Local structural variation with oxygen fugacity in $\text{Fe}_2\text{SiO}_{4+x}$ fayalitic iron silicate melts

O.L.G. Alderman^{a,b,*}, L. Lazareva^c, M.C. Wilding^d, C.J. Benmore^b, S. Heald^b, C.E. Johnson^e, J.A. Johnson^{e,f}, H.-Y. Hah^{e,f}, S. Sendelbach^a, A. Tamalonis^a, L.B. Skinner^{b,c}, J.B. Parise^c, J.K.R. Weber^{a,b}

Abstract

The structure of molten $\text{Fe}_2\text{SiO}_{4+x}$ has been studied using both high-energy x-ray diffraction and Fe K-edge x-ray absorption near-edge structure (XANES) spectroscopy, combined with aerodynamic levitation and laser beam heating. A wide range of Fe^{3+} contents were accessed by varying the levitation and atmospheric gas composition. Diffraction measurements were made in the temperature (T) and oxygen partial pressure ranges $1624(21) < T < 2183(94)$ K (uncertainties in parentheses) and $-5.6(3) < \Delta\text{FMQ} < +2.8(5)$ log units (relative to the Fayalite-Magnetite-Quartz buffer). Iron K-edge XANES measurements covered the ranges $1557(33) < T < 1994(36)$ K and $-2.1(3) < \Delta\text{FMQ} < +4.4(3)$ log units. Fe^{3+} contents, $x = \text{Fe}^{3+}/\Sigma\text{Fe}$, estimated directly from the pre-edge peaks of the XANES spectra varied between 0.15(1) and 0.40(2). While these agree in some cases with semi-empirical models, notable discrepancies are discussed in the context of the limitations in both the models and in the calibrations used to derive oxidation state from XANES spectra. XANES pre-edge peak areas imply average Fe-O coordination numbers, n_{FeO} , close to 5 for all $\text{Fe}^{3+}/\Sigma\text{Fe}$. Diffraction measurements yielded values of $4.4(2) < n_{\text{FeO}} <$

4.7(1). There is limited evidence for a linear trend $n_{\text{FeO}}(x) = 4.46(3) + 0.4(1)x$. Asymmetric Fe-O bond length distributions peak at around 1.96 Å and have a shoulder arising from longer interatomic distances. Mean r_{FeO} lie close to 2.06 Å, consistent with n_{FeO} close to 5. These observations suggest that Fe^{2+} is less efficient at stabilizing tetrahedral Fe^{3+} compared to large monovalent alkali cations.

Comparison of *in-situ* XANES estimates of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the melts to those of the quenched solids obtained from XANES as well as Mössbauer spectroscopy indicate rapid oxidation during cooling, enabled by stirring of the melt by the levitation gas flow. As such, the oxidation state of hot komatiitic and other highly fluid melts may not be retained, even during rapid cooling, as it is for cooler basaltic and more silicic magmas.

1. Introduction

Determining the local structure in molten silicates is important for understanding physical and transport properties relevant to geological magmatic and industrial smelting processes. The structure of a glass is often studied as a proxy for melt structure, but the assumption of short-range isomorphism can strictly only be applied to deeply supercooled melts in the glass transition region. This assumption has been shown to break down in many cases at higher temperatures (Alderman et al., 2016; Drewitt et al., 2012; Majerus et al., 2003; Wilding et al., 2010; Wilke, 2005; Wilke et al., 2007), and cannot be used at all for non-glass-forming melt compositions. Hence it is desirable to use *in-situ* methods of melt structure determination, despite the difficulties involved. Iron is the only major element of natural magmas which exists in multiple oxidation states, and the ferric/ferrous ratio is sensitive to temperature, T , and oxygen fugacity, $f(\text{O}_2)$. This property of iron makes it a valuable oxybarometer for estimating the conditions within parent magmas at depth, although this is complicated by the additional influences of pressure and bulk composition. The presence of both Fe^{3+} and Fe^{2+} , which have different formal charges and ionic radii and can adopt different (distributions of) coordination numbers to oxygen, makes the determination of local structure around iron in these important liquids particularly challenging.

Here we have chosen to study melts based on the fayalite (Fe_2SiO_4) composition, $\text{Fe}_2\text{SiO}_{4+x}$, under a variety of T , $f(\text{O}_2)$ conditions in an effort to discern structural changes with ferric iron content $x = \text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+}) = \text{Fe}^{3+}/\Sigma\text{Fe}$. The choice of a simple, iron-rich, composition is necessary to allow quantitative local structure determination by x-ray diffraction, see below. Fayalite is the ferrous endmember of the Fe_2SiO_4 – Mg_2SiO_4 olivine solid solution with forsterite. Olivine minerals on Earth dominate the mantle and have high average forsterite contents ($\approx 90\%$) (Frost and McCammon, 2008; McCammon et al., 2004; Woodland and Koch, 2003), whilst on other terrestrial planets such as Mars, iron contents can be higher (McSween, 2015; Shearer et al., 2013; Tuff et al., 2013). Although the concentration of fayalite in mantle olivines is restricted, studies of the end-members are important in order to understand the partial contribution of iron to the structural properties of liquids, such as iron enriched melts formed during differentiation of tholeiitic magmas (Scoon and Mitchell, 1994), including those formed *via* liquid-liquid immiscibility (Jakobsen et al., 2005; McBirney and Naslund, 1990). The earliest history of the Earth and the other terrestrial planets is believed to have been dominated by large fractions of melt, and processes such as planetary accretion and core-separation are all controlled by the structure-related properties of these liquids (Wade and Wood, 2005; Wood et al., 2006).

Fayalite-based slags are also important in non-ferrous metal processing and their thermodynamic and structural properties strongly influence copper metallurgy (Gorai et al., 2003; Zhang et al., 2015b). The presence of fayalite in historic slags has been identified as important in understanding the earliest developments of metal smelting (Ettler et al., 2015; Kramar et al., 2015), so from a wider perspective of materials and archeological significance, as well as a geochemical and geophysical viewpoint, direct measurements of fayalitic liquid structure are of interest.

In order to study fayalitic melts, we use the containerless processing method of aerodynamic levitation, combined with laser heating, to avoid problems such as the loss of Fe due to alloying with a Pt container (Darken and Gurry, 1945, 1946; Roskosz et al., 2008), as well as contamination of the melts by container material, particularly at the higher melting points encountered under oxidizing conditions. High-energy x-ray diffraction is employed to determine average Fe-O coordination numbers and bond length distributions within the melts, as has been applied successfully to other cations in refractory oxide liquids (Alderman et al., 2014; Benmore et al., 2010; Skinner et al., 2013a; Skinner et al., 2014a; Skinner et al., 2013b; Skinner et al., 2014b; Wilding et al., 2010). The choice of a simple iron-rich composition facilitates the quantitative measurement of Fe-O coordination numbers and bond length distributions by x-ray diffraction, something which is difficult or impossible for more complex melt compositions, and which cannot be achieved to the same level of accuracy using EXAFS. This is especially important when studying the subtle changes occurring due to redox and also obviates the need for more challenging techniques such as Fe isotope substitution combined with neutron diffraction. Fe K-edge x-ray absorption near-edge structure (XANES) spectroscopy is used to estimate $\text{Fe}^{3+}/\Sigma\text{Fe}$ redox ratios of the melts directly, as well as to provide complementary information on the average local structure about Fe. Very few x-ray absorption spectroscopic (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.

(Jackson et al., 1993) used x-ray absorption spectroscopy on a reduced fayalitic melt to determine that most Fe(II) ions were 4-fold coordinated to oxygen. Molten iron silicates have been studied previously using conventional x-ray diffraction (Waseda et al., 1980), with decreasing Fe-O coordination (n_{FeO}) with silica content reported, from $n_{\text{FeO}} \approx 5.5$ at 26 mol% SiO_2 to $n_{\text{FeO}} \approx 4.2$ at 39 mol% SiO_2 . These values showed little dependence on $2.0 \times 10^{-7} \leq p(\text{O}_2) \leq 2.0 \times 10^{-3}$ Pa or $1523 \leq T \leq 1623$ K. However, there are serious inconsistencies in the early data (Waseda et al., 1980) as critiqued recently (Drewitt et al., 2013). Drewitt *et al.* (2013) used aerodynamic levitation and laser beam heating to measure synchrotron x-ray diffraction patterns from iron bearing melts, including FeSiO_3 and Fe_2SiO_4 . Those authors found $n_{\text{FeO}} = 4.8(2)$ at 1623(30)K for Fe_2SiO_4 and $n_{\text{FeO}} = 5.1(2)$ at 1683(30)K for FeSiO_3 , however, the ferric iron contents were not quantified at the single $T, f(\text{O}_2)$ point sampled. Remarkably, even in the high- T melts, two separate peaks in the total correlation functions attributed to Fe-O distances were resolved and assigned to $[\text{FeO}_4]$ tetrahedra and $[\text{FeO}_6]$ octahedra. In the present work we seek to make measurements at multiple $T, f(\text{O}_2)$ points for systematic study of any structural changes associated with varying Fe^{3+} content of the fayalitic melt, and also to verify the splitting of the cation-oxygen bond length distribution.

2. Methods & Materials

2.1 Materials

For XANES and the higher energy (132 keV) x-ray diffraction experiments, $\text{Fe}_2\text{SiO}_{4+x}$ samples suitable for levitation were obtained by laser hearth melting approx. 30mg quantities of SiO_2 (Materion 99.9%) and Fe_2O_3 (Aldrich 99.999%) powders, taken from a pre-mixed 2 g batch with the correct 2:1 Fe:Si molar ratio. This 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).

Samples used for the lower energy (100 keV) x-ray diffraction experiments were obtained from a stock of pure fayalite and powders were pressed into 3mm sized pellets suitable for melting *in-situ* in the levitation nozzle. The fayalite was synthesized in a manner similar to Method 1 of Turnock et al. (1973): A 1:1 molar mixture of Fe_2O_3 and SiO_2 was ground together under ethanol in an agate mortar and placed in a platinum crucible that had previously been "soaked" with Fe to prevent Fe loss from the sample. The sample was heated overnight to 1473 K in a flowing mixture of CO and CO_2 , the ratio of which was adjusted to be well within the fayalite stability field.

We note that mass losses recorded during the course of each levitation measurement were small, corresponding to compositional drifts of < 1 mol% oxide, neglecting mass gain due to oxidation. The latter effect could mask larger compositional drifts. In the worst case, for oxidation of a fayalite sample to one with $\text{Fe}^{3+}_2\text{SiO}_5$ composition, the mass gained due to the additional O per formula unit could mask a compositional drift of up to -2.67mol% FeO.

2.2 Sample Environment

Sample beads approximately 3 mm in diameter were placed in a converging-diverging nozzle of an aerodynamic levitation system. This was contained within a purpose built water-cooled chamber approximately 1L in internal volume (see electronic supplemental information (ESI) Fig. S1). The chamber has several 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). The outlet port is conical and axially aligned with the sample in order to pass a large solid angle (30 degree half angle) of scattered x-rays. 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 $f(\text{O}_2)$ either by using a single supply of high purity O_2 , Ar, air, premixes of Ar:0.1vol.% O_2 , Ar:5vol.% CO_2 , 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 (Tables 2, 3, 4) were calculated based on the measured sample temperature, nominal gas composition and published Gibbs energies of formation for CO and CO_2 gases (Barin et al., 1993), and are also reported relative to the fayalite-magnetite- β -quartz (FMQ) buffer given by $\log f_{\text{O}_2} = -25096.3/T + 8.735$ (Frost et al., 1988) (see ESI, Fig. S4). Samples were heated from above with a CO_2 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 (see ESI Fig. S1) in order to

reduce 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 assumed for molten fayalite at the pyrometer wavelength of 0.9 μm . Pyrometer temperature was also corrected for reflection losses from a silica window and lens that were in the optical path. Melts were quenched rapidly after each measurement by switching off the heating laser whilst maintaining the gas flow. After about 2s of free cooling, recalescence was observed, signifying crystallization. The amount of supercooling varied depending on oxygen content, between about 100 and 200 K, for reduced and oxidized melts respectively.

2.3 X-ray diffraction

Diffraction measurements were made at beamline 6-ID-D of the Advanced Photon Source (Argonne, IL, USA) over the course of three separate campaigns (Table 4). The first two campaigns employed an x-ray energy of $E = 100.24 \text{ keV}$ ($\lambda = 0.12369 \text{ \AA}$) and the third a higher energy of $E = 131.80 \text{ keV}$ ($\lambda = 0.09407 \text{ \AA}$). A typical beam cross-section of 0.2 mm x 0.5 mm was used. Other than the x-ray wavelength, λ , the chamber window is the limiting factor on the maximum x-ray momentum transfer, $\hbar Q$, where $Q = 4\pi(\sin\theta)/\lambda$, because it imposes a maximum limit on the scattering angle, 2θ , for which x-rays can be detected. This is important because Q_{max} is reciprocally related to the resolution of the real-space Fourier transforms – the pair distribution or total correlation functions $T(r)$ – and so a large Q_{max} is desirable. An area x-ray detector (Perkin Elmer XRD1621, 2048 x 2048 pixels of 200 μm x 200 μm Tl doped CsI) was used with sample-to-detector distance (e.g. 370.7 mm at 100 keV, 357.5 mm at 132 keV) set to capture the entire diffraction pattern visible through the outlet window. The setup was calibrated using the diffraction pattern from polycrystalline CeO_2 powder coated onto a polystyrene bead that was placed in the levitator nozzle.

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 close to 2200 K in order to overcome temperature gradients across the partially molten sample (single sided heating) and to melt any refractory phases present or formed during heating, such as magnetite and SiO_2 . The initially large temperature gradient is reduced by convective mixing once melting is complete. The temperature was then lowered to that desired and diffraction patterns collected for 5 minutes (100 keV), with e.g. 0.5s exposures 600 times which were later averaged together. Longer measurements of 20 minutes were made at 132 keV due to the reduced x-ray flux at higher energy (campaign 3). Background patterns were collected with the same gas composition flowing into the chamber but without a sample in the nozzle. Detector dark current corrections were applied to all datasets. Quench products were measured as obtained, within the levitator nozzle, with the same experimental setup.

2.4 Fe K-edge XANES spectroscopy

X-ray Absorption Near Edge Structure (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. Molten samples were measured in three different gas mixtures (Table 2). The chamber (ESI Fig. S1) was rotated 90° compared to the configuration used for diffraction, such that the large x-ray outlet window was perpendicular to the incident x-ray beam and faced a 13-element Ge detector for measuring the fluorescence signal from the sample. 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 (see ESI Fig. S1). 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. Ionization chambers, one upstream 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. 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. The absorption length in molten Fe₂SiO₄ is about 57 µm at 7100 eV and decreases to about 12 µm above the edge, at 7200 eV. Levitation gas flow was reduced to zero when measuring the fluorescence signal from room-temperature beads quenched from the melts. This was to reduce noise due to motion of the more irregularly shaped (compared to melts) polycrystalline beads. The recovered beads were later pulverized and portions of the homogenized powder mounted on tape, positioned in front of the sample chamber and measured in transmission. Separate portions of the same powders were used for Mössbauer spectroscopy.

2.5 Mössbauer spectroscopy

Mössbauer spectra were obtained using a Rh⁵⁷Co source from samples recovered from XANES experiments and ground to a fine powder with an agate pestle and mortar. 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. No correction was made for the recoil-free fraction, which usually leads to a small overestimation of the ferric fraction (Zhang et al., 2015a).

2.6 Sample density and oxidation state estimates

The analysis, particularly of the diffraction data, requires knowledge of both the melt density and composition (Alderman et al., 2015; Alderman et al., 2014; Fischer et al., 2006; Keen, 2001). Liquid mass densities were estimated from measurements (Shiraishi et al., 1978) at 1573 K and 1673 K by linear interpolation or extrapolation using $\rho = 3.373 - 0.00028(T - 1573)$ in g cm⁻³ and K which yields densities

about 1% higher than some more recent measurements (Thomas et al., 2012). Hence the effect of Fe^{3+} on mass density was neglected, but was accounted for when calculating the atomic number densities.

The oxygen content in the formula $\text{Fe}_2\text{SiO}_{4+x}$ was calculated using a semi-empirical model given by Jayasuriya et al. (2004) (their equation 12)

$$\ln \left(\frac{X_{\text{Fe}_2^{3+}\text{O}_3}}{X_{\text{Fe}^{2+}\text{O}}} \right) = 0.1967 \ln f_{\text{O}_2} + \frac{12420}{T} - 7.054 + 1.377 X_{\text{FeO}_t} \quad (1)$$

where X_i are mole fractions of the i^{th} component. Note that we have eliminated correction terms involving components other than total iron oxide content, expressed as FeO_t . The Jayasuriya et al. (2004) model is an update of the Sack et al. (1980) model. The values of $100x = \text{Fe}^{3+}/\Sigma\text{Fe}$ in percent, calculated from equation 1, and based on the measured T and calculated $p(\text{O}_2)$ (Section 2.2), are given in Tables 2, 3 and 4. We note that all such empirical models are based on $\text{Fe}^{3+}/\Sigma\text{Fe}$ measured for complex geological glasses, such that, for the fayalitic melts in this study (which are silica poor, and lack major elements that have been shown to impact the relationship between $f(\text{O}_2)$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, such as Ca, Al, Na, K, P), considerable extrapolation in composition space is necessary and uncertainties in the expected $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are large. As such we used data based on melt-quench studies of pure iron oxide liquids from Darken and Gurry (1946) (see their Fig. 3B) to check the predictions of Jayasuriya et al. (2004) for fayalitic melts. This involved linear interpolation/extrapolation in temperature of Darken and Gurry's (linear) $\log p(\text{O}_2)$ versus O/Fe relations given at 3 discrete temperatures (1673, 1773 and 1873 K) which yielded

$$\frac{\text{Fe}^{3+}}{\Sigma\text{Fe}} = 2 \frac{X_{\text{Fe}_2^{3+}\text{O}_3}}{X_{\text{FeO}_t}} = 1.770 - (5.234 \times 10^{-4})T + ((7.920 \times 10^{-3}) - (4.620 \times 10^{-5})T) \log_{10} p_{\text{O}_2} \quad (2)$$

Predictions of both equations 1 and 2 are given in Tables 2, 3 and 4. Note that equation 2 cannot be written in the form of equation 1, and yields unphysical oxidation states at extreme values of T or $p(\text{O}_2)$, but gives reasonable values over most of the parameter space accessed in our experiments ($\text{Fe}^{3+}/\Sigma\text{Fe}$ becomes negative using equation 2 at our most reducing condition of $\log p(\text{O}_2) = -11.9$, $\Delta\text{FMQ} = -5.6$, but this is close to the stability field of metallic iron). The important result is that both equations 1 and 2 give similar predictions for $\text{Fe}^{3+}/\Sigma\text{Fe}$ in fayalitic melts. This is not the case for the original Sack et al. (1980) model, or the models of Kress and Carmichael (1991) which relatively under- and overestimate $\text{Fe}^{3+}/\Sigma\text{Fe}$ respectively. This suggests that the Jayasuriya et al. model should be favored for melt or glass compositions rich in iron, which may be due to the inclusion of data on iron rich (up to 30 wt. % Fe_2O_3) glasses in its derivation.

We note that the effect on Fe-O coordination numbers of *formally* changing the oxygen content within the diffraction data analysis is not large. An *upper bound* uncertainty of about 7% can be estimated based on the assumption that uncertainty is maximized for $x = 0.5$ (with $x = 0.5 \pm 0.5$), and the fact that n_{FeO} (as calculated) scales with $1/c_{\text{Fe}}$, the reciprocal of the atom fraction of iron. In the case of fayalitic $\text{Fe}_2\text{SiO}_{4+x}$ compositions, for $x = 0.5 \pm 0.5$, the fractional change in $1/c_{\text{Fe}}$ is $8/7.5 = 1.07$, yielding our 7%

estimate. The atomic number density also changes with x , and in particular, within our density model it increases with x , which leads to a compounded increase in n_{FeO} with x . However, we have found empirically that this is more than compensated for by normalization to a smaller average x-ray scattering form factor arising from the increased oxygen content, and so does not significantly alter our upper bound uncertainty estimate.

2.7 Electron microprobe

The compositions of two beads recovered from the high-energy x-ray diffraction experiments (campaign 3) were measured using electron microprobe analyses (EMPA), using a Cameca sx5 FEG electron microprobe analyser at the University of Oxford, 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 two samples, toward their centres, were performed using a 20 μm electron beam in order to average over the quenched textures, accelerating voltage was 20 kV and the beam current 20 nA. Synthetic MgO, albite and apatite were used to calibrate the analyses and the calibrations were verified using St John's Island Olivine and fayalite. Calcium and magnesium were not detected in the synthetic fayalite compositions studied here. Back scattered electron and secondary electron images show quench textures in the beads with skeletal fayalite crystals and excess quartz (lower mean electron density) and magnetite (ESI, Fig. S5).

3. Results

3.1 Electron microprobe analyses

The summary of the EMPA traverses for the two beads are presented as tables in the supplementary information (ESI, Tables S2 and S3) and plotted as a function of distance from the bead rims in ESI Fig. S6. Mean compositions (Fe:Si ratios) are close to that of the nominal fayalite stoichiometry ($66.7\text{FeO}\cdot33.3\text{SiO}_2$) at $62\text{FeO}\cdot38\text{SiO}_2$ with 2 mol% standard deviation (SD) for the sample melted in $\text{Ar:5vol\%}(1\text{CO:1CO}_2)$ gas, and $64\text{FeO}\cdot36\text{SiO}_2$ with 3 mol% SD for the sample melted in Ar. The variability across the samples reflects the heterogeneous quench textures and presence of all three FMQ phases. The mean iron contents are lower than expected from the small measured mass losses but remain close to the fayalite stoichiometry. The measured beads were recovered from the longest duration experiments, and so compositional drifts during all other experiments are expected to be correspondingly smaller. No discernible difference in average composition between the sample edges and the interiors was found, despite observed differences in microstructure (ESI, Fig. S5) which could arise by many mechanisms and are beyond the scope of the present study.

3.2 Fe K-edge XANES spectroscopy

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 one case (oxidized recovered bead) 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 dividing through 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. 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, and so for Fe K-edge measurements in $\text{Fe}_2\text{SiO}_{4+x}$, the effect is large and must be taken into account. Here we have used the Fluo algorithm (Haskel, 1999) available within Athena. This correction is applicable to flat-plate sample geometry, and therefore not necessarily suited to the liquid and solid beads of the present study (approx. 1.5 mm radii of curvature). However, we tested the algorithm on measurements of a pure iron sphere placed within the levitator nozzle and compared the results to that obtained by transmission measurement through a reference Fe foil. It was found empirically that the choice of 45° incident and 20° take-off angles gave a suitable correction at least up to about 100 eV above the edge, beyond which the intensities are overcorrected slightly, presumably due to the curved sample geometry. Nonetheless, the derived pre-edge intensities are subject to uncertainty resulting from this correction, which for the present case results in about a 50% reduction of the as-measured (isolated) pre-edge peak intensity. Note that in cases in which Fe is dilute or the absorption is dominated by heavier elements, then this correction can become small or even negligible.

In order to isolate the pre-edge peaks, up to two Lorentzian peaks were fitted to the main edge, with the energy range containing the pre-edge peaks excluded (Fig. 1). 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 (Table 1). The isolated pre-edge peak was then fitted typically with two Gaussian contributions, which were sufficient for simulating the spectra of molten samples (Fig. 1). In the case of crystallized oxidized samples an additional contribution to the pre-edge was usually observed at slightly higher energy 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 Fe^{3+} . 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 solids studied here.

Fig. 2 shows the isolated pre-edge spectra and Tables 2 and 3 give the parameters of the fitted peaks. Fig. 3 shows the average peak positions (centroids) plotted against total integrated area within the variogram determined by Wilke *et al.* (Wilke et al., 2001; Wilke et al., 2005). The three melt spectra have different centroid energies, corresponding to the different atmospheric gas mixtures (Table 2), and hence different Fe^{3+} contents. They all have similar total areas which lie intermediate between values expected for 4- or 6-fold Fe, indicating average Fe-O coordination numbers close to 5.

3.3 X-ray diffraction

The raw diffraction data were reduced from two dimensional images and corrected for the effects of polarization and geometry using the program Fit2d (Hammersley et al., 1996). The full azimuthal range

was used for the 100 keV measurements, whilst only the upper half of the diffraction cone was used for the 132 keV measurements in order to allow accurate corrections out to higher $Q_{\max}$. The reason for this arises from the intersection of the x-ray beam with the upper portion of the droplet, meaning that sample absorption is more severe in the lower portion of the diffraction pattern (Bendert et al., 2013). Additional geometrical corrections appropriate to flat panel detectors were also applied (Skinner et al., 2012b). The program GudrunX (Soper and Barney, 2011) was used for background subtraction, normalization and absorption and multiple scattering corrections. Any remaining slope on the resulting $S(Q)$ was accounted for by subtracting a constant from $I(Q)$ which approximately corrects for any fluorescence and secondary effects such as scattering in the sample followed by scattering (mostly Compton) in the air and other absorber layers between sample and detector. Any remaining weakly Q -dependent variations at this stage were removed using the Top-hat method (Soper and Barney, 2011), which amounts to an aesthetic correction suppressing unphysical oscillations in the r -space functions for $r < 1 \text{ \AA}$, similar to the back-transform method used elsewhere (Skinner et al., 2012a; Skinner et al., 2013a). The oxygen content in the formula $\text{Fe}_2\text{SiO}_{4+x}$ was calculated using equation 1, and the values based on the measured T and calculated $p(\text{O}_2)$ are given in Table 4 in the form $100x = \text{Fe}^{3+}/\Sigma\text{Fe}$ in percent. Liquid densities were estimated as described in section 2.6. Sample compositions used for analysis were based on the nominal 2:1 Fe:Si ratio which is partially justified on account of the small mass losses recorded during the course of each measurement (equivalent to drifts of $< 1 \text{ mol\%}$ oxide). Analyses based on SiO_2 richer compositions obtained from EMPA of recovered solids (section 3.1) revealed negligible differences in the extracted coordination numbers, n_{FeO} .

Structure factors, $S(Q)$, obtained are shown in Fig. 4, in the form of the Q -multiplied interference functions, $Q(S(Q) - 1)$, which emphasize the high- Q structure. Table 4 summarizes the conditions under which all of the measurements were made. The largest differences are seen between measurements made in pure O_2 or air and those under more reducing conditions in pure Ar or Ar:(CO-CO₂) buffers. A signature of the oxidizing conditions is the suppression of the $6.5 \text{ \AA}^{-1}$ shoulder (Fig. 4) which is much more prominent under reducing conditions. The effects of temperature and oxygen fugacity are not directly separable due to the higher temperatures required in oxidizing atmospheres to melt magnetite (and SiO_2) crystals, but from the systematics observed between all datasets, both T and $f(\text{O}_2)$ likely contribute to the changes in the $6.5 \text{ \AA}^{-1}$ feature, which arises predominantly from the Fe-Fe and Fe-Si partial structure factors, as discussed below.

The Fourier transforms (defined in (Alderman et al., 2015; Alderman et al., 2014)) of the diffraction data are presented in Fig. 5a and 5b in the form of $D(r)$ and $T(r)$. The changes with $f(\text{O}_2)$ are seen to be subtle, but are nonetheless systematic. In particular, the Fe-O bonds appear to contract in length, on average, and overlap more with the peak due to Si-O bond distances ($1.64 \text{ \AA}$) with increasing Fe^{3+} content, as expected for an increase in cation field strength (Fig. 6). Quantitative information on the nearest neighbor Fe-O pair correlations was extracted by means of peak fitting, the results of which are tabulated in Table 4, with an example plotted in Fig. 5b. Fitted peak shapes consisted of Gaussian distributions convolved with the Fourier transforms of both the x-ray pair weighting function $W_{ij}(Q)$ and the modification function, $M(Q)$, to match the experimental data (Alderman et al., 2015). For the measurements made at 100 keV, which have lower resolution, the Si-O peak was simulated (rather than

fitted) with bond-length $r_{\text{SiO}} = 1.64 \text{ \AA}$, root-mean-square deviation $\langle u_{\text{SiO}}^2 \rangle^{1/2} = 0.095 \text{ \AA}$, and coordination number $n_{\text{SiO}} = 4$, estimated from measurements at similar temperatures on pure liquid SiO_2 (Skinner et al., 2013b). The intratetrahedral O-O peak was also simulated assuming ideal geometry such that $r_{\text{OO}} = (8/3)^{1/2} r_{\text{SiO}}$, an estimate $\langle u_{\text{OO}}^2 \rangle^{1/2} = \langle 2u_{\text{SiO}}^2 \rangle^{1/2}$ and $n_{\text{OO}} = 3$ which is the minimum coordination number possible based on complete depolymerisation of the tetrahedra into $[\text{SiO}_4]^{4-}$ monomers, as in crystalline fayalite. This component of the O-O contribution is nonetheless small in the x-ray data and the assumptions have relatively little effect on the results obtained. The $T(r)$ minus the modelled Si-O and O-O peaks was then fitted with a single Fe-O distribution up to $2.0 \text{ \AA}$. The residuals consistently revealed a peak *circa* $2.25 \text{ \AA}$ which was assigned to longer Fe-O bonds and fitted up to $2.4 \text{ \AA}$. The higher resolution of the measurements made at 132 keV (Fig. 5b) allowed the parameters r_{SiO} and $\langle u_{\text{SiO}}^2 \rangle^{1/2}$ to be fitted simultaneously with the first Fe-O peak. Results are given in Table 5. The width of the peak is a little narrower than that estimated from measurements on pure molten silica at similar temperatures (Skinner et al., 2013b), but this is likely due to the lower $Q_{\text{max}} = 16.75 \text{ \AA}^{-1}$ used by (Skinner et al., 2013b). Although the $\langle u_{ij}^2 \rangle^{1/2}$ parameters are formally independent of Q_{max} or the form of any modification function, in practice both truncation in Q -space or use of a $M(Q)$ which suppresses high- Q amplitudes tend to lead to lower sensitivity to, and inflated values of, the underlying $\langle u_{ij}^2 \rangle^{1/2}$. This can also be seen in the $\langle u_{\text{SiO}}^2 \rangle^{1/2}$ obtained from the $T(r)$ without modification (step modification), which are smaller still (see also Fig. 5b). Such small values ($0.061(2) \text{ \AA}$) are only a little larger than values measured for pure vitreous SiO_2 under ambient conditions using high resolution neutron diffraction (Wright, 1994) ($0.045(2) \text{ \AA}$), and may be a result of the predominance of $[\text{SiO}_4]^{4-}$ monomers, as opposed to the more highly stressed polymerized $[\text{SiO}_{4/2}]$ in silica glass. Note that the use of a step modification allows the Si-O peak to become fully resolved, Fig 5b, as compared to the shoulder observed using Lorch modification. Meanwhile, changes in the Fe-O peaks are much more modest. This demonstrates that the highest Q oscillations observed at $Q > 25 \text{ \AA}^{-1}$, Fig. 4, are due predominantly to the Si-O partial structure factor. Nonetheless, use of the Lorch $M(Q)$ not only suppresses the effects of truncation, but has the additional benefit of suppressing the noise at high Q where the coherent scattering signal is extremely small.

Q -space representations of the r -space fits (Fig. 4c) show reasonable agreement only as low as 6 or $7 \text{ \AA}^{-1}$. At lower $Q \lesssim 7 \text{ \AA}^{-1}$, the Fe-Fe and Fe-Si partial structure factors, which have relatively large weightings, become important, but are damped away at higher Q . Making reasonable estimates for nearest neighbor Fe-Fe and Fe-Si Gaussian distributions, it was possible to obtain reasonable reproductions of the $S(Q)$, including the two dominant peaks, at $Q \lesssim 7 \text{ \AA}^{-1}$. Furthermore, the $6.5 \text{ \AA}^{-1}$ shoulder mentioned above could be reproduced, suggesting that increased disorder in the Fe-Fe and Fe-Si distributions at higher $f(\text{O}_2)$ and T is responsible for the observed changes in its intensity.

4. Discussion

4.1 Local structure about Fe^{2+} and Fe^{3+} in $\text{Fe}_2\text{SiO}_{4+x}$ melts

X-ray diffraction reveals Fe-O coordination numbers of between $4.4(2)$ and $4.7(1)$ (Fig. 6a, Table 4). Note that these are averaged over all iron sites, irrespective of valence state. XANES pre-peak areas imply values of n_{FeO} close to 5 (Fig. 3, Table 2) and are therefore in qualitative agreement. Note however

that longer Fe-O bonds may not be accounted for in the fits to diffraction data. In fact the Fe-O partial pair distribution, $g_{\text{FeO}}(r)$, may not return to zero after its first peak, implying that coordination numbers are not well defined and are a function of radial cut-off. Such bond length distributions are typical in oxide melts (Alderman et al., 2014; Skinner et al., 2013a; Skinner et al., 2014a; Skinner et al., 2014b) and glasses (Weigel et al., 2008a, b; Weigel et al., 2006; Wright et al., 2014), for all but the highest field strength cations, such as Si^{4+} and B^{3+} . As such, if $g_{\text{FeO}}(r)$ could be extracted (e.g. by neutron diffraction with Fe isotope substitution, or modelling) and n_{FeO} calculated to higher r (e.g. to the first minimum in $g_{\text{FeO}}(r)$), then values closer to 5 might be expected. Note that our results for n_{FeO} are in good agreement with a recent x-ray diffraction study by (Drewitt et al., 2013) who give $n_{\text{FeO}} = 4.8(2)$ (this study is discussed in detail below), and with the early results of (Waseda et al., 1980), n_{FeO} between 4.3(3) and 4.9(3). In contrast to an early Fe K-edge x-ray absorption study (Jackson et al., 1993), which concluded that on average $n_{\text{Fe(II)O}} = 4$, we assert that the fayalitic melts also contain significant fractions of more highly coordinated (5- and/or 6-fold) Fe. A classical molecular dynamics simulation of molten Fe_2SiO_4 also yields a similar value of $n_{\text{Fe(II)O}} = 4.7$ (Guillot and Sator, 2007), as does a recent *ab initio* molecular dynamics study (Muñoz Ramo and Stixrude, 2014). Average coordination numbers of between 4 and 5 are also typical of more complex Fe-bearing glasses (Drewitt et al., 2013; Farges et al., 2004; Jackson et al., 2005; Rossano et al., 2000a; Rossano et al., 2000b; Waychunas et al., 1988; Weigel et al., 2008a, b; Weigel et al., 2006; Wilke et al., 2007; Wilke et al., 2005; Wright et al., 2014) and melts (Drewitt et al., 2013; Guillot and Sator, 2007; Waychunas et al., 1988; Wilke et al., 2007).

It is important to note that the Fe-O coordination numbers measured by diffraction support the interpretation that XANES pre-edge peak intensities increase (in melts *cf.* crystals) due to decreasing coordination, and not simply due to increased distortion of more highly coordinated polyhedra at high temperature.

Considering all 9 data points in Fig. 6a, little systematic variation of $n_{\text{FeO}}(x)$ with $x = \text{Fe}^{3+}/\Sigma\text{Fe}$ is apparent, a linear fit yielding $n_{\text{FeO}}(x) = 4.48(4) + 0.2(1)x$ (adjusted $R^2 = 0.19$, $N = 9$), while the weighted average is $\langle n_{\text{FeO}} \rangle = 4.5(1)$. If the data point from the measurement which has the poorest signal-to-noise is excluded (that made in air, Fig. 4a), a weak positive correlation between n_{FeO} and $x = \text{Fe}^{3+}/\Sigma\text{Fe}$ is apparent. The fitted correlation $n_{\text{FeO}}(x) = 4.46(3) + 0.4(1)x$ has adjusted $R^2 = 0.55$, $N = 8$. If the trend were to continue in a linear fashion up to $x = 1$, then it goes against the conventional view that Fe^{3+} has a preference for tetrahedral environments in glassy and molten silicates, and Fe^{2+} for higher coordination numbers ((Holland et al., 1999; Mysen, 2006; Mysen et al., 1980; Mysen et al., 1985a; Mysen et al., 1985b; Mysen et al., 1984; Wright et al., 2014; Wright et al., 2008) and references therein). This is likely due to the highly depolymerized nature of the melts studied herein, as opposed to the more-polymerized, glass-forming compositions of the works cited. One should exercise caution with this result given that: i) the effect of temperature on the Fe-O coordination number distributions is neglected, although comparisons of glasses and melts (Wilke et al., 2007) imply that such dependencies are weak, at least in highly silicious systems; ii) there is no particular reason to expect a linear relationship and the data alone do not justify such a choice; iii) up to about 1/3 of the slope may be a systematic effect arising from the use of a constant cut-off (2.4 Å) for fitting, i.e. as the average cation field strength increases with $\text{Fe}^{3+}/\Sigma\text{Fe}$, so the bond lengths decrease and more of the Fe-O bond length

distribution is included below the cut-off, and iv) the experimental calibrations used to calculate $\text{Fe}^{3+}/\Sigma\text{Fe}$ are not intended for application to fayalitic melts and as such, it is possible that the true variation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ of melts in this study is not captured by our calculations. It would be instructive to test this result using e.g. molecular dynamics modelling and/or neutron diffraction with Fe isotope substitution.

The above trend can be rationalized to some extent by considering the electrostatic bond-strength (EBS) sums at the oxygen sites (Hannon, 2016). Firstly, the vast majority of O atoms are expected to be non-bridging,^a because the ratio $\text{O}/\text{Si} \geq 4$, that is to say that they bond to exactly one $[\text{SiO}_4]^{4-}$ tetrahedron with $\text{EBS} = v_{\text{Si}}/n_{\text{SiO}} = 1$, where v_i represents formal valence of the i^{th} species. Then there remains $\text{EBS} = v_{\text{O}} - 1 = 1$ for bonding to Fe. In the limiting case with $x = 0$, i.e. all iron divalent Fe^{2+} , the diffraction data indicate that n_{FeO} is low, about 4.4, such that there are very few 6-fold Fe-O polyhedra, and therefore the most optimal O environment corresponds to two tetrahedral Fe, $[\text{OSi}^{\text{IV}}\text{Fe}^{2+}_2]$ (Fig. 7a) with $\text{EBS} = v_{\text{O}} = 2$ (as proposed by (Jackson et al., 1993), although not all O environments exist in this configuration since $n_{\text{FeO}} > 4$). As Fe^{3+} content is increased, the optimal configurations ($\text{EBS} = v_{\text{O}}$) involving Si, Fe^{2+} and Fe^{3+} are $[\text{OSi}^{\text{IV}}\text{Fe}^{2+}_2\text{Fe}^{3+}]$ and $[\text{OSi}^{\text{IV}}\text{Fe}^{2+}\text{Fe}^{3+}_2]$ (Fig. 7b and 7c) and importantly these have average Fe-O coordination numbers of 5, which means that they will act to increase the n_{FeO} of the melt overall. Of course, there will be a concomitant increase of the number of oxygen bonded only to Fe cations, O_{Fe} , because for $x > 0$, $\text{O}/\text{Si} > 4$. There is a minimum of $x \text{ O}_{\text{Fe}}$ per formula unit $\text{Fe}_2\text{SiO}_{4+x}$, but it remains a minority species so long as there is no significant polymerization of the silicate anions. Silicate polymerization does occur at high $x > 2/3$ (Bowen and Schairer, 1932; Muan, 1955; Phillips and Muan, 1959) *via* phase separation (or formation of crystalline SiO_2 and magnetite at lower T). At the maximum $x = 0.56$ covered by our data, the probability $x^2 = 0.31$, for neighboring pairs of Fe^{3+} is still quite low, and these probably bridge mostly *via* the O_{Fe} . The broad distribution of Fe-O bond lengths observed allows for a wide variety of bond valences, and a greater degree of disorder in local atomic environments than considered above. Nonetheless the above simplified picture goes some way toward rationalizing the tentatively observed modest increase in n_{FeO} with Fe^{3+} content. Note that since our arguments are based on the majority of O species being non-bridging, in $[\text{SiO}_4]^{4-}$ moieties, then this mechanism for correlation between n_{FeO} and $\text{Fe}^{3+}/\Sigma\text{Fe}$ does not transfer directly to more polymerized melt compositions. Indeed, Farges *et al.* (Farges et al., 2004) have used Fe K-edge XANES on silicate rich glasses, dilute in iron ($\leq 2 \text{ wt.}\% \text{ Fe}_2\text{O}_3$), to infer composition dependent changes in n_{FeO} with $\text{Fe}^{3+}/\Sigma\text{Fe}$. For example, n_{FeO} is apparently constant at 4.6(1) with $\text{Fe}^{3+}/\Sigma\text{Fe}$ in a $\text{CaO-Na}_2\text{O-SiO}_2$ glass composition, but decreases, from 4.9(1) at $\text{Fe}^{3+}/\Sigma\text{Fe} = 0$ to 4.3(1) at $\text{Fe}^{3+}/\Sigma\text{Fe} = 100\%$ in an analogous $\text{MgO-Na}_2\text{O-SiO}_2$ glass. Similarly, Wilke *et al.* found average Fe-O coordination numbers close to 5 over the whole $\text{Fe}^{3+}/\Sigma\text{Fe}$ range in basaltic and sodium silicate glasses (Wilke et al., 2005) and a slight reduction in n_{FeO} with increased $\text{Fe}^{3+}/\Sigma\text{Fe}$ in alkali silicate and aluminosilicate melts (Wilke et al., 2007). Mössbauer spectroscopic evidence supports a decreasing average n_{FeO} with $\text{Fe}^{3+}/\Sigma\text{Fe}$ increasing, in various polymerized glass-forming silicates (Mysen, 2006; Mysen et al., 1980; Mysen et al., 1985a; Mysen et al.,

^a This is the case even for slightly more silica rich compositions, such as those measured by EMPA on recovered solids (section 3.1), and holds true for moderate amounts of disproportionation (polymerization) $2\text{NBO} \rightarrow \text{MBO} + \text{BO}$, where MBO denotes metal (iron) bridging oxygen (O_{Fe}) not bonded to any Si atoms.

1985b; Mysen et al., 1984). This latter tendency is suggestive of the stabilization of tetrahedral Fe^{3+} by alkali cations, illustrated in Fig. 7d for the case of 8-fold coordinated potassium ions. The important point to note is that Fe^{2+} , like other small divalent cations such as Mg^{2+} , tends to have lower coordination numbers to oxygen and higher EBS and field strength, and hence does not tend to stabilize $^{\text{IV}}\text{Fe}^{3+}$ as readily, as illustrated in Fig. 7b and 7c. This may go toward explaining the larger published viscosity variations with $\text{Fe}^{3+}/\Sigma\text{Fe}$ in alkali-, compared to alkaline earth-iron silicate melts (Dingwell, 1991; Dingwell and Virgo, 1987).

The overall broad and asymmetric Fe-O bond length distribution in the $\text{Fe}_2\text{SiO}_{4+x}$ melts peaks at 1.93 to 1.98 Å, about the expected distance for $[\text{Fe}^{2+}\text{O}_4]$ or $[\text{Fe}^{3+}\text{O}_5]$, but has a high r tail characterized by a 2nd Gaussian distribution peaked at 2.22 to 2.38 Å. This 2nd contribution has been attributed to 6-fold Fe by (Drewitt et al., 2013). We do not see any reason to exclude the presence of 5-fold units, and rather infer the presence of a distribution of distorted coordination units with 4, 5 and/or 6 oxygen ligands, as is typical for iron at ambient pressure ($4 \leq n_{\text{FeO}} \leq 6$). From the average n_{FeO} (Table 4) 4-fold or 5-fold units must dominate the distribution, and there can be at most 20(5)% to 35(5)% 6-fold units in the limiting case of a bimodal distribution with zero 5-fold polyhedra.

Fig. 6b shows the average Fe-O bond lengths as a function of calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$. As expected, there is a general decrease in r_{FeO} as $\text{Fe}^{3+}/\Sigma\text{Fe}$ increases, due to the increasing (average) field strength of the Fe ions. This decrease is somewhat less than expected from bond-valence considerations for constant coordination number (diagonal lines, Fig. 6b). There are at least two contributing factors to this effect: i) measurements under oxidizing conditions were made at higher temperatures and therefore there is increased thermal expansion of the bonds; ii) if the Fe-O coordination number increases as implied by the data in Fig. 6a, then this will contribute to increasing r_{FeO} as $\text{Fe}^{3+}/\Sigma\text{Fe}$ increases. From crystallographic measurements of the temperature dependence of the Fe^{2+} -O bonds in crystalline fayalite (Smyth, 1975), the bond length thermal expansion coefficient $\alpha_{\text{FeO}} = (1.4 \pm 0.1) \times 10^{-5} \text{ K}^{-1}$ can be derived (similar to those for the unit cell edges). One would expect the value for Fe^{3+} -O bonds to be similar or smaller than this. Given the ΔT of 50 to 400 K across our three datasets (different symbols in Fig. 6), such a value for α_{FeO} would lead to Δr_{FeO} of 0.001 to 0.01 Å. These predicted Δr_{FeO} are smaller than the observed deviations (from the bond-valence slopes) of 0.026 to 0.038 Å, and as such, the r_{FeO} data support an increasing n_{FeO} coordination number with $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 6a). Bond valence predictions imply $\Delta r_{\text{FeO}}/\Delta n_{\text{FeO}}$ of $\approx 0.08 \text{ Å}$ per atom and so the observed deviations Δr_{FeO} are consistent with the observed Δn_{FeO} of up to 0.35(23) (Table 4).

4.2 Comparison to Drewitt *et al.*

(Drewitt et al., 2013) recently measured the x-ray structure factor for molten fayalite by very similar means to those used herein, i.e. using high-energy (99.554 keV) synchrotron x-rays combined with aerodynamic levitation and laser beam heating. A measurement at a single $f(\text{O}_2)$, at $T = 1623(30) \text{ K}$ was made in Argon levitation gas “under normal atmospheric conditions”, i.e. open to the air. We were not able to reproduce exactly these conditions in our own experiments because in an open chamber (one chamber port uncovered) ingestion of air led to oxidation of the sample, sufficient to raise the melting point well above 1623 K with the concomitant formation of magnetite (and presumably SiO_2) crystals.

We were able to obtain a measurement on a crystal-free liquid, in high-purity Ar at 1677(23) K, only in a closed chamber (single conical opening for gas outlet at chamber apex, ESI Fig. S1), as used for measurements made with other levitation gas mixtures. The result can be seen in Fig. 4a to be broadly similar to that of (Drewitt et al., 2013), as well as to another measurement made with 132 keV x-rays in an atmosphere containing equal amounts of CO and CO₂. Fig. 4b shows that the low Q peaks in our measurement fall at Q values about $0.2 \text{ \AA}^{-1}$ higher than those of (Drewitt et al., 2013). Since this is also the case for all our other measurements, we can rule out the effect being due to T or $f(\text{O}_2)$ differences. We have confidence in our peak positions given that those of well-known materials (crystalline CeO₂, amorphous SiO₂) are well reproduced by our experimental setup. Since the low Q peaks include strong contributions from the metal-metal partial structure factors $s_{\text{FeFe}}(Q)$ and $s_{\text{FeSi}}(Q)$, one of the effects of shifting them to lower Q is to shift the nearest neighbor Fe-Fe and Fe-Si peaks in r -space to higher r , and increase their separation from the bonding Si-O and Fe-O peaks, as can be seen in Fig. 5b.

A final quantitative difference can be seen in Fig. 4a where, beyond about $Q = 16.5 \text{ \AA}^{-1}$, the oscillation amplitudes of the published result (Drewitt et al., 2013) are enhanced with respect to those of the structure factors presented herein. Since this is only evident at higher Q , it implies less damping, or smaller Debye-Waller factors, of the published measurement (Drewitt et al., 2013). The difference may arise due to inaccuracies in the various Q -dependent multiplicative corrections applied to either data, all of which increase in magnitude with Q (Bendert et al., 2013; Skinner et al., 2012b). Regardless of the origin, there is an important consequence in that the smaller damping in the published measurement gives rise to resolution of two separate peaks, attributed by (Drewitt et al., 2013) to Fe-O correlations for tetrahedral [FeO₄] and octahedral [FeO₆] iron environments. These two peaks were yet more clearly resolved for other iron-bearing melt compositions as well as glasses measured under ambient conditions (Drewitt et al., 2013). We observe no such resolution of two Fe-O peaks in our measurements, and we attribute the structure factor oscillations at the highest Q ($\geq 23 \text{ \AA}^{-1}$) to the Si-O partial structure factor, on the basis of the (unique) resolution of a separate Si-O peak in the $T(r)$ obtained without Lorch modification and $Q_{\text{max}} = 30.4 \text{ \AA}^{-1}$, Fig. 5b. As such, we have no evidence to suggest a bimodal Fe-O coordination number distribution (into 4- and 6-fold Fe), indeed, strictly speaking, the scattering data cannot be used to show this directly, with or without the resolution of two separate Fe-O peaks. Results from our analysis of the $S(Q)$ from (Drewitt et al., 2013) are given in the final rows of Table 4.

4.3 Oxidation state of iron

It has been shown that the centroid of the pre-edge feature in Fe K-edge XANES spectra can be used as a quantitative measure of oxidation state (Berry et al., 2003; Cottrell and Kelley, 2011; Cottrell et al., 2009; Knipping et al., 2015; Wilke et al., 2007; Wilke et al., 2005; Zhang et al., 2016). Such quantification typically relies upon calibration to a series of glasses of varying and known (by other means) Fe³⁺/ΣFe, but otherwise fixed composition, and has been shown to depend somewhat on the bulk composition. Given that the Fe₂SiO_{4+x} melts cannot typically be quenched to form glasses, such a calibration cannot be performed, because it relies on the assumption of local structural similarity between calibrants and the material of interest. In lieu of an alternative technique suitable for estimation of Fe³⁺/ΣFe directly from measurements on fluid melts, we have chosen to rely upon the calibrations made by (Wilke et al., 2005)

for basaltic glasses, to enable estimation of the oxidation state for the $\text{Fe}_2\text{SiO}_{4+x}$ melts, accepting the uncertainty this entails.

(Wilke et al., 2005) give two methods for extracting $\text{Fe}^{3+}/\Sigma\text{Fe}$ from the pre-edge peak position, one directly from the centroid position C , and one *via* $F = I(\text{Fe}^{3+})/[I(\text{Fe}^{2+}) + I(\text{Fe}^{3+})]$ 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 Fig. 2 by the vertical lines. During our analysis we noticed that the coefficients for the quadratic calibration curves given by Wilke *et al.* (Wilke et al., 2005) did not exactly match their graphical data. Therefore we have made our own fits to the basaltic glass data digitized from (Wilke et al., 2005), 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 3 percentage points. Recently (Knipping et al., 2015) have pointed out that the Mössbauer based calibrations of (Wilke et al., 2005) tend to underestimate $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to wet chemical analyses of alkali silicate glasses. We have included $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated using the calibration of (Knipping et al., 2015) for alkali trisilicate glasses in Tables 2 and 3 to illustrate the differences that can be obtained simply based on the choice of calibration curve.

Table 2 compares model $\text{Fe}^{3+}/\Sigma\text{Fe}$ values with those estimated directly from the C and F values calculated from the XANES spectra of the melts. For the oxidized case (50Ar:50O₂), it can be seen that the model calculation is slightly higher than the values determined from the different calibrations. In the most reducing case (88CO₂:12CO), the model appears to give a good estimate of $\text{Fe}^{3+}/\Sigma\text{Fe}$ compared to the XANES calibrations. The values for the Ar:0.1%O₂ atmosphere disagree, being significantly smaller as determined by XANES, compared to the model prediction. What to make of the various discrepancies? The most obvious source, is the choice of XANES calibration. The underlying reason that different calibrations are required for different compositions is the sensitivity of the pre-edge absorption features to the local structure about iron. The relatively robust result from diffraction analyses, that average n_{FeO} *does not decrease*, but likely increases, with $\text{Fe}^{3+}/\Sigma\text{Fe}$ increasing, means that the centroid energy $C(R)$ will vary differently than in the case where n_{FeO} *decreases* with $\text{Fe}^{3+}/\Sigma\text{Fe}$ increasing. This latter scenario does hold for at least some of the alkali containing silicate calibration glasses (Knipping et al., 2015), which can lead to an underestimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the fayalitic melts, as qualitatively observed. However, the basaltic glasses (Wilke et al., 2005) apparently show little variation of n_{FeO} with $\text{Fe}^{3+}/\Sigma\text{Fe}$, with similar pre-edge centroids and intensities to the fayalitic melts (Fig. 3). This does not necessarily mean that the basaltic calibration is suitable for the fayalitic melts, because individual coordination numbers for $\text{Fe}^{2+}\text{-O}$ and $\text{Fe}^{3+}\text{-O}$ may vary differently with $\text{Fe}^{3+}/\Sigma\text{Fe}$, and/or site symmetry may vary, independently from the average n_{FeO} or individual $n_{\text{Fe(II)O}}$ and $n_{\text{Fe(III)O}}$. Ultimately, use of a calibration curve $C(R)$ to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ always relies on the assumption of local structural similarity (about both ferric and ferrous iron) between the calibrant materials, and that under investigation.

The semi-empirical thermodynamic model used (Jayasuriya et al., 2004) is another possible source of discrepancy between calculated and XANES derived $\text{Fe}^{3+}/\Sigma\text{Fe}$. The model is based on measurements of

Fe³⁺/ΣFe made on quenched glasses of necessarily different composition to the fayalitic melts of this study, and may not apply to the equilibrium molten state, or the iron-rich, silica-poor fayalitic compositions. Nonetheless, it does agree well with the measurements of (Darken and Gurry, 1946) on materials quenched from pure molten iron oxides (Section 2.6, Tables 2, 3 and 4), suggesting that the extrapolation to iron-rich compositions is reasonable. On the other hand, the basis of all such models on *quenched* materials is itself a possible source of systematic error, as noted by (Darken and Gurry, 1946). Rapid oxidation occurring during quenching in the original experiments of Darken and Gurry is a possible explanation for the XANES determination of the oxidized melts as more reduced than the calculations (Equations 1 and 2) predict (Table 2, see section 4.4). There is potential for greatly expanding the range of compositions used in constraining models of iron oxidation state by using *in-situ* iron K-edge measurements on melts, although the issue of calibration remains a barrier. To this end, independent structural information e.g. from diffraction experiments, could be used to determine appropriate calibration compositions with local structural similarity to the materials of interest.

Another possible cause for disagreement in model and XANES Fe³⁺/ΣFe values is redox disequilibrium of the melts studied herein, and this may be a key contribution to the largest discrepancy, for the Ar:0.1%O₂ atmosphere measurement. During each run, the temperature of the sample had to be raised relatively high (≈ 2300 K) initially, in order to overcome temperature gradients, and ensure complete melting of any refractory phases present (e.g. magnetite and SiO₂) before being lowered to the hold temperature for XANES measurement. In the case of Ar:CO-CO₂ atmospheres, the *f*(O₂) is buffered and Fe³⁺/ΣFe depends only weakly on *T*, such that effects of *T* change prior to measurement are diminished. For the 50Ar:50O₂ atmosphere, although there is no such buffering effect, *T* was lowered only by ≈ 200 K prior to measurement, in order to avoid crystallization at lower *T*, and the higher *T* = 1994(36) K of the measurement presumably reduces equilibration time. However, for the Ar:0.1%O₂ atmosphere, a larger drop in *T* of ≈ 720 K was applied and this could explain the apparently low (e.g. Fe³⁺/ΣFe = 23(1)%) result from the XANES measurement, compared to the predicted Fe³⁺/ΣFe = 76(3)% at 1557 K. At the pre-measurement *T* = 2260 K, the predicted Fe³⁺/ΣFe = 21(3)% is close to the observed 23(1)%, suggestive of little, or only partial relaxation in the melt, from about 21% toward the predicted equilibrium value of 76%. This is supported by measurements on the recovered crystallized solid (Table 3, Fig. 2) where the centroid occurs at higher *E*, indicative of a more oxidized material resulting from the melt being held at 1557 K for the full 8 minute measurement duration. Note that oxidation from 21% to 76% Fe³⁺/ΣFe requires uptake of 1.3mg of O₂ for a typical sample mass of 31 mg. Given the unbuffered Ar:0.1%O₂ gas composition, the ~1 L chamber contains only 1.4 mg O₂ at a given instance, whilst only about 0.7 mg O₂ are supplied, per minute, through the levitator nozzle. Given the comparable amounts of required and available O₂, a disequilibrium effect seems possible. An alternative explanation is that oxidation occurred during the quenching process, which took only 1s between initiation of cooling and the onset of crystallization. This seems unlikely based on the limited available oxygen in Ar:0.1%O₂, but is a possibility in the O₂ and CO₂ rich gas compositions used, and is discussed below in section 4.4.

Based on the effective redox diffusivities of 10⁻¹⁰ to 10⁻⁹ m²s⁻¹ determined by (Magnien et al., 2008) for pyroxene melts in the high *T* region relevant to our study, characteristic times for 99% equilibration of 7 to 65 minutes result, for a sample radius of 1.25 mm (cf. XANES pre-edges measured within 2 minutes,

diffraction patterns in 5 to 20 minutes). We do not expect the equilibration of the melts in our study with the surrounding gas to be diffusion-limited, on account of the observed 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. Indeed, molten Fe_2SiO_4 at 1573 K has a low viscosity of about 0.06 Pa s (Shiraishi et al., 1978) and Schmidt numbers for the melt are therefore of order $Sc \approx 10^4$ to 10^5 , such that viscous transport is expected to strongly dominate over diffusive transport. The viscous flow is driven by the levitation gas jet, which has a velocity through the nozzle orifice of order 10 m s^{-1} , and 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). Reynolds numbers for the melt are therefore of order $Re \approx 10^{-1}$ to 10^0 , implying laminar flow, devoid of turbulent mixing. Nonetheless, it is worth considering the implications of minute timescale equilibration on the diffraction measurements: Any effect is diminished because these were made either i) in CO-CO₂ buffers; ii) at higher T where relaxation is more rapid; and iii) the entire diffraction pattern represents an average over the length of the experiment, as opposed to XANES where the lower the spectral energy, the earlier during the measurement the intensity value is recorded. The only measurement similar to the XANES measurement in Ar:0.1%O₂ is the 132 keV (campaign 3) measurement in Ar, i.e. unbuffered atmosphere, and large T reduction prior to measurement. Here we rely on point iii) above and the longer measurement time of 20 minutes. Nonetheless, some influence of disequilibrium on the results cannot be ruled out and future work should involve the modeling of fluid flow in the context of aerodynamically levitated molten droplets and measurement of redox dynamics by time-resolved techniques (Ginder-Vogel et al., 2009).

4.4 Changes in structure and Fe oxidation state on melt-quenching

Upon quenching, gross structural changes are expected as the melt crystallizes to form an FMQ assemblage. Redox changes are also expected due to forced convection by the gas jet, given the estimated melt flow rates of mm s^{-1} to cm s^{-1} , mm sample size and quench interval of 1 to 2 s between blocking the heating laser and the pyrometric observation of recalescence signifying crystallization. Redox heterogeneity may therefore be present in samples quenched from homogeneous melts. The XANES data in Fig. 2 and Tables 2 and 3 show a shift in the pre-edge peaks to higher E upon melt-quenching. Such changes imply oxidation during melt-quenching, which appears to be supported by the Mössbauer measurements (Table 3, ESI Fig. S3) on the recovered solids which show average $\text{Fe}^{3+}/\Sigma\text{Fe}$ larger than those derived for the melts from XANES spectroscopy. If the melts are mixed sufficiently rapidly to allow partial equilibration with the atmosphere *during rapid quenching* down to the recalescence temperatures (Table 3), then some oxidation is expected in the O₂ rich mixtures, Table 6, as observed. However, for Ar:(CO-CO₂) mixtures, the expected changes are almost negligible (Table 6) due to the buffering gas phase equilibrium, whilst the observed oxidation appears to be large. A possible explanation for this is differential local structural changes about Fe^{2+} and Fe^{3+} . In the reduced melt the average n_{FeO} is low, about 4.4. Upon quenching, the melt crystallizes, forming mostly fayalite, and some magnetite and quartz (ESI Fig. S2). The solid assemblage then has all Fe^{2+} in octahedral environments, but the Fe^{3+} in magnetite is split approximately evenly between tetrahedral and octahedral sites, with average $n_{\text{FeO}} = 5$. Assuming the average n_{FeO} for Fe^{2+} and Fe^{3+} are initially similar in

the melt, crystallization causes larger increases in n_{FeO} for Fe^{2+} than for Fe^{3+} , and as such, the portion of the pre-edge feature arising from Fe^{2+} reduces in area more than that for Fe^{3+} . The result is a shift in pre-edge peak centroid to higher energy due to structural changes, *independent of* any oxidation. A similar argument has been made by (Métrich et al., 2006) for the changes observed during melt quenching to glass of a hydrous peralkaline rhyolitic inclusion. Whilst this goes toward explaining the XANES observations, it does not account for the apparent oxidation during quenching (in Ar:(CO-CO₂)) implied by comparison of the Mössbauer $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the solid (Table 3) to the XANES $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the melt (Table 2).

We note that measurements on the recovered polycrystalline solids differ somewhat between those made on the bead in the levitator nozzle in fluorescence mode, and those made on the finely powdered sample in transmission mode (Fig. 2), at least in the two more reducing gas mixtures. The fluorescence measurements are subject to the inhomogeneity of the samples which consist of quartz, fayalite, and magnetite crystals (ESI Fig. S2 and S3), as well as self-absorption effects associated with any changes in sample size and shape upon crystallization (e.g. non-sphericity and roughness), and furthermore probe only the surface $\approx 50\ \mu\text{m}$. The transmission measurements on the other hand should represent an average over the sample volume, free from any self-absorption effect. The discrepancies between fluorescence-from-bead and powder transmission measurements for the Ar:0.1%O₂ and 88CO₂:12CO atmosphere measurements may however arise from the fact that they were made 8 months later than the rest of the measurements, allowing for possible oxidation over time. It is also possible that the grinding of the samples in air prior to measurement induced oxidation, but this is deemed unlikely as it does not appear to have affected the Mössbauer measurements as dramatically (they agree more closely with the fluorescence-from-bead measurements).

Taken as a whole, the results highlight the fact that the oxidation state of any multivalent element, even within a rapidly quenched solid, will not represent that of the melt if any stirring mechanism exists capable of driving the redox reaction towards equilibrium on short timescales comparable with that defined by the cooling rate. Such effects are largest under conditions similar to those of our experiments e.g. low viscosity melts of small volume (high surface area), under forced convection conditions (flow induced by shear forces arising from the gas jet-melt surface interaction). These conditions may be similar to hot ultramafic komatiitic eruptions dominant during the Archean (Berry et al., 2008; Huppert and Sparks, 1985), and for iron-rich compositions found more commonly on the moon and Mars (Chevrel et al., 2013). These effects on iron-rich lunar and Martian compositions may have important implications for *in-situ* resource utilization for space exploration (Curreri et al., 2006; Vai et al., 2010). On the other hand, evidence suggests that oxidation state is indeed 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).

4.5 Comparison to Mg₂SiO₄ liquid and glass

Mg-O coordination in molten Mg₂SiO₄ (2300 K, ambient pressure) has been reported to be $n_{\text{MgO}} = 5.1(2)$ (Wilding et al., 2010), similar to the value of about $n_{\text{MgO}} = 5.0(1)$ in the corresponding glass (Kohara et al., 2004; Wilding et al., 2010). Both of these values are higher than n_{FeO} measured herein for any of the

Fe₂SiO_{4+x} melts, and in particular the value $n_{\text{FeO}} = 4.4(1)$ inferred for the ferrous end-member, Fe₂SiO₄ (Fig. 6a). This lack of isomorphism between olivine *liquid* endmembers has implications for liquids along the Mg₂SiO₄–Fe₂SiO₄ join. Although there is far less constraint on the local structure of a cation doped into a liquid, as opposed to a crystal structure, the bulk liquid structure can nonetheless exert influence on the dopant (Kushiro and Mysen, 2002). If Fe ions doped into Mg₂SiO₄ liquid have any affinity for the sites of the host divalent cations, then one would expect an increase in Fe-O coordination in Mg rich olivine melts, as compared to the pure Fe endmember. Similarly the converse would be true for Mg in Fe rich molten olivines.

There is some evidence for a similar effect in ternary SiO₂ rich glasses, M₍₂₎O–M'O–SiO₂, doped with 0.2 to 2.0 wt.% levels of iron oxide (Farges et al., 2004). The data (Farges et al., 2004) indicate an apparent tendency toward higher Fe²⁺–O coordination where M, M' = Na, Mg or Ca, Mg, as compared to Mg free glasses. This effect can also be seen in MD simulations of complex iron-bearing silicate melts (Guillot and Sator, 2007) where n_{FeO} tends to be larger (and similar to n_{MgO}) when Mg is present and is greater than or comparable to Fe²⁺ content.

4.6 Implications for the properties of iron-rich silicate melts

Molten Fe₂SiO₄ at 1573 K has a low viscosity (η) of about 0.06 Pa s (Shiraishi et al., 1978), which is similar to those measured for highly inviscid, carbonatite forming, carbonate melts (Jones et al., 2013), and only a factor of about 60 times that of ambient water. Such low viscosities are also possible for hot komatiitic magmas (Huppert and Sparks, 1985). For Fe₂SiO_{4+x}, as Fe³⁺/ΣFe increases, viscosity has been shown to decrease modestly (Kaiura et al., 1977), which is the opposite trend to that observed in polymerized silicate melts (Dingwell, 1991). The present results do not show *strong* changes in Fe-O coordination over the Fe³⁺/ΣFe range studied. Therefore the effect of adding oxygen to the fayalite composition (O/Si = 4), inevitably as mobile O_{Fe} ions (not bonded to silicon, since O/Si > 4), likely decreases the viscosity to a greater extent than the formation of stronger Fe³⁺–O bonds increases it. It is worth noting that despite an anomalous local maximum in viscosity as a function of SiO₂ content at the fayalite composition (Shiraishi et al., 1978), and the recently measured anomalous (for a depolymerized melt) decrease in molten fayalite viscosity with pressure (P) (Spice et al., 2015), the dependencies of η on $p(\text{O}_2)$, T and P are all weak. This means that fayalitic melts maintain very low η over a large parameter space. To the extent that fayalitic melts can be considered a model system for iron-rich melts produced during differentiation of tholeiitic magmas, either by crystallization or liquid-liquid immiscibility (Jakobsen et al., 2005; McBirney and Naslund, 1990; Scoon and Mitchell, 1994), then such liquids can be expected to maintain their propensity to form intrusions and accelerate the differentiation processes at a wide range of depths and conditions. However, as discussed above, the local structure about Fe is sensitive to the melt composition. In particular the coordination of ferric iron tends to be lowered in the presence of heavy alkali cations, and this means that in natural iron-rich melts, viscosity may be somewhat more sensitive to intensive variables such as $p(\text{O}_2)$, T and P . For example, the viscosity variations with Fe³⁺/ΣFe are larger in alkali-, compared to alkaline earth-iron silicate melts (Dingwell, 1991; Dingwell and Virgo, 1987).

5. Conclusions

The local structure of fayalitic melts along the Fe_2SiO_4 – Fe_2SiO_5 join have been studied as a function of Fe^{3+} content using an aerodynamic levitation furnace and a combination of high-energy x-ray diffraction and Fe K-edge XANES spectroscopy. Iron occupies sites with low oxygen coordination numbers of $4.4(2) < n_{\text{FeO}} < 4.7(1)$, with the higher values obtained for higher $\text{Fe}^{3+}/\Sigma\text{Fe}$. There is limited evidence for a linear trend $n_{\text{FeO}}(x) = 4.46(3) + 0.4(1)x$, where $x = \text{Fe}^{3+}/\Sigma\text{Fe}$. These observations suggest that Fe^{2+} , and presumably Mg^{2+} etc., are less efficient at stabilizing tetrahedral Fe^{3+} as compared to (particularly the larger) monovalent alkali cations. Mean Fe-O bond lengths lie close to $2.06 \text{ \AA}$, as expected for n_{FeO} close to 5, with individual values displaying the influences of thermal expansion, variable Fe field strength and Fe-O coordination. Fe^{3+} contents estimated directly from the pre-edge peaks of Fe K-edge XANES spectra varied between $15(1) < x < 40(2) \%$. These agreed in some cases with semi-empirical calculations, with some notable discrepancies which were discussed in the context of the Fe redox equilibrium and limitations in both the semi-empirical thermodynamic models and the calibrations used to derive oxidation state from XANES spectra. Although equilibrium is expected to be established rapidly in our experiments due to levitation gas jet induced mixing, both measurement of the kinetics with suitable time-resolved techniques (Ginder-Vogel et al., 2009), and modelling of fluid flow within aerodynamically levitated droplets would be beneficial, as has been demonstrated in the context of electromagnetically and electrostatically levitated droplets (Hyers, 2005; Hyers et al., 2004). Comparison of *in-situ* XANES estimates of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the melts to those of the quenched solids obtained from XANES as well as Mössbauer spectroscopy indicate rapid oxidation during cooling, enabled by stirring of the melt by the levitation gas jet. As such, the oxidation state of hot komatiitic and iron-rich lunar and Martian melts may not be retained, even during rapid cooling, as is the case for cooler basaltic and more silicic magmas. The modest dependence of Fe-O coordination on $\text{Fe}^{3+}/\Sigma\text{Fe}$ in fayalitic melts results in a weak dependence of viscosity on $p(\text{O}_2)$, which, combined with the similarly weak dependencies of viscosity on pressure and temperature, means that fayalitic and other depolymerized iron-rich melts maintain their propensity to form intrusions and accelerate differentiation processes at a wide range of conditions and depths. This is in contrast to alkali bearing, more polymerized melts, which show stronger dependence on $p(\text{O}_2)$.

Acknowledgements

We thank Dr. Jon Wade, Oxford University Earth Sciences Department for assistance with electron microprobe analysis. We thank Dr. James Drewitt for helpful discussions regarding the x-ray structure factor of molten fayalite and access to numerical data (Drewitt et al., 2013). Dr. Robert Mayanovic, Dr. Mahaling Balasubramanian and Dr. Matthew Newville are thanked for helpful preliminary discussion regarding XANES measurements on levitated droplets, and Dr. M. Wilke, H. L. Zhang and Prof. M. M. Hirschmann for helpful correspondence. Dr. Mahaling Balasubramanian is also thanked for provision of the iron K-edge XANES spectrum for $\alpha\text{-Fe}_2\text{O}_3$. Thanks to Prof. D. H. Lindsley for provision of crystalline fayalite, and W. R. Woerner and A. Whale for help with preliminary experiments. Thanks also to Rick Spence, Douglas Robinson and Altug Hasozbek for technical support and useful discussions, and to M. J. Toplis (editor), Roman Botcharnikov (reviewer) and two anonymous reviewers for helpful suggestions leading to significant improvement of the manuscript. Work was supported by U.S. Department of Energy (DOE) under grant number SBIR DE-SC0007564 (OLGA, AT, SS, RW) and the

U.S. DOE, office of Basic Energy Sciences (BES), grant BES DE-FG02-09ER46650 (LBS, LL and JBP). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. We acknowledge support from the Center for Laser Applications and the University of Tennessee Space institute (CEJ, JAJ, H-YH).

References

- Alderman, O.L.G., Ferlat, G., Baroni, A., Salanne, M., Micoulaut, M., Benmore, C.J., Lin, A., Tamalonis, A. and Weber, J.K.R. (2015) Liquid B_2O_3 up to 1700K: X-ray Diffraction and Boroxol Ring Dissolution. *J. Phys.: Condens. Matter* **27**, 455104.
- Alderman, O.L.G., Liska, M., Machacek, J., Benmore, C.J., Lin, A., Tamalonis, A. and Weber, J.K.R. (2016) Temperature-Driven Structural Transitions in Molten Sodium Borates $Na_2O-B_2O_3$: X-ray Diffraction, Thermodynamic Modelling and Implications for Topological Constraint Theory. *J. Phys. Chem. C* **120**, 553-560.
- Alderman, O.L.G., Skinner, L.B., Benmore, C.J., Tamalonis, A. and Weber, J.K.R. (2014) Structure of Molten Titanium Dioxide. *Phys. Rev. B* **90**, 094204.
- Barin, I., Sauert, F., Schultze-Rhonhof, E. and Sheng, W.S. (1993) Thermochemical data of pure substances. VCH Weinheim.
- Bendert, J., Blodgett, M. and Kelton, K. (2013) Calculation of absorption and secondary scattering of X-rays by spherical amorphous materials in an asymmetric transmission geometry. *Acta Crystallogr. A* **69**, 131-139.
- Benmore, C.J., Weber, J.K.R., Wilding, M.C., Du, J. and Parise, J.B. (2010) Temperature-dependent structural heterogeneity in calcium silicate liquids. *Phys. Rev. B* **82**, 224202.
- Berry, A.J., Danyushevsky, L.V., O'Neill, H.S.C., Newville, M. and Sutton, S.R. (2008) Oxidation state of iron in komatiitic melt inclusions indicates hot Archaean mantle. *Nature* **455**, 960-963.
- Berry, A.J., O'Neill, H.S.C., Jayasuriya, K.D., Campbell, S.J. and Foran, G.J. (2003) XANES calibrations for the oxidation state of iron in a silicate glass. *Am. Mineral.* **88**, 967-977.
- Boubnov, A., Lichtenberg, H., Mangold, S. and Grunwaldt, J.-D. (2015) Identification of the iron oxidation state and coordination geometry in iron oxide- and zeolite-based catalysts using pre-edge XAS analysis. *J. Synchrotron Radiat.* **22**, 410-426.
- Bowen, N.L. and Schairer, J.F. (1932) The system, $FeO-SiO_2$. *Am. J. Sci.*, 177-213.
- Brown, I.D. and Altermatt, D. (1985) Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database. *Acta Crystallogr.* **B41**, 244-247.
- Capron, M., Florian, P., Fayon, F., Trumeau, D., Hennet, L., Gaihlanou, M., Thiaudière, D., Landron, C., Douy, A. and Massiot, D. (2001) Local structure and dynamics of high temperature $SrO-Al_2O_3$ liquids studied by ^{27}Al NMR and Sr K-edge XAS spectroscopy. *J. Non-Cryst. Solids* **293**, 496-501.
- Chevrel, M.O., Giordano, D., Potuzak, M., Courtial, P. and Dingwell, D.B. (2013) Physical properties of $CaAl_2Si_2O_8-CaMgSi_2O_6-FeO-Fe_2O_3$ melts: Analogues for extra-terrestrial basalt. *Chem. Geol.* **346**, 93-105.
- Cottrell, E. and Kelley, K.A. (2011) The oxidation state of Fe in MORB glasses and the oxygen fugacity of the upper mantle. *Earth. Planet. Sci. Lett.* **305**, 270-282.
- Cottrell, E., Kelley, K.A., Lanzirotti, A. and Fischer, R.A. (2009) High-precision determination of iron oxidation state in silicate glasses using XANES. *Chem. Geol.* **268**, 167-179.
- Curreri, P.A., Ethridge, E.C., Hudson, S.B., Miller, T.Y., Grugel, R.N., Sen, S. and Sadoway, D.R. (2006) Process Demonstration For Lunar In Situ Resource Utilization—Molten Oxide Electrolysis. *NASA Marshall Space Flight Center. MSFC Independent Research and Development Project.*

849 Darken, L.S. and Gurry, R.W. (1945) The system iron-oxygen. I. The wüstite field and related equilibria. *J.*
850 *Am. Chem. Soc.* **67**, 1398-1412.

851 Darken, L.S. and Gurry, R.W. (1946) The System Iron—Oxygen. II. Equilibrium and Thermodynamics of
852 Liquid Oxide and Other Phases. *J. Am. Chem. Soc.* **68**, 798-816.

853 Dingwell, D.B. (1991) Redox viscometry of some Fe-bearing silicate melts. *Am. Mineral.*, 1560-1562.

854 Dingwell, D.B. and Virgo, D. (1987) The effect of oxidation state on the viscosity of melts in the system
855 $\text{Na}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$. *Geochim. Cosmochim. Ac.* **51**, 195-205.

856 Drewitt, J.W., Sanloup, C., Bytchkov, A., Brassamin, S. and Hennet, L. (2013) Structure of $(\text{Fe}_x\text{Ca}_{1-x})\text{O}_y(\text{SiO}_2)_{1-y}$ liquids and glasses from high-energy x-ray diffraction: Implications for the structure of
857 natural basaltic magmas. *Phys. Rev. B* **87**, 224201.

858 Drewitt, J.W.E., Hennet, L., Zeidler, A., Jahn, S., Salmon, P.S., Neuville, D.R. and Fischer, H.E. (2012)
860 Structural Transformations on Vitrification in the Fragile Glass-Forming System CaAl_2O_4 . *Phys. Rev. Lett.*
861 **109**, 235501.

862 Ettler, V., Johan, Z., Zavřel, J., Selmi Wallisová, M., Mihaljevič, M. and Šebek, O. (2015) Slag remains from
863 the Na Slupi site (Prague, Czech Republic): evidence for early medieval non-ferrous metal smelting. *J.*
864 *Archaeol. Sci.* **53**, 72-83.

865 Farges, F., Lefrère, Y., Rossano, S., Berthereau, A., Calas, G. and Brown Jr, G.E. (2004) The effect of redox
866 state on the local structural environment of iron in silicate glasses: a combined XAFS spectroscopy,
867 molecular dynamics, and bond valence study. *J. Non-Cryst. Solids* **344**, 176-188.

868 Fischer, H.E., Barnes, A.C. and Salmon, P.S. (2006) Neutron and x-ray diffraction studies of liquids and
869 glasses. *Rep Prog Phys* **69**, 233-299.

870 Frost, B.R., Lindsley, D.H. and Andersen, D.J. (1988) Fe-Ti oxide-silicate equilibria; assemblages with
871 fayalitic olivine. *Am. Mineral.* **73**, 727-740.

872 Frost, D.J. and McCammon, C.A. (2008) The redox state of Earth's mantle. *Annu. Rev. Earth Planet. Sci.*
873 **36**, 389-420.

874 Ginder-Vogel, M., Landrot, G., Fischel, J.S. and Sparks, D.L. (2009) Quantification of rapid environmental
875 redox processes with quick-scanning x-ray absorption spectroscopy (Q-XAS). *Proc. Natl. Acad. Sci. USA*
876 **106**, 16124-16128.

877 Glatzel, P., Sikora, M. and Fernandez-Garcia, M. (2009) Resonant X-ray spectroscopy to study K
878 absorption pre-edges in 3d transition metal compounds. *Eur. Phys. J. Spec. Top.* **169**, 207-214.

879 Gorai, B., Jana, R.K. and Premchand (2003) Characteristics and utilisation of copper slag—a review.
880 *Resour. Conserv. Recy.* **39**, 299-313.

881 Guillot, B. and Sator, N. (2007) A computer simulation study of natural silicate melts. Part I: Low
882 pressure properties. *Geochim. Cosmochim. Ac.* **71**, 1249-1265.

883 Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N. and Hausermann, D. (1996) Two-dimensional
884 detector software: From real detector to idealised image or two-theta scan. *High Pressure Res.* **14**, 235-
885 248.

886 Hannon, A.C. (2016) Bonding and structure in network glasses. *J. Non-Cryst. Solids* **451**, 56-67.

887 Haskell, D. (1999) FLUO: Correcting XANES for Self-Absorption in Fluorescence Measurements. *Computer*
888 *program and documentation [online]. Available from*
889 <http://www.aps.anl.gov/xfd/people/haskell/fluo.html> (accessed January 4, 2009).

890 Hennet, L., Landron, C., Berthet, P., Coutures, J.-P., Jenkins, T., Aletru, C. and Greaves, N. (1999) X-Ray
891 Diffraction and Near Edge Studies of Iron Oxides and Alumina at High Temperatures Using Aerodynamic
892 Levitation and Laser Heating. *Jpn. J. Appl. Phys.* **38**, 115-117.

893 Holland, D., Mekki, A., Gee, I.A., McConville, C.F., Johnson, J.A., Johnson, C.E., Appleyard, P. and Thomas,
894 M. (1999) The structure of sodium iron silicate glass - a multi-technique approach. *J. Non-Cryst. Solids*
895 **253**, 192-202.

896 Huppert, H.E. and Sparks, R.S.J. (1985) Komatiites I: Eruption and flow. *J. Petrol.* **26**, 694-725.

897 Hyers, R.W. (2005) Fluid flow effects in levitated droplets. *Meas. Sci. Technol.* **16**, 394.
 898 Hyers, R.W., Matson, D.M., Kelton, K.F. and Rogers, J.R. (2004) Convection in Containerless Processing.
 899 *Ann. N.Y. Acad. Sci.* **1027**, 474-494.
 900 Jackson, W.E., de Leon, J.M., Brown, G.E., Waychunas, G.A., Conradson, S.D. and Combes, J.-M. (1993)
 901 High-Temperature XAS Study of Fe₂SiO₄ Liquid: Reduced Coordination of Ferrous Iron. *Science* **262**, 229-
 902 233.
 903 Jackson, W.E., Farges, F., Yeager, M., Mabrouk, P.A., Rossano, S., Waychunas, G.A., Solomon, E.I. and
 904 Brown Jr, G.E. (2005) Multi-spectroscopic study of Fe(II) in silicate glasses: Implications for the
 905 coordination environment of Fe(II) in silicate melts. *Geochim. Cosmochim. Ac.* **69**, 4315-4332.
 906 Jakobsen, J.K., Veksler, I., Tegner, C. and Brooks, C.K. (2005) Immiscible iron-and silica-rich melts in
 907 basalt petrogenesis documented in the Skaergaard intrusion. *Geo* **33**, 885-888.
 908 Jayasuriya, K.D., O'Neill, H.S.C., Berry, A.J. and Campbell, S.J. (2004) A Mössbauer study of the oxidation
 909 state of Fe in silicate melts. *Am. Mineral.* **89**, 1597-1609.
 910 Jones, A.P., Genge, M. and Carmody, L. (2013) Carbonate melts and carbonatites. *Rev. Mineral.*
 911 *Geochem.* **75**, 289-322.
 912 Kaiura, G., Toguri, J. and Marchant, G. (1977) Viscosity of fayalite-based slags. *Can. Metall. Quart.* **16**,
 913 156-160.
 914 Keen, D.A. (2001) A comparison of various commonly used correlation functions for describing total
 915 scattering. *J. Appl. Cryst.* **34**, 172-177.
 916 Knipping, J.L., Behrens, H., Wilke, M., Goettlicher, J. and Stabile, P. (2015) Effect of oxygen fugacity on
 917 the coordination and oxidation state of iron in alkali bearing silicate melts. *Chem. Geol.* **411**, 143-154.
 918 Kohara, S., Suzuya, K., Takeuchi, K., Loong, C.K., Grimsditch, M., Weber, J.K.R., Tangeman, J.A. and Key,
 919 T.S. (2004) Glass formation at the limit of insufficient network formers. *Science* **303**, 1649-1652.
 920 Kramar, S., Tratnik, V., Hrovatin, I.M., Mladenović, A., Pristacz, H. and Rogan Šmuc, N. (2015)
 921 Mineralogical and Chemical Characterization of Roman Slag from the Archaeological Site of Castra
 922 (Ajdovščina, Slovenia). *Archaeometry* **57**, 704-719.
 923 Krause, M.O. and Oliver, J. (1979) Natural Widths of Atomic K and L Levels, K α X-ray Lines and Several
 924 KLL Auger Lines. *J. Phys. Chem. Ref. Data* **8**, 329-338.
 925 Kress, V.C. and Carmichael, I.S. (1991) The compressibility of silicate liquids containing Fe₂O₃ and the
 926 effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contrib.*
 927 *Mineral. Petr.* **108**, 82-92.
 928 Kushiro, I. and Mysen, B.O. (2002) A possible effect of melt structure on the Mg-Fe²⁺ partitioning
 929 between olivine and melt. *Geochim. Cosmochim. Ac.* **66**, 2267-2272.
 930 Landron, C., Hennet, L. and Thiaudiere, D. (2001) Combining measurements of synchrotron radiation
 931 and neutrons from liquids at high temperature. *Anal. Sci.* **17**, i165.
 932 Landron, C., Hennet, L., Thiaudiere, D., Price, D.L. and Greaves, G.N. (2003) Structure of liquid oxides at
 933 very high temperatures. *Nucl. Instrum. Meth. B* **199**, 481-488.
 934 Magnien, V., Neuville, D.R., Cormier, L., Roux, J., Hazemann, J.L., de Ligny, D., Pascarelli, S., Vickridge, I.,
 935 Pinet, O. and Richet, P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The
 936 effects of temperature and alkali cations. *Geochim. Cosmochim. Ac.* **72**, 2157-2168.
 937 Majerus, O., Cormier, L., Calas, G. and Beuneu, B. (2003) Temperature-Induced Boron Coordination
 938 Change in Alkali Borate Glasses and Melts. *Phys. Rev. B* **67**, 024210.
 939 McBirney, A.R. and Naslund, H.R. (1990) The differentiation of the Skaergaard Intrusion. *Contrib.*
 940 *Mineral. Petr.* **104**, 235-240.
 941 McCammon, C.A., Frost, D.J., Smyth, J.R., Laustsen, H.M.S., Kawamoto, T., Ross, N.L. and Van Aken, P.A.
 942 (2004) Oxidation state of iron in hydrous mantle phases: implications for subduction and mantle oxygen
 943 fugacity. *Phys. Earth. Planet. In.* **143**, 157-169.
 944 McSween, H.Y. (2015) Petrology on Mars. *Am. Mineral.* **100**, 2380-2395.

945 Métrich, N., Susini, J., Foy, E., Farges, F., Massare, D., Sylla, L., Lequien, S. and Bonnin-Mosbah, M. (2006)
 946 Redox state of iron in peralkaline rhyolitic glass/melt: X-ray absorption micro-spectroscopy experiments
 947 at high temperature. *Chem. Geol.* **231**, 350-363.
 948 Muan, A. (1955) Phase equilibria in the system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$. *J. Met.* **7**, 965-976.
 949 Muñoz Ramo, D. and Stixrude, L. (2014) Spin crossover in Fe_2SiO_4 liquid at high pressure. *Geophys. Res.*
 950 *Lett.* **41**, 4512-4518.
 951 Mysen, B.O. (2006) The structural behavior of ferric and ferrous iron in aluminosilicate glass near meta-
 952 aluminosilicate joins. *Geochim. Cosmochim. Ac.* **70**, 2337-2353.
 953 Mysen, B.O., Seifert, F. and Virgo, D. (1980) Structure and Redox Equilibria of Iron-Bearing Silicate Melts.
 954 *Am. Mineral.* **65**, 867-884.
 955 Mysen, B.O., Virgo, D., Neumann, E.-R. and Seifert, F.A. (1985a) Redox equilibria and the structural
 956 states of ferric and ferrous iron in melts in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe-O}$; relationships between
 957 redox equilibria, melt structure and liquidus phase equilibria. *Am. Mineral.* **70**, 317-331.
 958 Mysen, B.O., Virgo, D., Scarfe, C.M. and Cronin, D. (1985b) Viscosity and structure of iron-and aluminum-
 959 bearing calcium silicate melts at 1 atm. *Am. Mineral.* **70**, 487-498.
 960 Mysen, B.O., Virgo, D. and Seifert, F.A. (1984) Redox Equilibria of Iron in Alkaline-Earth Silicate Melts -
 961 Relationships between Melt Structure, Oxygen Fugacity, Temperature and Properties of Iron-Bearing
 962 Silicate Liquids. *Am. Mineral.* **69**, 834-847.
 963 Newville, M. (2001) IFEFFIT: Interactive XAFS Analysis and FEFF Fitting. *J. Synchrotron Radiat.* **8**, 322-324.
 964 Phillips, B. and Muan, A. (1959) Phase Equilibria in the System $\text{CaO-Iron Oxide-SiO}_2$, in Air. *J. Am. Ceram.*
 965 *Soc.* **42**, 413-423.
 966 Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-ray Absorption
 967 Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537-541.
 968 Roskosz, M., Toplis, M.J., Neuville, D.R. and Mysen, B.O. (2008) Quantification of the kinetics of iron
 969 oxidation in silicate melts using Raman spectroscopy and assessment of the role of oxygen diffusion.
 970 *Am. Mineral.* **93**, 1749-1759.
 971 Rossano, S., Ramos, A., Delaye, J.-M., Creux, S., Filipponi, A., Brouder, C. and Calas, G. (2000a) EXAFS and
 972 Molecular Dynamics combined study of CaO-FeO-2SiO_2 glass. New insight into site significance in
 973 silicate glasses. *Europhys. Lett.* **49**, 597.
 974 Rossano, S., Ramos, A.Y. and Delaye, J.M. (2000b) Environment of ferrous iron in $\text{CaFeSi}_2\text{O}_6$ glass;
 975 contributions of EXAFS and molecular dynamics. *J. Non-Cryst. Solids* **273**, 48-52.
 976 Sack, R., Carmichael, I., Rivers, M. and Ghiorso, M. (1980) Ferric-ferrous equilibria in natural silicate
 977 liquids at 1 bar. *Contrib. Mineral. Petr.* **75**, 369-376.
 978 Scoon, R.N. and Mitchell, A.A. (1994) Discordant Iron-Rich Ultramafic Pegmatites in the Bushveld
 979 Complex and their Relationship to Iron-Rich Intercumulus and Residual Liquids. *J. Petrol.* **35**, 881-917.
 980 Shearer, C.K., Aaron, P.M., Burger, P.V., Guan, Y., Bell, A.S. and Papike, J.J. (2013) Petrogenetic linkages
 981 among fO_2 , isotopic enrichments-depletions and crystallization history in Martian basalts. Evidence from
 982 the distribution of phosphorus in olivine megacrysts. *Geochim. Cosmochim. Ac.* **120**, 17-38.
 983 Shiraishi, Y., Ikeda, K., Tamura, A. and Saito, T. (1978) On the viscosity and density of the molten FeO-
 984 SiO_2 system. *T. Jpn. I. Met.* **19**, 264-274.
 985 Skinner, L.B., Barnes, A.C., Salmon, P.S., Fischer, H.E., Drewitt, J.W.E. and Honkimaki, V. (2012a)
 986 Structure and Triclustering in Ba-Al-O Glass. *Phys. Rev. B* **85**, 064201.
 987 Skinner, L.B., Barnes, A.C., Salmon, P.S., Hennet, L., Fischer, H.E., Benmore, C.J., Kohara, S., Weber,
 988 J.K.R., Bytchkov, A., Wilding, M.C., Parise, J.B., Farmer, T.O., Pozdnyakova, I., Tumber, S.K. and Ohara, K.
 989 (2013a) Joint diffraction and modeling approach to the structure of liquid alumina. *Phys. Rev. B* **87**,
 990 024201.
 991 Skinner, L.B., Benmore, C.J. and Parise, J.B. (2012b) Area detector corrections for high quality
 992 synchrotron X-ray structure factor measurements. *Nucl. Instrum. Meth. A* **662**, 61-70.

993 Skinner, L.B., Benmore, C.J., Weber, J.K.R., Du, J., Neuefeind, J., Tumber, S.K. and Parise, J.B. (2014a) Low
 994 cation coordination in oxide melts. *Phys. Rev. Lett.* **112**, 157801.
 995 Skinner, L.B., Benmore, C.J., Weber, J.K.R., Wilding, M.C., Tumber, S.K. and Parise, J.B. (2013b) A time
 996 resolved high energy x-ray diffraction study of cooling liquid SiO₂. *Phys. Chem. Chem. Phys.* **15**, 8566-
 997 8572.
 998 Skinner, L.B., Benmore, C.J., Weber, J.K.R., Williamson, M.A., Tamalonis, A., Hebden, A., Wiencek, T.,
 999 Alderman, O.L.G., Guthrie, M., Leibowitz, L. and Parise, J.B. (2014b) Molten uranium dioxide structure
 1000 and dynamics. *Science* **346**, 984-987.
 1001 Smyth, J.R. (1975) High temperature crystal chemistry of fayalite. *Am. Mineral.* **60**, 1092-1097.
 1002 Soper, A.K. and Barney, E.R. (2011) Extracting the pair distribution function from white-beam X-ray total
 1003 scattering data. *J. Appl. Cryst.* **44**, 714-726.
 1004 Spice, H., Sanloup, C., Cochain, B., de Grouchy, C. and Kono, Y. (2015) Viscosity of liquid fayalite up to 9
 1005 GPa. *Geochim. Cosmochim. Ac.* **148**, 219-227.
 1006 Thomas, C.W., Liu, Q., Agee, C.B., Asimow, P.D. and Lange, R.A. (2012) Multi-technique equation of state
 1007 for Fe₂SiO₄ melt and the density of Fe-bearing silicate melts from 0 to 161 GPa. *Journal of Geophysical*
 1008 *Research: Solid Earth (1978-2012)* **117**.
 1009 Tuff, J., Wade, J. and Wood, B.J. (2013) Volcanism on Mars controlled by early oxidation of the upper
 1010 mantle. *Nature* **498**, 342-345.
 1011 Turnock, A.C., Lindsley, D.H. and Grover, J.E. (1973) The synthesis and unit cell parameters of Ca-Mg-Fe
 1012 pyroxenes. *Am. Mineral.* **58**, 50-59.
 1013 Vai, A., Yurko, J., Wang, D. and Sadoway, D. (2010) Molten oxide electrolysis for lunar oxygen generation
 1014 using in situ resources. Minerals, Metals and Materials Society/AIME, 420 Commonwealth Dr., P. O. Box
 1015 430 Warrendale PA 15086 USA.
 1016 Wade, J. and Wood, B.J. (2005) Core formation and the oxidation state of the Earth. *Earth. Planet. Sci.*
 1017 *Lett.* **236**, 78-95.
 1018 Waseda, Y., Shiraishi, Y. and Toguri, J.M. (1980) The Structure of the Molten FeO-Fe₂O₃-SiO₂ System by
 1019 X-Ray-Diffraction. *T. Jpn. I. Met.* **21**, 51-62.
 1020 Waychunas, G.A., Brown, G.E., Ponader, C.W. and Jackson, W.E. (1988) Evidence from X-ray absorption
 1021 for network-forming Fe²⁺ in molten alkali silicates. *Nature* **332**, 251-253.
 1022 Weber, J.K.R., Felten, J.J. and Nordine, P.C. (1996) Laser Hearth Melt Processing of Ceramic Materials.
 1023 *Rev. Sci. Instrum.* **67**, 522-524.
 1024 Weber, J.K.R., Krishnan, S., Anderson, C.D. and Nordine, P.C. (1995) Spectral Absorption Coefficient of
 1025 Molten Aluminum Oxide from 0.385 to 0.780 μm. *J. Am. Ceram. Soc.* **78**, 583-587.
 1026 Weigel, C., Cormier, L., Calas, G., Galois, L. and Bowron, D.T. (2008a) Intermediate-range order in the
 1027 silicate network glasses NaFe_xAl_{1-x}Si₂O₆ (x=0, 0.5, 0.8, 1): A neutron diffraction and empirical potential
 1028 structure refinement modeling investigation. *Phys. Rev. B* **78**, 064202.
 1029 Weigel, C., Cormier, L., Calas, G., Galois, L. and Bowron, D.T. (2008b) Nature and distribution of iron
 1030 sites in a sodium silicate glass investigated by neutron diffraction and EPSR simulation. *J. Non-Cryst.*
 1031 *Solids* **354**, 5378-5385.
 1032 Weigel, C., Cormier, L., Galois, L., Calas, G., Bowron, D. and Beuneu, B. (2006) Determination of Fe³⁺
 1033 sites in a NaFeSi₂O₆ glass by neutron diffraction with isotopic substitution coupled with numerical
 1034 simulation. *Appl. Phys. Lett.* **89**, 141911.
 1035 Wilding, M.C., Benmore, C.J. and Weber, J.K.R. (2010) Changes in the local environment surrounding
 1036 magnesium ions in fragile MgO-SiO₂ liquids. *Europhys. Lett.* **89**, 26005.
 1037 Wilke, M. (2005) Fe in magma-An overview. *Ann. Geophys.* **48**, 609-617.
 1038 Wilke, M., Farges, F., Partzsch, G.M., Schmidt, C. and Behrens, H. (2007) Speciation of Fe in silicate
 1039 glasses and melts by in-situ XANES spectroscopy. *Am. Mineral.* **92**, 44-56.

Wilke, M., Farges, F., Petit, P.-E., Brown, G.E. and Martin, F. (2001) Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *Am. Mineral.* **86**, 714-730.
 Wilke, M., Partzsch, G.M., Bernhardt, R. and Lattard, D. (2005) Determination of the iron oxidation state in basaltic glasses using XANES at the K-edge. *Chem. Geol.* **220**, 143-161.
 Wood, B.J., Walter, M.J. and Wade, J. (2006) Accretion of the Earth and segregation of its core. *Nature* **441**, 825-833.
 Woodland, A. and Koch, M. (2003) Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth. Planet. Sci. Lett.* **214**, 295-310.
 Wright, A.C. (1994) Neutron-Scattering from Vitreous Silica .5. The Structure of Vitreous Silica - What Have We Learned from 60 Years of Diffraction Studies. *J. Non-Cryst. Solids* **179**, 84-115.
 Wright, A.C., Clarke, S.J., Howard, C.K., Bingham, P.A., Forder, S.D., Holland, D., Martlew, D. and Fischer, H.E. (2014) The environment of Fe²⁺/Fe³⁺ cations in a soda–lime–silica glass. *Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B-European Journal of Glass Science and Technology Part B* **55**, 243-252.
 Wright, A.C., Sinclair, R.N., Shaw, J.L., Haworth, R., Marasinghe, G.K. and Day, D.E. (2008) A neutron diffraction study of the structure of iron phosphate glasses. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* **49**, 1-7.
 Zhang, H.L., Hirschmann, M.M., Cottrell, E., Newville, M. and Lanzirotti, A. (2016) Structural environment of iron and accurate determination of Fe³⁺/ΣFe ratios in andesitic glasses by XANES and Mössbauer spectroscopy. *Chem. Geol.* **428**, 48-58.
 Zhang, H.L., Solheid, P.A., Lange, R.A., von der Handt, A. and Hirschmann, M.M. (2015a) Accurate determination of Fe³⁺/ΣFe of andesitic glass by Mössbauer spectroscopy. *Am. Mineral.* **100**, 1967-1977.
 Zhang, J., Qi, Y.-h., Yan, D.-l., Cheng, X.-l. and He, P. (2015b) Characteristics and Mechanism of Reduction and Smelting-separation Process of Copper Slag. *J. Iron Steel Res. Int.* **22**, 121-127.

Table 1: Transmission Fe K-edge XANES measurements for standard materials at room temperature. Results from peak fitting to the normalized isolated pre-edge peaks. Rows including full-width at half-maximum (FWHM) values correspond to individual peak parameters. Values in italics correspond to average centroid and total pre-peak areas reported in the literature, with references given in the final column.

Material	Fe ³⁺ /ΣFe ideal (%)	n _{FeO}	Centroid (eV) ± 0.1	FWHM (eV)	Intensity (eV)	Fe ³⁺ /ΣFe centroid (%)	Fe ³⁺ /ΣFe ratio (%)	Ref.
FeO (Wüstite)	0	6	7112.0		0.11(1)	1(3)	13(1)	This work
			7110.68	0.94	0.012			This work
			7112.15	2.18	0.098			This work
			<i>7112.45</i>		<i>0.0834</i>			(Wilke et al., 2001)
			<i>7112.26</i>		<i>0.108</i>			(Boubnov et al., 2015)
Fe ₃ O ₄ (Magnetite)	66.7	5.33	7112.5		0.17(2)	20(4)	21(1)	This work
			7112.60	1.70 ^c	0.159			This work
			7110.01	1.70 ^c	0.007			This work
			7114.72 ^b	1.70 ^c	0.038			This work
			<i>7112.92</i>		<i>0.212</i>			(Boubnov et al., 2015)
γ-Fe ₂ O ₃ (Maghemite)	100	5.25	7113.1		0.21(2)	58(9)	35(3)	This work
			7112.7	1.70 ^c	0.166			This work
			7114.8	1.70 ^c	0.044			This work
			7116.0	1.36 ^c	0.033			This work
			<i>7113.29</i>		<i>0.219</i>			(Boubnov et al., 2015)
α-Fe ₂ O ₃ (Hematite)	100	6	7113.4		0.13(1)	100(30) ^a	55(2)	This work
			7112.5	1.70 ^c	0.053			This work
			7114.0	1.70 ^c	0.076			This work
			7116.2 ^b	1.36 ^c	0.033			This work
			<i>7113.47</i>		<i>0.1236</i>			(Wilke et al., 2001)
Ferrihydrite	100	5.6	7112.9		0.15(1)	40(6)	37(3)	This work
			7112.90	1.97	0.148			This work
			7115.94 ^b	1.89	0.055			This work
			<i>7113.47</i>		<i>0.1193</i>			(Wilke et al., 2001)

a. Our quadratic equation fitted to Wilke et al.'s (Wilke et al., 2005) basalt glass data yields 100% Fe³⁺ at $E = 7113.37$ eV, albeit with large uncertainty due to the shallow gradient of the curve at high Fe³⁺. b. Peaks assumed to have non-local origin not included in averaged centroid or total pre-peak area sum. c. Fixed during fitting.

1076 Table 2: Conditions for Fe K-edge XANES measurements on molten $\text{Fe}_2\text{SiO}_{4+x}$, along with results from
1077 peak fitting to the normalized isolated pre-edge peaks.

Gas mix ^a	T (K)	$\log p(\text{O}_2)$	ΔFMQ	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%) ^b	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%) ^c	Centroid (eV) ± 0.1	FWHM (eV)	Intensity (eV)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^d (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio ^d (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^e (%)
50O ₂ :50Ar	1994(36)	-0.3	+3.5(2)	66(3)	70(2)	7112.9		0.18(4)	40(6)	40(2)	57(7)
						7111.56	1.27	0.027			
						7113.13	1.74	0.148			
Ar:0.1% O ₂	1557(33)	-3.0	+4.4(3)	76(3)	72(2)	7112.5		0.16(4)	20(4)	23(1)	31(6)
						7111.60	1.25	0.071			
						7113.18	1.41	0.092			
88CO ₂ :12CO	1560(20)	-9.4(2)	-2.1(3)	15(2)	20(3)	7112.4		0.12(3)	15(4)	15(1)	24(6)
						7111.45	1.08	0.041			
						7112.85	1.65	0.081			

1078 a. All CO₂-CO mixtures are 5 vol.% in argon. b. (Jayasuriya et al., 2004) (their equation 12). c. Based on
1079 (Darken and Gurry, 1946) (their Fig. 3B). d. (Wilke et al., 2005) calibration. e. (Knipping et al., 2015)
1080 calibration.

1081

1082 Table 3: Fe K-edge XANES measurements at room temperature on recovered Fe₂SiO_{4+x} beads, along
 1083 with results from peak fitting to the normalized isolated pre-edge peaks. Results from powder
 1084 transmission are italicized. Observed temperatures of recalcrescence (crystallization) are given, at which
 1085 $p(\text{O}_2)$ and $\text{Fe}^{3+}/\Sigma\text{Fe}$ were calculated.

Gas mix ^a	$T_{\text{Recalcrescence}}$ (K)	$\log p(\text{O}_2)$	ΔFMQ	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%) ^b	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Calc. (%) ^c	Centroid (eV) ± 0.1	FWHM (eV)	Intensity (eV)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^g (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio ^g (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ centroid ^h (%)	$\text{Fe}^{3+}/\Sigma\text{Fe}$ Mössbauer (%) ± 1
50O ₂ :50Ar	1660(20)	-0.3	+6.2(2)	87(1)	87(1)	7113.1 7112.02 7113.24 7115.36 ^d	 1.09 1.54 1.36	0.10(2) 0.012 0.090 0.0182	54(8)	56(2)	73(8)	70
50O ₂ :50Ar ^e	1660(20)	-0.3	+6.2(2)	87(1)	87(1)	7113.1 7112.88 7113.38 7115.37 ^d	 1.54 1.44 1.36	0.14(1) 0.074 0.065 0.026	55(8)	62(5)	75(8)	70
Ar:0.1% O ₂	1264(14)	-3	+8.2(2)	95(1)	91(1)	7112.6 7111.07 7113.02	 1.11 1.62	0.09(2) 0.019 0.075	26(5)	38(3)	39(7)	50
Ar:0.1% O ₂ ^e	1264(14)	-3	+8.2(2)	95(1)	91(1)	7113.2 7111.47 7113.32 7114.72 ^d _f	 0.71 1.52 1.70 ^f	0.10(1) 0.005 0.094 0.007	65(10)	66(6)	83(8)	50
88CO ₂ :12CO	1240(14)	-14.3(1)	-2.8(3)	13(2)	19(3)	7112.8 7110.99 7113.03 7114.91 ^d	 1.21 1.61 0.85 ^f	0.14(3) 0.019 0.120 0.009	33(5)	44(2)	48(7)	33
88CO ₂ :12CO ^e	1240(14)	-14.3(1)	-2.8(3)	13(2)	19(3)	7113.1 7111.45 7113.33	 0.85 1.59	0.08(1) 0.010 0.073	54(8)	56(5)	74(8)	33

1086 a. All CO₂-CO mixtures are 5 vol.% in argon. b. (Jayasuriya et al., 2004) (their equation 12). c. Based on
 1087 (Darken and Gurry, 1946) (their Fig. 3B). d. Peaks assumed to have non-local origin not included in
 1088 averaged centroid or total pre-peak area sum. e. Powder transmission measurements. Those for the
 1089 Ar:0.1%O₂ and 88CO₂:12CO atmospheres were made 8 months later than the rest of the measurements.
 1090 f. Fixed during fitting. g. (Wilke et al., 2005) calibration. h. (Knipping et al., 2015) calibration.

1091

Table 4: Conditions for high-energy x-ray diffraction measurements on molten $\text{Fe}_2\text{SiO}_{4+x}$, along with results from Fe-O peak fitting to $T(r)$. Weighted average Fe-O bond lengths and total Fe-O coordination numbers are given in bold type. Uncertainties are given in parentheses, and for the individual fitting parameters represent statistical (fitting) values only.

Gas mix ^a	T (K)	$\log p(\text{O}_2)$	ΔFMQ	Density (g cm ⁻³) ^b	Fe ³⁺ /ΣFe Calc. (%) ^c	Fe ³⁺ /ΣFe Calc. (%) ^d	r_{FeO} (Å)	$\langle u_{\text{FeO}}^2 \rangle^{1/2}$ (Å)	n_{FeO}
Campaign 3: $Q_{\text{max}} = 30.4 \text{ \AA}^{-1}$, 132 keV, Lorch									
Ar	1677(23)	$\lesssim -6$	+0.4(2)	3.71(1)	$\lesssim 32(2)$	$\lesssim 38(2)$	1.950(1)	0.125(1)	3.25(3)
							2.273(4)	0.113(5)	1.33(4)
							2.044(2)		4.58(8)
1CO ₂ :1CO	1624(21)	-10.4(2)	-3.7(3)	3.73(1)	7(1)	5(3)	1.952(1)	0.118(1)	3.06(3)
							2.262(4)	0.110(5)	1.37(4)
							2.048(2)		4.43(7)
Campaign 3: $Q_{\text{max}} = 30.4 \text{ \AA}^{-1}$, 132 keV, Step									
1CO ₂ :1CO	1624(21)	-10.4(2)	-3.7(3)	3.73(1)	7(1)	5(3)	1.930(4)	0.114(3)	2.84(8)
							2.218(5)	0.131(5)	1.65(5)
							2.036(3)		4.49(11)
Campaign 2: $Q_{\text{max}} = 22.1 \text{ \AA}^{-1}$, 100 keV, Lorch									
O ₂	2183(94)	0	+2.8(5)	3.57(3)	56(6)	63(5)	1.949(1)	0.143(1)	3.43(2)
							2.333(6)	0.117(6)	1.27(4)
							2.053(2)		4.70(13)
CO ₂	1751(48)	-3.9(2)	+1.7(5)	3.69(1)	47(6)	51(4)	1.971(1)	0.145(1)	3.62(3)
							2.349(5)	0.105(5)	1.12(4)
							2.060(2)		4.74(13)
2CO ₂ :1CO	1862(40)	-7.5(3)	-2.8(4)	3.66(1)	10(2)	9(6)	1.975(2)	0.143(2)	3.37(3)
							2.352(6)	0.107(5)	1.10(4)
							2.068(2)		4.47(9)
1CO ₂ :1CO ^e	1855(97)	-8.2(8)	-3.4(1.1)	3.66(3)	8(7)	3(22)	1.980(2)	0.142(1)	3.23(3)
							2.351(6)	0.109(5)	1.16(4)
							2.080(2)		4.39(19)
Campaign 1: $Q_{\text{max}} = 21.2 \text{ \AA}^{-1}$, 100 keV, Lorch									
Air	2094(55)	-0.68	+2.6(3)	3.60(2)	55(4)	60(3)	1.936(2)	0.115(2)	3.10(4)
							2.276(4)	0.107(5)	1.39(3)
							2.041(2)		4.50(10)
9CO ₂ :1CO	1641(29)	-8.3(3)	-1.8(4)	3.71(1)	16(3)	21(5)	1.973(2)	0.141(1)	3.44(3)
							2.351(4)	0.113(4)	1.10(3)
							2.065(2)		4.54(10)
1CO ₂ :9CO	1665(23)	-11.9(2)	-5.6(3)	3.72(1)	3.3(6)	-11(4)	1.978(2)	0.151(1)	3.55(3)
							2.381(5)	0.106(4)	1.01(3)
							2.067(2)		4.55(7)
Drewitt <i>et al.</i> (Drewitt et al., 2013), $Q_{\text{max}} = 26.45 \text{ \AA}^{-1}$, 100 keV, Cosine									
Ar	1623(30)	$\lesssim -6$	+0.7(4)	3.67(4)	$\lesssim 36(4)$	$\lesssim 41(3)$	1.93(1)	-	-
							2.20(2)	-	-
							-		4.8(2)
Fit to Drewitt <i>et al.</i> (Drewitt et al., 2013), $Q_{\text{max}} = 26.45 \text{ \AA}^{-1}$, 100 keV, Step									
Ar	1623(30)	$\lesssim -6$	+0.7(4)	3.72(1)	$\lesssim 36(4)$	$\lesssim 41(3)$	1.938(2)	0.102(2)	2.99(6)

2.222(2) 0.111(2) 2.18(3)
2.057(2) 5.17(12)

1096 a. All CO₂-CO mixtures are 5 vol.% in argon. b. Extrapolated from Shiraishi *et al.* (Shiraishi *et al.*, 1978).
 1097 c. (Jayasuriya *et al.*, 2004) (their equation 12). d. Based on (Darken and Gurry, 1946) (their Fig. 3B). e.
 1098 Very small Bragg peaks present.

1099

1100 Table 5: Si-O peak parameters extracted from the highest real-space resolution measurements on
 1101 molten Fe₂SiO_{4+x}, along with measurement conditions repeated from Table 4. $n_{\text{SiO}} = 4$ was fixed during
 1102 fitting.

Gas mix ^a	<i>T</i> (K)	log <i>p</i> (O ₂)	ΔFMQ	Density (g cm ⁻³) ^b	Fe ³⁺ /ΣFe Calc. (%) ^c	Fe ³⁺ /ΣFe Calc. (%) ^d	<i>r</i> _{SiO} (Å)	$\langle u_{\text{SiO}}^2 \rangle^{1/2}$ (Å)	<i>n</i> _{SiO}
<i>Q</i>_{max} = 30.4 Å⁻¹, 132 keV, Lorch									
Ar	1677(23)	≤ -6	+0.4(2)	3.71(1)	≤ 32(2)	≤ 38(2)	1.646(1)	0.088(1)	4
1CO ₂ :1CO	1624(21)	-10.4(2)	-3.7(3)	3.73(1)	7(1)	5(3)	1.646(1)	0.084(1)	4
<i>Q</i>_{max} = 30.4 Å⁻¹, 132 keV, Step									
1CO ₂ :1CO	1624(21)	-10.4(2)	-3.7(3)	3.73(1)	7(1)	5(3)	1.628(2)	0.061(2)	4
Drewitt <i>et al.</i> (Drewitt <i>et al.</i>, 2013), <i>Q</i>_{max} = 26.45 Å⁻¹, 100 keV, Cosine									
Ar	1623(30)	≤ -6	+0.7(4)	3.72(1)	≤ 36(4)	≤ 41(3)	1.64(1)	-	4.0(1)
Fit to Drewitt <i>et al.</i> (Drewitt <i>et al.</i>, 2013), <i>Q</i>_{max} = 26.45 Å⁻¹, 100 keV, Step									
Ar	1623(30)	≤ -6	+0.7(4)	3.72(1)	≤ 36(4)	≤ 41(3)	1.641(2)	0.057(2)	4

1103 a. All CO₂-CO mixtures are 5 vol.% in argon. b. Extrapolated from Shiraishi *et al.* (Shiraishi *et al.*, 1978).
 1104 c. (Jayasuriya *et al.*, 2004) (their equation 12). d. Based on (Darken and Gurry, 1946) (their Fig. 3B).

1105

1106 Table 6: Changes in Fe K-edge XANES pre-edge peak on quenching. Calculated ΔFe³⁺/ΣFe assume
 1107 equilibrium is maintained until crystallization.

Gas mix ^a	Δ Fe ³⁺ /ΣFe Calc. (%) ^c	Δ Fe ³⁺ /ΣFe Calc. (%) ^d	Δ Centroid (eV) ± 0.14	Δ Intensity (eV)	Δ Intensity (%)	Δ Fe ³⁺ /ΣFe centroid (%)	Δ Fe ³⁺ /ΣFe ratio (%)
50O ₂ :50Ar	+21(3)	+17(2)	+0.20	-0.07(5)	-42(28)	+13(10)	+16(3)
50O ₂ :50Ar ^b	+21(3)	+17(2)	+0.22	-0.04(4)	-21(24)	+15(10)	+22(5)
0.1% O ₂ in Ar	+19(3)	+19(2)	+0.13	-0.07(4)	-42(28)	+6(6)	+15(3)
0.1% O ₂ in Ar ^b	+19(3)	+19(2)	+0.73	-0.06(4)	-39(25)	+45(11)	+43(6)
88CO ₂ :12CO	-2 (3)	-1(4)	+0.55	+0.03(4)	+23(36)	+27(7)	+29(2)
88CO ₂ :12CO ^b	-2(3)	-1(4)	+0.72	-0.04(3)	-31(24)	+39(9)	+40(5)

1108 a. All CO₂-CO mixtures are 5 vol.% in argon. b. Refers to powder transmission measurement of the solid.
 1109 c. (Jayasuriya *et al.*, 2004) (their equation 12). d. Based on (Darken and Gurry, 1946) (their Fig. 3B).

1110

Figure 1: Fe K-edge XANES spectrum for molten $\text{Fe}_2\text{SiO}_{4+x}$ (1975(35) K) in an oxidizing atmosphere ($50\text{Ar}:50\text{O}_2$). 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 2: Isolated pre-edge features of the Fe K-edge XANES spectra of molten and quenched $\text{Fe}_2\text{SiO}_{4+x}$. Both experimental data (points) and fits (solid curves) are shown, with peaks assigned to non-local transitions shown by broken curves. Each plot compares the melt to the recovered quenched product measured as bulk bead and in powder transmission (shaded area curves), except for the lower right plot which compares spectra for three melts at different $f(\text{O}_2)$. See Tables 2 and 3. Vertical lines denote regions integrated over to extract the average Fe oxidation state by the ratio method of Wilke *et al.* (Wilke *et al.*, 2005). Note that the spectra for the solid (FMQ) beads may be affected by inhomogeneity and preferred orientation of crystallites, and also have larger uncertainties in their amplitudes owing to self-absorption effects of surface roughness and shape irregularity not present for the molten (spherical) beads, or for the transmission measurements.

Figure 3: Variogram after (Wilke et al., 2001; Wilke et al., 2005) showing data for molten $\text{Fe}_2\text{SiO}_{4+x}$ (Table 2) with ΔFMQ values adjacent (filled red circles). The open black circles are data for basaltic glasses from (Wilke et al., 2005). The reason that the three measurements are not ordered in centroid energy according to their ΔFMQ values is discussed in the text, but may also arise from the necessary extrapolation of the buffer equation well beyond its stated maximum temperature of 1473K (Frost et al., 1988).

Figure 4: Interference functions, $Q(S(Q) - 1)$, measured from molten $\text{Fe}_2\text{SiO}_{4+x}$ by high-energy x-ray diffraction. Refer to Table 4 and main text for full details. All $\text{CO}_2:\text{CO}$ mixtures at 5vol.% in Ar. Part a) compares measurements at different $f(\text{O}_2)$ and T , b) compares the low Q region to published data (Drewitt et al., 2013) and c) compares the Q -space manifestations of fits made to the short range peaks in r -space (Fig. 5) to the measured data.

Figure 5: a) $D(r)$ curves transformed from interference functions (O_2 , CO_2 , $2CO_2:1CO$) shown in Fig. 4a, with $Q_{\max} = 22.1 \text{ \AA}^{-1}$ and Lorch modification. b) The corresponding $T(r)$ at top. Offset by -1 is the $1CO:1CO_2$ measurement with $Q_{\max} = 30.4 \text{ \AA}^{-1}$ and with (black) and without (orange) Lorch modification. Offset by -2 is the $T(r)$ obtained by transforming the $S(Q)$ of Drewitt *et al.* (Drewitt *et al.*, 2013) with $Q_{\max} = 26.45 \text{ \AA}^{-1}$ and no modification (step function). The $1CO:1CO_2$ measurement with $Q_{\max} = 30.4 \text{ \AA}^{-1}$ and Lorch modification is shown again, offset by -3 along with the corresponding fitted real-space peaks ($n_{\text{SiO}} = 4$ and intratetrahedral O-O peak held fixed), their sum (dashed) and the residual (dash dot).

1154

1155

1156

Figure 6: a) Average Fe-O coordination numbers and b) average Fe-O bond lengths in molten $\text{Fe}_2\text{SiO}_{4+x}$ from high-energy x-ray diffraction (Table 4). Diamonds with points, $Q_{\text{max}} = 30.4 \text{ \AA}^{-1}$; circles, $Q_{\text{max}} = 21.2 \text{ \AA}^{-1}$; diamonds with crosses, $Q_{\text{max}} = 22.1 \text{ \AA}^{-1}$. In a) a linear fit to the data is shown ($N = 9$ points) along with a second fit ($N = 8$ points, steeper gradient) excluding the ‘air’ dataset which has the lowest statistical quality ($Q_{\text{max}} = 21.2 \text{ \AA}^{-1}$, Fig. 4a), and with 95% confidence bounds shown by the shaded area. Filled diamonds represent relevant minerals, as labelled. In b) comparison is made to bond-valence (Brown and Altermatt, 1985) derived r_{FeO} values at room temperature (broken lines), and estimated at high temperature (shaded bands, 1600 to 2200 K) using the Fe-O bond length thermal expansion coefficient derived from (Smyth, 1975), for crystalline fayalite. Each point in b) is labelled by the mean measurement temperature in Kelvin (see Table 4).

1167

1168 Figure 7: Illustrations of simple electrostatic bond-strength (EBS) sums at non-bridging oxygen sites (one
 1169 Si neighbor). a) $[\text{OSi}^{\text{IV}}\text{Fe}^{2+}_2]$ as proposed by (Jackson et al., 1993) for pure molten fayalite. b) Mixed iron
 1170 valence $[\text{OSi}^{\text{V}}\text{Fe}^{2+}\text{Fe}^{3+}]$ and c) $[\text{OSi}^{\text{IV}}\text{Fe}^{2+}\text{Fe}^{3+}]$, both with average Fe-O coordination numbers of 5. d)
 1171 Stabilization of tetrahedral Fe^{3+} by a large, low valence cation, potassium in this case, $[\text{OSi}^{\text{VIII}}\text{K}_2^+\text{Fe}^{3+}]$.
 1172 Note that $^{\text{VIII}}\text{K}_2^+$ may be replaced by divalent $^{\text{VIII}}\text{Ba}^{2+}$, whereas the smaller alkaline earths such as Mg^{2+} and
 1173 Ca^{2+} , as well as Fe^{2+} , tend to have lower coordination numbers and hence do not tend to stabilize $^{\text{IV}}\text{Fe}^{3+}$
 1174 as readily (see b) and c)).