ₂ SiO ₄ ^b	1264(14)	Ceramic	-3.0	+8.1(2)	95(1)	7113.2	0.10(1)	65(10)	66(6)	83(8)	50
Fe ₂ SiO ₄	1240(14)	Ceramic	-14.3(3)	-2.8(4)	13(2)	7112.8	0.15(3)	33(5)	44(2)	48(7)	33
Fe ₂ SiO ₄ ^b	1240(14)	Ceramic	-14.3(3)	-2.8(4)	13(2)	7113.1	0.08(1)	54(8)	56(5)	74(8)	33
FeSiO ₃	1584(19)	Ceramic	-0.3	+6.8(2)	88(1)	7113.4	0.20(4)	85(27)	60(3)	94(8)	
FeSiO ₃	1310(15)	Ceramic	-3.0	+7.4(2)	92(1)	7113.0	0.14(3)	49(7)	48(4)	68(8)	
FeSiO ₃	1312(15)	Ceramic	-13.7(3)	-3.3(3)	8(1)	7112.4	0.11(2)	18(4)	28(1)	28(6)	
MgFeSiO ₄	1408(16)	Ceramic	-0.3	+8.8(2)	92(1)	7113.2	0.22(4)	64(10)	72(3)	82(8)	
MgFeSiO ₄	1485(17)	Ceramic	-0.3	+7.9(2)	88(1)	7113.0	0.20(4)	49(7)	58(2)	68(8)	
MgFeSiO ₄	1420(16)	Ceramic	-3.0	+5.9(2)	76(2)	7112.7	0.09(2)	30(5)	43(3)	44(7)	
MgFeSiO ₄	1445(17)	Ceramic	-11.6(2)	-3.0(3)	5(1)	7112.3	0.09(2)	10(4)	24(1)	16(6)	
Fe _{0.5} Mg _{0.5} SiO ₃	1431(31)	Ceramic	-0.3	+8.5(4)	92(1)	7113.0	0.20(3)	49(7)	60(3)	69(8)	
Fe _{0.5} Mg _{0.5} SiO ₃	1023(27)	Ceramic	-3.0	+12.8(7)	99(1)	7112.3	0.14(2)	11(4)	19(1)	17(6)	
Fe _{0.5} Mg _{0.5} SiO ₃	1023(27)	Glass	-19.9(7)	-4.1(1.0)	5(4)	7112.1	0.15(2)	4(4)	13(1)	8(5)	
Fe _{0.25} Mg _{0.75} SiO ₃	1414(24)	Ceramic	-0.3	+8.7(0.3)	91(1)	NA	NA	NA	NA	-(-)	
Fe _{0.25} Mg _{0.75} SiO ₃	1023(27)	Glass	-3.0	+12.8(7)	99(1)	7111.9	0.13(2)	-1(3)	5(1)	1(3)	
Fe _{0.25} Mg _{0.75} SiO ₃	1544(25)	Ceramic	-10.3(3)	-2.8(4)	5(1)	NA	NA	NA	NA	-(-)	
Fe _{0.25} Mg _{0.75} SiO ₃	1023(27)	Glass	-20.0(7)	-4.2(1.0)	4(3)	7111.9	0.15(2)	-2(3)	6(1)	1(3)	
Fe _{0.25} Mg _{0.75} SiO ₃	1023(27)	Glass	-20.0(7)	-4.2(1.0)	4(3)	7112.0	0.13(2)	1(4)	6(1)	3(4)	
Fe _{0.25} Mg _{0.75} SiO ₃	1023(27)	Glass	-20.0(7)	-4.2(1.0)	4(3)	7112.1	0.14(2)	3(4)	7(1)	6(5)	
Aluminosilicate ^a	1033(27)	Ceramic	0.0	+15.6(6)	99.6(1)	7113.3	0.25(2)	69(12)	75(4)	86(8)	
Aluminosilicate ^a	1033(27)	Glass	0.0	+15.6(6)	99.6(1)	7113.2	0.24(2)	67(11)	70(3)	85(8)	
Aluminosilicate ^a	1033(27)	Glass	-3.0	+12.6(6)	99(1)	7112.6	0.18(2)	24(5)	32(1)	37(7)	
Aluminosilicate ^a	1033(27)	Glass	-19.1(7)	-3.5(1.0)	4(4)	7112.2	0.17(2)	7(4)	12(1)	12(5)	

BiFeO ₃	1094(20)	Ceramic	0.0	+14.2(4)	99.8(1)	7113.3	0.11(1)	70(12)	54(2)	87(8)	
BiFeO ₃	1132(19)	Ceramic	-6.0(3)	+7.4(5)	96(1)	7113.2	0.10(1)	65(10)	54(2)	83(8)	
BiFeO ₃	1132(19)	Ceramic	-6.0(3)	+7.4(5)	96(1)	7113.2	0.10(1)	61(9)	56(2)	80(8)	
(FeO) ₁₀ ·(CaSiO ₃) ₄₅	1023(27)	Glass	0.0	+15.8(6)	99.9(1)	7113.3	0.20(2)	74(15)	76(4)	89(8)	
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^f	1023(27)	Glass	0.0	+15.8(6)	99.9(1)	7113.3	0.20(2)	73(14)	76(4)	89(8)	85 (77) ^e
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^b	1023(27)	Glass	0.0	+15.8(6)	99.9(1)	7113.2	0.16(2)	61(9)	64(3)	80(8)	85 (77) ^e
(FeO) ₁₀ ·(CaSiO ₃) ₄₅	1023(27)	Glass	-3.0	+12.8(6)	99.6(2)	7112.9	0.15(2)	42(6)	48(2)	60(7)	37
(FeO) ₁₀ ·(CaSiO ₃) ₄₅	1023(27)	Glass	-19.9(7)	-4.1(1.0)	11(9)	7112.5	0.15(2)	20(4)	30(1)	30(6)	26
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^b	1023(27)	Glass	-19.9(7)	-4.1(1.0)	11(9)	7112.5	0.13(1)	19(4)	27(1)	29(6)	26
(FeO) ₁₀ ·(CaSiO ₃) ₄₅ ^b	1023(27)	Glass	-3.0	+12.8(6)	99.6(1)	7112.8	0.15(3)	35(5)	48(2)	51(7)	37
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	1295(18)	Ceramic	-0.3	+10.3(3)	98.6(2)	7113.2	0.24(3)	61(9)	73(3)	80(8)	
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	1661(28)	Ceramic	-3.0	+3.4(3)	72(3)	7113.0	0.14(2)	44(6)	54(2)	63(7)	
(FeO) ₃₀ ·(CaSiO ₃) ₃₅	1191(13)	Ceramic	-15.8(3)	-3.5(4)	13(2)	7112.7	0.14(2)	30(5)	38(2)	46(7)	
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	1288(15)	Ceramic	-0.3	+10.4(2)	98.8(1)	7113.1	0.18(2)	55(8)	70(3)	75(8)	
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	1390(18)	Ceramic	-3.0	+6.3(2)	92(1)	7113.1	0.16(2)	54(8)	52(4)	74(8)	
(FeO) ₅₀ ·(CaSiO ₃) ₂₅	1329(15)	Ceramic	-13.2(3)	-3.1(3)	15(2)	7112.6	0.11(1)	25(5)	30(1)	38(7)	

a. 9FeO·17CaO·13Al₂O₃·61SiO₂, see ESI. b. Powder transmission measurement. c. Wilke et al. (2004) calibration. d. Knipping et al. (2015) calibration. e. Measured at $T = 6$ K. f. Repeat measurement on separate sample.

Table 3: Parameters derived from ^{57}Fe Mössbauer spectra for $(\text{FeO})_{10}(\text{CaSiO}_3)_{45}$ glasses quenched from melts at different $f(\text{O}_2)$ (see Tables 1 and 2).

Gas mix	$T_{\text{Möss}}$ (K)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ (%) ± 1	$\delta'(\text{Fe}^{2+})$ (mm/s)	$\Delta(\text{Fe}^{2+})$ (mm/s)	$\delta'(\text{Fe}^{3+})$ (mm/s)	$\Delta(\text{Fe}^{3+})$ (mm/s)
O_2	6	77	1.15(2)	2.26(4)	0.41(1)	1.24(1)
O_2	293	85	0.98(1)	1.96(2)	0.29(1)	1.15(1)
$\text{Ar:0.1\%O}_2$	293	37	0.97(3)	2.04(6)	0.45(4)	0.9(1)
$80\text{CO}_2:20\text{CO}$	293	26	0.97 ^a	2.04 ^a	0.47(2)	0.83 ^a

a. Fixed during fitting

Table 4: Estimated end-member coordination numbers for Fe^{2+} and Fe^{3+} by linear extrapolation or interpolation of the Fe K-edge pre-edge peak area-centroid data, Fig. 8. N is the number of data points fitted to.

Melt/glass series	N	End-member coordination number		FeO (mol%)	NBO/T ^a
		$\text{Fe}^{2+}\text{-O}$	$\text{Fe}^{3+}\text{-O}$		
Aluminosilicate melts + glasses	7	4.8(1)	4.7(1)	9	0.3
Aluminosilicate melts	4	4.8(2)	4.7(3)	9	0.3
$\text{CaSiO}_3\text{-FeO}$ melts + glasses	15	5.3(1)	4.9(1)	10 – 50	2.4 – 4
$\text{CaSiO}_3\text{-FeO}$ melts	11	5.4(1)	4.8(1)	10 – 50	2.4 – 4
$\text{CaSiO}_3\text{-FeO}$ glasses	4	5.4(5)	5.0(2)	10	2.4
MgO-FeO-SiO_2 melts + glasses	17	4.89(3)	4.9(1)	12.5 – 33.3	2 – 4
MgO-FeO-SiO_2 melts	12	4.8(1)	4.9(1)	12.5 – 33.3	2 – 4
FeO-SiO_2 melts	6	5.0(2)	5.2(3)	50 – 66.7	2 – 4
FeO melts	4	5.6(3)	5.1(2)	100	n.a.
Average (Standard deviation)	49	5.0(2)	4.9(1)		
Data below from Farges et al. (2004)					
$\text{CaO-Na}_2\text{O-SiO}_2$ glasses (CNF)	18	4.6	4.6	< 2	0.8
$\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glasses (ALB)	2	4.3	4.4	< 2	0
CaO-MgO-SiO_2 glasses (DIO)	3	4.9	4.8	< 2	2
$\text{MgO-Na}_2\text{O-SiO}_2$ glasses (MNF)	7	4.9	4.4	< 2	0.8
$\text{CaO-K}_2\text{O-SiO}_2$ glasses (CKF)	2	4.3	4.4	< 2	0.8
Average (Standard deviation)	32	4.6(3)	4.5(2)		

a. The degree of network polymerization is often approximated by $\text{NBO/T} = (2c_{\text{O}} - 4c_{\text{T}})/c_{\text{T}}$ where NBO refers to “non-bridging oxygen” bonded to a single tetrahedral cation (denoted by T, where T = Si, Al in the present case), and c_{T} and c_{O} are atomic fractions of T cations and oxygen respectively. The preceding formula assumes all O ions are bonded to one or two T cations. The compositions of the present study are all relatively iron-rich, with $8 \leq \text{mol\% FeO} \leq 100$, as well as depolymerized, $0.7 \leq \text{NBO/T} \leq 4$, with some compositions containing O unbonded to any T (such that nonsensical values of $\text{NBO/T} > 4$ are calculated from the above formula, e.g. $(\text{FeO})_{50}(\text{CaSiO}_3)_{25}$).

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997 Figure 1: Illustration of the self-absorption corrections for extreme cases. a) Molten
998 $10\text{FeO}.45\text{CaO}.45\text{SiO}_2$, requiring only a small correction; b) Molten Fe_2SiO_4 , requiring a large correction.

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Figure 2: Fe K-edge XANES spectrum for molten $10\text{FeO} \cdot 45\text{CaO} \cdot 45\text{SiO}_2$ (2068(29) K) in one atm. O_2 . The measured pre-edge region is shown (open points) with bi-Lorentzian fit to the main edge (dashed grey), two fitted Gaussian pre-edge peak components (solid black) and the sum (solid red). Inset: XANES data over an extended energy range.

Figure 3: Illustrating the effect of sample stability on the X-ray absorption spectrum. At higher temperatures and gas flow rates molten samples can deform from sphericity, and become ellipsoidal. The ellipsoids tend to rotate (actually precess given that the melt is circulating about a different axis) about a vertical axis. a) Photograph of a stable, close to spherical, molten sample at lower gas flow rate. b) Rotating ellipsoidal sample at higher gas flow rate. c) Comparison of spectra obtained from a fayalitic melt in spherical and ellipsoidal levitation modes. For the ellipsoidal melt, the rotation period was larger than the measurement time-step resulting in a periodically varying component due to the oscillating sample geometry, and hence fluorescence signal, presented to the detector. Videos of the different behaviors shown in a) and b) are provided as online supplemental material.

Figure 4: Fe K-edge XANES spectra for melts levitated in different gas compositions and hence different $f(\text{O}_2)$. a) Molten $10\text{FeO}.45\text{CaO}.45\text{SiO}_2$; b) molten MgFeSiO_4 .

Figure 5: Fe K-edge XANES spectra for melts of varying chemical composition. a) Molten $y\text{FeO} \cdot (50 - y/2)\text{CaSiO}_3$, $y = 10, 30, 50$ and 100 . Note that for the pure FeO melt ($y = 100$) the gas composition was slightly different to that labelled on the plot for the other melts ($y < 100$), being $\text{Ar}:5\%(\text{77CO}_2:\text{23CO})$. b) Molten $\text{Mg}_z\text{Fe}_{1-z}\text{SiO}_3$, $z = 0, 0.5, 0.75$. Note that the large difference in pre-edge feature for $z = 0.5$ is attributed to the lower measurement temperature and hence higher $\text{Fe}^{3+}/\Sigma\text{Fe}$.

Figure 6: Comparison of Fe K-edge XANES spectra for melts and their corresponding glasses obtained by switching off the heating laser beam. a) to c) $10\text{FeO} \cdot 45\text{CaO} \cdot 45\text{SiO}_2$ in three different levitation gas compositions, showing fluorescence mode measurements on melts and glass beads in the levitator nozzle, as well as transmission mode measurements on powdered glasses. d) to f) Synthetic aluminosilicate composition $(\text{FeO})_9(\text{CaO})_{17}(\text{Al}_2\text{O}_3)_{13}(\text{SiO}_2)_{61}$ in three different levitation gas compositions, showing fluorescence mode measurements on melts and glass beads in the levitator nozzle. Insets show the isolated pre-edge peaks, where shaded areas indicate $\pm 1\sigma$ confidence bounds.

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1043 Figure 7: Comparison of Fe K-edge XANES fluorescence spectra for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{SiO}_3$ melts and their
 1044 corresponding glasses obtained by switching off the heating laser beam. The glass beads were
 1045 measured as obtained in the levitator nozzle, analogously to the melts. Insets show the isolated pre-
 1046 edge peaks, where shaded areas indicate $\pm 1\sigma$ confidence bounds.

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Figure 8: Variograms after (Wilke et al., 2001; Wilke et al., 2004, 2005) compared to present data for a) and b) molten silicates and oxides, and c) silicate melts (filled symbols) and corresponding glasses (open symbols). Shaded region in b) represents X-ray diffraction derived trend (95% confidence bands) for fayalitic $\text{Fe}_2\text{SiO}_{4+x}$ melts from Alderman et al. (2017), and is based on the modified Wilke et al. (2004) calibration between centroid and $\text{Fe}^{3+}/\Sigma\text{Fe}$. Arrows in c) connect melt-glass pairs where large differences are apparent. Dashed lines represent binary mixtures of end-member minerals, with vertical ticks indicating 10 mol% intervals. Open circles are the basaltic glass data of Wilke et al. (2004), open squares the phonolitic glass data of (Giuli et al., 2011). Note that the shaded areas representing 5-fold Fe(II) and Fe(III) are at the positions for 1:1 mixtures of 4-fold and 6-fold Fe bearing minerals given by Wilke et al. (2004), which are at slightly higher total area values than the shaded areas shown in the same paper.

Figure 9: $T = 293 \text{ K}$ ^{57}Fe Mössbauer spectra for $(\text{FeO})_{10} \cdot (\text{CaSiO}_3)_{45}$ glasses quenched from levitated melts at different $f(\text{O}_2)$ (see Tables 1 and 2). Vertical offsets have been applied for clarity. See Table 3 for fit parameters.

Figure 10: Results of unweighted non-linear least squares refinement of the parameters A_0 , B and C in the empirical equations a) $A_{\text{calc}} = A_0 + B/T + C \log_{10} f(\text{O}_2)$ and b) $A_{\text{calc}} = A_0 + B/T + C \text{Fe}^{3+}/\Sigma\text{Fe}$ to the measured Fe K-edge pre-edge peak areas (A_{meas}) of molten silicates and oxides. Symbols are the same as in Fig. 8. The dashed lines represent $A_{\text{calc}} = A_{\text{meas}}$. The model equations amount to attributing all observed variations in A_{meas} , and hence in Fe-O coordination, to variations in $\text{Fe}^{3+}/\Sigma\text{Fe}$ (a function of T and $f(\text{O}_2)$) and independent temperature-driven variations. The fact that the standard deviations between A_{calc} and A_{meas} , σ_{calc} are smaller than the average experimental uncertainty, $\langle \sigma_{\text{meas}} \rangle$, on A_{meas} implies that the model is reasonable and that variations due to bulk composition changes are below the detection limit. Nonetheless, there is still weak evidence that FeO, FeSiO_3 , Fe_2SiO_4 (below line) tend to have higher Fe-O coordination numbers, for a given $\text{Fe}^{3+}/\Sigma\text{Fe}$ (or T and $f(\text{O}_2)$), than the Mg-rich compositions (above line). Linear fits to the data shown result in adjusted R^2 , gradient and intercept of a) 0.70, 0.96(10) and 0.00(2) eV and b) 0.70, 1.03(11) and -0.01(2) eV.

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1082 Figure 11: Comparison of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in melts (Table 1) estimated from XANES using reported calibrations,
 1083 to those calculated using a semi-empirical thermodynamic model Jayasuriya et al. (2004). a) Ratio
 1084 method (Wilke et al., 2004, 2005), b) centroid method (Wilke et al., 2004, 2005), c) centroid method
 1085 (Knipping et al., 2015). The blue dashed line is the one-to-one correspondence; red solid lines are linear
 1086 regressions.

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1089 Figure 12: Histograms illustrating changes in Fe K-edge pre-edge peak parameters on quenching from
 1090 melt to solid, for all of the materials studied herein. a) Centroid energy change $\Delta E = E_{\text{solid}} - E_{\text{melt}}$.
 1091 Uncertainty ± 0.14 eV. b) Relative change in pre-edge peak area $\Delta I / I = (I_{\text{solid}} - I_{\text{melt}}) / I_{\text{melt}}$. Mean
 1092 uncertainty ± 20 .

Figure 13: Typical cooling curves measured by pyrometer for a) a 10FeO.45CaO.45SiO₂ glass-forming composition and b) FeO, a non-glass forming composition showing dramatic recalescence due to crystallization after supercooling by about 170 K. Approximate glass-transition and melting temperatures are indicated. The Fe³⁺/ΣFe at maximum *T* are calculated (Jayasuriya et al., 2004) to be a) 50(2)% and b) 10(1)%. The sample in a) begins cooling at -1300 K/s, which reduces to -100 K/s at the glass transition. The sample b) begins cooling at -500 K/s which reduces to -200 K/s at the point of recalescence.