THE EFFECT OF THE [Na/(Na+K)] RATIO ON Fe SPECIATION IN PHONOLITIC GLASSES

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Highlights

- By using Fe K-edge XAS spectra (both XANES and EXAFS), we determined the Fe geochemical role in phonolitic glasses.

- The effect of different alkalis [Na/(Na+K)] ratio on the Fe structural role has been investigated.

- The results are discussed in terms of the contrasting effects of T, fO2 and alkali ratio.

- The [Na/(Na+K)] ratio has a strong effect on the Fe^{3+}/(Fe^{2+} + Fe^{3+}) ratio.
The effect of the [Na/(Na+K)] ratio on Fe speciation in phonolitic glasses

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ABSTRACT

Natural iron-bearing sodic phonolitic melts represent an extreme compositional range of the effect of the [Na/(Na+K)] ratio on the geochemical behavior of Fe in volcanic systems. Yet phonolitic melts have not been well-investigated. The glasses studied here have been synthesized from liquids equilibrated over a range of oxygen fugacity conditions (log10(fO2) from -0.68 to -11) in order to elucidate the role of the alkali ratio in influencing the local environment around both divalent and trivalent Fe. In this study, the Fe K-edge XAS spectra (XANES and EXAFS) have been employed, in order to constrain the Fe structural role (oxidation state, coordination number, bond distances) in phonolitic glasses as a function of synthesis temperature (T), [Na/(Na+K)] ratio (= 0.0, 0.25, 0.5, 0.75, 1.0) and redox state.

We verify that at constant oxygen fugacity, the [Na/(Na+K)] ratio has a strong effect on the Fe³⁺/(Fe²⁺+Fe³⁺) ratio. The results obtained are parameterized and discussed in terms of the contrasting effects of T, fO2 and alkali ratio.

Keywords: alkalis, iron, oxidation state, phonolitic glasses, XAS

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INTRODUCTION

The speciation of iron in magmatic systems influences both phase equilibria and physical properties of magma. This speciation is known to depend significantly on temperature, redox state and chemical composition (e.g. Mysen and Richet 2005). Ultimately, sufficiently robust and comprehensive characterization of Fe redox and coordination states may provide the data necessary for constructing thermodynamic models of the role of reduced and oxidized iron in both volcanic and technologically significant systems that is so badly needed.

Iron can be found in a variety of oxidation states and coordination geometries in both melts and crystals. The common Fe species interpreted from investigations of silicate melts and glasses include $[^4]Fe^{2+}$, $[^5]Fe^{2+}$, $[^4]Fe^{3+}$, and $[^5]Fe^{3+}$ (see Wilke et al. 2001; Giuli et al. 2002, 2011, 2012a; Farges et al. 2004; Jackson et al. 2005; Métrich et al. 2006; Rossano et al. 2008). The presence of $[^6]Fe^{2+}$ (e.g. Calas and Petiau 1983; Virgo and Mysen 1985; Dingwell and Virgo 1987) and a minor presence of $[^6]Fe^{3+}$ (Wilke et al. 2007) have been reported. Variation of the relative proportions of these species influences the $<Fe - O>$ distances and bond strengths, thus likely affecting all aspects of glass/melt structure, including melt polymerization, basicity, as well as melt properties; such as density and viscosity (e.g. Dingwell and Virgo 1987; Dingwell 1991; Liebske et al. 2003).

The $Fe^{3+}/Fe^{2+}$ ratio is also widely used as a monitor of the redox conditions of magmatic systems (e.g. Fudali 1965; Carmichael 1991). Several empirical and theoretical models have been proposed (e.g. Kilinc 1983; Kress and Carmichael 1988, 1991; Ottonello et al. 2001), and most of them assume a linear dependence of log ($Fe^{3+}/Fe^{2+}$) on the mole fractions of the main components of the silicate melts. However, some differences have been observed for alkali- and alkali earth-bearing materials. In particular, it has been verified that the different ionization potential ($Z/r$) of cations influences the Fe redox ratio (e.g. Paul and Douglas 1965) and the iron-oxygen coordination geometry (e.g. Mysen 2006). These effects have been related to the steric factors associated with charge-balance of $Fe^{3+}$ 4-fold coordinated (Mysen 2006). In particular, several studies suggest a stabilization of $[^4]Fe^{3+}$ by charge-balancing $K_2O$ (Sack et al. 1980; Kilinc et al. 1983; Dickenson and Hess 1981; Kress and Carmichael 1988). In contrast, Tangeman et al. (2001) observed that in very Fe-rich $K_2O-FeO-SiO_2$ glasses an increase of $K_2O$ leads to an increase of the ferrous iron.

It follows from the above that a full understanding of the parameters that influence Fe coordination and oxidation state in silicate melts should be a research priority. Alkali content is one of the melt chemical
parameters which exhibit a very strong influence on melt structure and properties. It is known to affect virtually all glass properties (Isard 1969) as well as the Fe oxidation state itself in silicate melts (see Dickenson and Hess 1981; Duffy, 1993; Moretti and Ottonello 2003 and references therein). It also exerts a first order effect on the viscosity of silicate liquids at high temperatures (Giordano et al. 2008). Nevertheless few data are available to assess quantitatively to which extent the Na/(Na+K) ratio can modify the Fe structural role in multicomponent glasses and melts. Le Losq and Neuville (2013) have recently studied the effect of Na/K ratio on the structure and rheology of silica-rich glasses, proposing the occurrence of two sub-networks in mixed alkali tectosilicate glasses. In previous experiments on phonolitic glasses (with constant alkali content), we determined that the oxidation of Fe produces an increase in polymerization as well as shorter (and stronger) Fe-O bonds (Giuli et al. 2011).

2. MATERIALS AND METHODS

Five melt compositions have been synthesized at high temperature and atmospheric pressure over a wide range of oxygen fugacity ($f_{O_2}$) conditions. The compositions have been prepared starting from a mixture of oxides and carbonates calculated on the base of a phonolitic bulk composition. Each blank was prepared with a different relative Na and K contents, to provide samples containing a nominal [Na/(Na+K)] ratio respectively of 0, 0.25, 0.5, 0.75 and 1, (named Ph0, Ph0.25, Ph0.5, Ph0.75 and Ph1, respectively).

The powders of oxides and carbonates, previously dried at 110°C were mixed in an agate mortar and then placed in a Pt crucible for heating in a muffle furnace. After decarbonation the mixture was heated to the final temperature (1250°C or 1400°C) for 24 hours and the melt produced was cooled quickly in air. To ensure homogeneity of the samples, the glasses were finely ground and melted again. Samples Ph0 and Ph0.25 were optically inhomogeneous even after four cycles of grinding, melting at 1250°C, and quenching. Moreover the compositions with [Na/(Na+K)] ratio < 0.5 stabilized small amounts of a Fe-bearing leucite phase (K(Al,Fe)Si2O8, as determined by XRD). Thus, these two compositions were synthetized only at higher temperatures. The chemical compositions of the starting glasses used in this study are reported in Table 1.
Aliquots on the order of 1 g of each glass were melted in alumina crucibles in a vertical furnace, at two different temperatures (1250 or 1400°C, called LT and HT, respectively). The oxygen fugacity conditions were controlled by CO₂/CO gas mixtures. The temperature and \( f_{O_2} \) (in the range of \( f_{O_2} \) from 10E-0.68 to 10E-9.7 atm/10E-11.26 atm depending on temperature) were monitored continuously using a Type B thermocouple and a yttria-stabilized zirconia oxygen sensor placed close to the sample. Additional kinetic experiments have been done in order to assess the Fe redox kinetics at the reducing conditions corresponding to the iron-wüstite (IW) buffer. The kinetic experiments have been performed by dip-sampling melt droplets with an alumina rod at different dwell times.

Homogeneity and absence of crystalline phases of each sample was checked via X-ray Powder Diffraction (XRPD), Optical Microscopy and Scanning Electron Microscopy (SEM) analysis at the University of Camerino. The analyses confirmed the absence of microcrystals or inhomogeneous regions for all the samples, except for Ph0 glasses synthesized at FMQ-2 and IW (Table 2). Chemical compositions were collected using a CAMECA SX50 electron microprobe (CNR, Padova) and are reported in Table 1.

Fe K-edge X-ray Absorption Spectroscopy (XAS) spectra were collected at the bending magnet BM08 GILDA beamline of ESRF (Grenoble, F) in the range 7000-7400 eV for XANES data and 6980-8000 eV for EXAFS data. Fe model compounds and powdered glasses for XAS measurement were prepared by smearing finely ground powder on a Kapton tape. The flat sample surface was placed 45° from the X-ray beam directed toward the detector. The spectra were acquired in fluorescence mode by using a Ge 12-elements detector and a Si(311) crystal monochromator was used, providing an energy resolution of about 0.2 eV at the Fe K-edge. However, the main limitation for energy resolution is the finite core-hole width of the absorbing element (approximately 1.15 eV at the Fe K-edge; Krause and Oliver 1979), resulting in a convoluted energy resolution full-width half maximum (FWHM) of about 1.4 eV. The energy was calibrated by defining the first derivative peak of a metallic Fe reference foil (7112.0 eV) acquired simultaneously to the samples.

The standards used for XANES measurements are: a synthetic Fe-akermanite for Fe²⁺ in tetrahedral coordination and a synthetic orthopyroxene for Fe²⁺ in octahedral coordination; a natural tetra-ferriphlogopite and a synthetic Fe-kimzeyite for Fe³⁺ in 4-fold coordination (Giuli et al. 2012b). The Fe model compounds used in this study were checked for purity by both Optical Microscopy and X-ray powder Diffraction.
Potassium dichromate titration was used to determine the Fe$^{2+}$ content for some of the Fe-bearing glasses and to verify the reliability of the XAS data (see Giuli et al. 2011 for details on the procedure).

3. DATA ANALYSIS

XANES spectra were reduced by background subtraction with a linear function and then normalized for atomic absorption on the average absorption coefficient of the spectral region from 7170 to 7400 eV. The threshold energy was taken as the first maximum of the first derivative of the spectra, whereas the main peak positions were obtained by calculating the second derivative of the spectra. In addition to the position of the main edge, particular attention has been given to the analysis of the pre-edge peak. This small peak is due to an s-d like electronic transition. Although dipole-forbidden, it becomes partially allowed by mixing of the d-states of the transition metal with the p-states of the surrounding oxygen atoms. This implies that the pre-edge peak energy position and intensity are greatly affected by the Fe oxidation state and coordination (Calas and Petiau 1983; Brown et al. 1995; Wilke et al. 2001). In particular, the accurate assessment of the centroid energy position and of the integrated intensity of the pre-edge peak allows comparison with those of Fe model compounds. As a result it can provide quantitative information on both Fe oxidation state and coordination environment (see Wilke et al. 2001; Farges 2001; Giuli et al. 2002).

In this study, the pre-edge peak analysis was carried out following the procedure reported in Wilke et al. (2001) and Giuli et al. (2002). The pre-edge peak was fitted by a sum of pseudo-Voigt (pV) functions, and their intensities along with energy positions were compared with those of the standards analyzed here and others from the literature (e.g., Wilke et al. 2001; Farges 2001; Giuli et al. 2012b) to extract information on Fe oxidation state and coordination number in the glasses studied. Particular care was taken in using the smallest possible number of components in the pre-edge peak fitting procedure. The number of the mathematical functions used was constrained to be equal to the minima found in the second derivative of the pre-edge peak. Moreover, also the energy values derive from the minima of the second derivative. Concerning peak fitting, after the background subtraction, we followed two procedures: i) by using pV components with different FWHM or Lorentzian coefficient; ii) by using pV components constrained to have the same FWHM and Lorentzian coefficient. The second method produced the best results in terms of scatter of pre-edge peak energy and integrated intensity (Giuli et al. 2010).
XAS spectra in the extended region (Extended X-ray Absorption Fine Structure - EXAFS) were collected in the energy region from 6980 to 8000 eV. EXAFS data reduction and analysis was done by means of the GNXAS package (Filipponi and Di Cicco 2000). This program extracts the EXAFS signal \( [\chi(k)] \) from the raw spectrum without performing Fourier filtering and thus avoids possible bias derived from incorrect background subtraction. The theoretical amplitudes and phase shifts are calculated \textit{ab initio} according to the muffin-tin approximation. The Hedin-Lundquist complex potential (Hedin and Lundquist 1971) was used for the exchange-correlation potential of the excited state. The amplitude reduction factor \( S_0^2 \) has been fixed to 0.83, in agreement with the values observed for several crystalline standard and natural glasses (Giuli et al. 2002, 2012b) and this value is close to those used by Farges et al. (1994) (0.82), and Di Cicco et al. (1994) (0.85).

4. RESULTS

4.1 Synthesis in Air – Alkali effects

Figure 1a shows the normalized XANES spectra collected at the Fe K-edge for the 5 glasses synthesized in air at 1400°C. The main edge energy, as determined by first derivative, indicates the presence of predominantly trivalent Fe. However, the shape and edge energy positions vary depending on the \( [\text{Na}/(\text{Na+K})] \) ratio, and these differences point to variations in the Fe oxidation state. The clear trend observed, both in the main edge and in the pre-edge region (inset Fig. 1a) is in agreement with the \( [\text{Na}/(\text{Na+K})] \) ratio. In fact, by passing from the sample with only K (Ph0) to the sample with only Na (Ph1), the Fe main edge shift to lower energies (from 7124.7 eV to 7123.5 eV, respectively for Ph0 and Ph1). The only exception is the sample Ph0.25, which was synthesized at lower temperature (1325°C).

Each pre-edge peak has been fitted with two components, whose energies (ca. 7112.65 and 7114.4 eV) are consistent with those of trivalent Fe model compounds. There are strong differences between the two end-members both in energy positions and relative intensities, and in particular the sample rich in K (Ph0) has a more intense peak at higher energy. The integrated intensity of the pre-edge peaks vs. their centroid energies are plotted (Figure 1b) along with the data of Fe model compounds analyzed here and elsewhere (Wilke et al. 2001; Farges 2001; Giuli et al. 2002, 2012b). For the sake of simplicity, the relative energy is plotted (0 refers to the first maximum of the first derivative of metallic Fe spectrum) to avoid confusions when comparing data with literature data where a different energy
value of metallic Fe was chosen. In Figure 1b all divalent Fe model compounds plot at energies close to 0.9 eV above the metallic Fe edge, whereas trivalent Fe model compounds plot at energies close to 2.4 eV. At constant energy, the intensity of the model compounds pre-edge peaks varies according to the Fe coordination geometry (the shaded ellipses refer to the range of coordination numbers in Fe model compounds analysed here and from literature data; e.g. Wilke et al. 2001; Farges et al. 2001; Giuli et al. 2002, 2012b). The five phonolitic glasses data (full symbols) plot along a narrow trend going from the region of $^{1}^{1}$Fe$^{3+}$ model compounds toward to lower energies and intensities, by increasing the [Na/(Na+K)] ratio. As already observed in the XANES region, the only exception is the sample Ph0.25 (down triangle in Fig. 1b), which was synthesized at 1325°C.

Mixing lines that best fits the experimental points have been calculated (dotted line with small crosses) and the comparison between the experimental pre-edge peak data and the calculated mixing lines provide quantitative Fe$^{3+}$/(Fe$^{2+}$+Fe$^{3+}$) ratios ranging from 0.8 to 0.6 respectively for Ph0 and Ph1 (Table 2). Sample Ph0.25 (down triangle in Fig. 1b) has the highest amount of trivalent species (Fe$^{3+}$/(Fe$^{2+}$+Fe$^{3+}$) = 0.82) and it is the only sample that do not follow the trend. Based on the precision of the energy, we estimate the error in the Fe$^{3+}$/(Fe$^{2+}$+Fe$^{3+}$) ratios to be within ± 0.05.

4.2 Kinetic experiments

The kinetic of Fe oxidation-reduction for the composition Ph1 has been studied at two different temperatures (1400°C and 1250°C, respectively named HT and LT) under reducing conditions (IW buffer). Samples of the melt have been obtained at different time intervals, from 1 h to 72 h. All the quenched glasses obtained have been studied by XAS at the Fe K-edge, and in order to verify the reliability of the method, the iron redox ratio of some of the kinetic samples has been determined also by wet chemical analyses (Table 2).

The normalized XANES spectra of Ph1 glasses, sampled at different times (1, 2, 4, 6, 12, 24, 36, 48 hours, respectively) are reported in Figures 2a-b along with the spectra collected for the glass synthesized at the same temperatures, but in air. Clear variations in the intensity and energy position are visible in both the edge regions and in the pre-edge peaks, at increasing time. Whilst for the samples synthesized at higher temperature (Fig. 2a) no significant changes were observed after 10 hours, the glasses done at lower temperature (Fig. 2b) needed longer time to achieve the Fe oxidation state equilibrium. The background subtracted pre-edge peaks of each glass were fitted and the resulting
integrated intensities of the pre-edge peaks vs. their centroid energies are plotted in Figure 2c. The two series follow the same reduction trend and, as expected, the kinetic of the redox reactions is faster at higher temperatures. However, it is important to notice that glasses synthesized at LT achieved equilibrium about 6x slower with respect to the same samples synthesized at HT. Mixing lines allowed the estimation of the Fe$^{3+}$(Fe$^{2+}$+Fe$^{3+}$) ratios for each sample, and it was possible to determine the progressive decrease of Fe$^{3+}$(Fe$^{2+}$+Fe$^{3+}$) ratios with time: from 0.6 to the equilibrium value of 0.01 for samples synthesized at HT and from 0.9 to 0.05 for those synthesized at LT.

The time dependence of redox ratios as determined by XANES for the glass Ph1, both at HT and LT, is plotted in Figure 2d. As shown by Magnien et al. (2006), the evolution of Fe$^{3+}$(Fe$^{2+}$+Fe$^{3+}$) ratio with time at a given temperature can be reproduced by expressions of the form

\[(F_t - F_{eq}) = (F_0 - F_{eq}) \exp(-t/\tau), \quad (\text{Eq. 1})\]

where $F_t$ is the redox ratio at time $t$, $F_0$ the initial ratio, $F_{eq}$ the equilibrium value and $\tau$ a characteristic time determined from a least-squares fit of Eq. (1) to the experimental redox data. As reported by Magnien et al. (2006, 2008) the time for redox equilibration is arbitrarily defined as the time at which the redox ratio reaches 99% of the equilibrium value as derived from Eq. (1). The values extrapolated for the synthesis at HT and LT are 197 and 347 minutes, respectively (Fig. 2d).

4.3 Synthesis at different redox conditions

The glasses of different composition have been synthesized also under reducing atmospheres (FMQ, FMQ-2, IW) to investigate how redox conditions affect the Fe oxidation state. As expected, the XAS data indicate a clear shift of the absorption edge from higher to lower energies when decreasing the oxygen fugacity as well as changes in the pre-edge peaks (P). Passing from air to IW conditions the P peaks exhibit a shoulder on the lower energy side, which is typical of Fe$^{2+}$ compounds, and a consequent decreasing of the intensity of the component at higher energy, characteristic feature of Fe$^{3+}$. The background subtracted pre-edge peaks of each glass synthesized at HT and at different $f_{O_2}$ (FMQ, FMQ-2 and IW) were fitted and the resulting integrated intensities of the pre-edge peaks vs. their centroid energies are plotted in Figure 3 along with the glass samples synthesized in air.

Different mixing lines have been calculated by taking into account several combinations between pre-edge peak intensity and energy values representative of possible Fe structural roles in silicate glasses. All the pre-edge peak data are compatible with the presence of $^{(4)}$Fe$^{3+}$ and with an intensity for the
ferrous species close to that of grandidierite ([5]Fe2+). Thus, Figure 3 shows different mixing lines (dotted lines) that best match the experimental data. Moreover, Figure 3 shows that by decreasing the [Na/(Na+K)] ratio from 1 to 0, there is an increase of the amount of ferric iron, both under oxidizing (air) and reducing conditions. The integrated intensities of the pre-edge peaks can also provide information on the average Fe coordination number and thus on the mean Fe coordination environment.

The pre-edge peak analysis suggest that ferric iron is mainly 4-fold coordinated, whereas the ferrous iron, although laying close to the 5-fold region, could be compatible also with the presence of both [6]Fe2+, [4]Fe2+ or, alternatively, of [5]Fe2+, [3]Fe2+, and [6]Fe2+.

4.4 EXAFS

The Extended X-ray Absorption Fine Structure (EXAFS) analysis of the first coordination shell around Fe, for the two end-members synthesized in air, is reported in Figure 4. The experimental (circles), and theoretical (solid line) EXAFS signals of both glasses are shown in Figure 4a, whereas their Fourier Transforms are shown in Figure 4b. There are some differences in the EXAFS signals of the two end-members (Ph1 and Ph0 glasses) synthesized in air at HT. The K-rich sample (Ph0), respect to the Ph1 sample, shows greater amplitude of the oscillations, but interestingly, the oscillations seem to be in-phase, which can be interpreted as similar <Fe-O> distances. A satisfactory fit of both EXAFS spectra has been obtained with the Fe3+ 4-fold coordinated in a regular tetrahedral geometry. The result of the fit using this small cluster, composed of the absorber and the first coordination shell of oxygens, shows that the major oscillations can be well reproduced by the cluster with the [6]Fe3+. However, although the fit was acceptable, a residual was still evident and we have tried to improve the fitting procedure by adding the contribution of divalent iron, according to the percentage estimated by the pre-edge peak analysis in each sample. The best fit shows that in both glasses trivalent iron is 4-fold coordinated (CN = 4 ± 0.5), with average distances <Fe3+-O> = 1.88 Å (± 0.02). This result is consistent with the pre-edge peaks results and also with the shape of the EXAFS signals, since both glasses analyzed present oscillations with almost the same frequencies. Usually, changes in EXAFS amplitudes are interpreted as differences in the average number of nearest-neighbors around the absorber (e.g. Stöhr 1984). In our signals, the different amplitudes of the EXAFS spectra derive from the different contribution (i.e. amount) of Fe2+. 
Preliminary results from the EXAFS analysis of the Ph1 glass synthesized at IW (Fe$^{3+}$/[(Fe$^{2+}$+Fe$^{3+}$) = 0.99 as estimated from pre-edge analysis) shown that acceptable fit can be obtained either considering the presence of both [4]Fe$^{2+}$, and [6]Fe$^{2+}$ or only the presence of [5]Fe$^{2+}$. Thus, the data obtained by EXAFS analysis confirm the indications on the Fe oxidation state and average coordination number derived from the XANES spectra. All the relevant structural parameters obtained from the EXAFS fit are reported in Table 3.

5. DISCUSSION

This XAS study has yielded the determination of Fe oxidation state and coordination environment in glasses of phonolitic composition, with different [Na/(Na+K)] ratios. From the obtained results it may be observed that several factors (T, $f$O$_2$ and composition) have an effect on the Fe oxidation state. Each factor is discussed below in detail.

Influence of the temperature

The five glass series of phonolitic compositions ([Na/(Na+K)] ratios 0.0, 0.25, 0.5, 0.75, 1.0) have been synthesized at two different temperatures (1400°C - HT and 1250°C - LT). Unfortunately, compositions with [Na/(Na+K)] ratio < 0.5, synthesized at 1250°C, stabilized small amounts of a Fe-bearing leucite phase, thus no Fe K-edge spectra were collected for those samples. For samples synthesized in air at HT, divalent iron increases with the [Na/(Na+K)] ratio (Figure 1). In contrast, XAS data analyses for the glasses synthesized in air at LT (1250°C) show no clear variation with the [Na/(Na+K)] ratio, within experimental error. In fact, by comparing the centroid energy positions of each pre-edge peak vs. the [Na/(Na+K)] ratio of samples synthesized in air, two distinct trends can be observed, for HT and LT samples (Figure 5). With only three points available for synthesis at LT, robust analysis is not possible, even if the two series have differing behaviours (Figure 5). Speculating, if we extend the trend line of the samples LT toward lower [Na/(Na+K)] ratios (dotted line in Fig. 5), it would seem to coincide with the value obtained at 1400°C. Thus, at LT the [Na/(Na+K)] ratio seems to have little effect on the Fe redox ratio.

It is important to note here that kinetic experiments and the values extrapolated from Magnien equation (Eq. 1) indicated the achievement of equilibrium at both LT and HT. Then the differences observed in Figure 5 could be explained by considering the diffusion of oxygen and cations at different
temperatures. Passing from superliquidus temperature to lower temperatures the reaction kinetics could be increasingly influenced by the distinct diffusivities of the alkaline cations.

Influence of the redox state

The iron redox reaction may be parameterized in terms of $f_O^2$ by the expression $\log[Fe^{2+}/Fe^{3+}] = 0.25 \log(f_O^2) + c$. Several authors (e.g. Fudali 1965; Lauer and Morris 1977; Mysen et al. 1984) have demonstrated a linear relationship between $\log(f_O^2)$ and $\log[Fe^{2+}/Fe^{3+}]$. A theoretical slope value of 0.25 might be expected, however it has been demonstrated that the slope of the fugacity-redox state relationship varies depending on the bulk composition (e.g. Fudali 1965; Mysen et al. 1984; Jayasuriya et al. 2004).

The equilibrium dependence of the $Fe^{2+}/Fe^{3+}$ ratio on oxygen fugacity for our phonolitic glasses (Figure 6) also shows a systematic slope variation with composition varying systematically with the $[Na/(Na+K)]$ ratio. The slope of the straight lines decreases from about 0.23 for the Ph1 composition to about 0.14 for the Ph0 composition. The slope of the equilibrium dependence of the $Fe^{2+}/Fe^{3+}$ ratio on the oxygen fugacity observed for the samples synthesized at HT can be observed as well in samples synthesized at LT. The results of linear regressions ($y = mx+b$) for the glasses synthesized at 1250°C are supplied in Table 4, along with those obtained for the samples synthesised at 1400°C.

The value of 0.23 of the Na-rich phonolites (Ph1 and Ph0.75) is very similar to that reported by Johnston (1964) for sodium disilicate glasses. For alkaline earth silicate melts, Mysen et al. (1984) observed a decrease of the slope according to the ionic potential of the alkaline earth cation. In the present study, the $\log[Fe^{2+}/Fe^{3+}]$ is a linear function of $\log(f_O^2)$, with the slope depending on the $[Na/(Na+K)]$ ratio, according to the ionic potential of the cations (Figure 6).

Alkali effect

By plotting the $[Na/(Na+K)]$ ratio vs. $\log[Fe^{2+}/Fe^{3+}]$ for the five series of glasses, synthesized at HT, it is possible to observe a clear trend for samples synthesized at both oxidizing and reducing conditions (Fig. 7): by increasing the $[Na/(Na+K)]$ ratio there is an increase of the ferrous iron in glasses. This effect is visible in air, and even more at reducing conditions.

Dickenson and Hess (1981) observed that the variation of the Fe oxidation state as a function of $K_2O/(K_2O+Al_2O_3)$ ratio follows two trends depending on the K/Al ratio: in peralkaline systems the
Fe\textsuperscript{2+}/Fe\textsubscript{tot} ratio weakly increases by adding K, whereas in peraluminous compositions there is a sharp
linear decrease of the Fe\textsuperscript{2+}/Fe\textsubscript{tot} ratio with increasing K content. For simple peralkaline compositions,
Tangeman and coauthors (2001) reported similar behaviour, with an increase of Fe\textsuperscript{2+}/Fe\textsubscript{tot} ratio with
increasing K\textsubscript{2}O content. Recently, Vetere et al. (2014) observed that in peralkaline phonotephritic
glasses both high NBO/T and high Na/(Na + K) stabilize Fe\textsuperscript{3+} in the melt.

Our glasses, fall close to the metaluminous join, thus residing (according to Dickenson and Hess 1981)
in the redox minimum, where the maximum concentration of Fe\textsuperscript{3+} is correlated with a melt
composition having K\textsubscript{2}O/(Al\textsubscript{2}O\textsubscript{3}+K\textsubscript{2}O) slightly in excess of Al\textsubscript{2}O\textsubscript{3}. Aluminum in alkali-bearing silicate
melts and glasses is essentially present in tetrahedral coordination and when alkali cations are present,
they can play a charge-compensating role of the Al\textsuperscript{3+} to ensure the system’s electroneutrality. Previous
studies suggest stabilization of ferric iron by alkali or alkaline earth cations (Mysen et al. 1980; Weigel
et al. 2006) and from Figure 7, the results show that substitution of K for Na stabilizes more ferric iron.

Optical Basicity

In order to further discuss the results obtained in terms of their compositional control, we have
calculated the optical basicity of our glasses. The optical basicity concept has been developed for
quantitative determination of the acid-basic properties of mixtures containing a large number of oxides
in glasses, alloys, slags, molten salts, etc. (e.g. Duffy and Ingram 1976; Duffy 1993). In this concept
the oxygen behaves as base in the Lewis sense and the metal ions behave as Lewis acids (Moretti 2005)
and the ability of oxygen to transfer electron density to surrounding cations depends on the degree of
its polarization.

It is possible to calculate the so-called theoretical optical basicity of multi-component glass on the basis
of the equation proposed by Duffy and Ingram (1976), which expresses the average bulk basicity from
all oxide species. In this study we calculated the optical basicity from the models of Duffy (1993) and
Ottonello et al. (2001) and we employed the equation of Duffy (1993) in order to correlate the log
(Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) and the optical basicity (Λ) of each glass:

\[
\log(\text{Fe}^{2+}/\text{Fe}^{3+}) = 3.2 - 6.5 \Lambda
\]

Figure 8 reports the calculated log(Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) from the two models vs. the Na/(Na+K) ratio and the
log(Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) estimated from the XANES data analysis, for the glasses synthesized in air at HT (solid
lines) and at LT (dashed lines). Both the models and our experimental data indicate that there is a sharp
decrease of the ferric Fe with increasing sodium, although there are differences in the magnitude of the
trends between the models and the experimental results here obtained. The calculated log(Fe^{2+}/Fe^{3+})
from Ottonello’s model for samples synthesized at LT are similar to the data obtained for the HT
synthesis. On the contrary, the (Fe^{2+}/Fe^{3+}) ratios determined experimentally in this study (empty
triangles in Fig. 8a) show that the trend is completely different. Thus, our data qualitatively confirm the
results of Duffy (1993) and Ottonello et al. (2001) for samples synthesized in air at HT. In fact, there is
a drop in the (Fe^{2+}/Fe^{3+}) ratio as the basicity rises (Fig. 8b) by increasing the content of the alkali oxide
(i.e. K increases the basicity of the glass). However, models are not able to reproduce the differences
observed experimentally between synthesis at HT and LT.

**Implications and concluding remarks**

Because of the wide use of the Fe oxidation state to infer the redox conditions of terrestrial materials
and its strong effect on melt physical properties, it is mandatory to have a fully understanding of the
parameter that influences Fe speciation (oxidation state and local geometry). However, the effect of
high Al and/or alkali content on Fe in silicate melts still remains largely unconstrained (e.g. Giordano
et al. 2006; Mysen and Toplis 2007; Peccerillo et al. 2007). The major consequence of the lack of
experimental data is that current models for predicting the viscosity of natural melts at geological
conditions treat iron as a single species and do not account for variable valence states.

The XAS spectra of the samples synthesized in air and at 1400°C show that the Fe^{3+}/(Fe^{2+}+Fe^{3+}) ratio
decreases by increasing the [Na/(Na+K)] ratio. This behaviour suggests that ferric iron is stabilised by
network-modifier cations with lower ionic potential (i.e. K) and it prefers the tetrahedral coordination
when sufficient alkalis are available for charge balance. Therefore, ferric iron behaves as a structural
analogous of Al^{3+}. Moreover, since Fe^{3+} acts as network former (tetrahedrally coordinated) we presume
that decreasing the [Na/(Na+K)] ratio will increase the polymerization.

The different [Na/(Na+K)] ratios strongly affect the Fe^{3+}/(Fe^{2+}+Fe^{3+}) ratio for any oxygen fugacity
conditions, as observed from the linear relationship between log(O_2) and log[Fe^{2+}/Fe^{3+}], which
gradually decreases from 0.23 to 0.14 by changing the Na/Na+K content from 1 to 0. Furthermore, the
trend of the log[Fe^{2+}/Fe^{3+}] shows a systematic variation of the slope according to the change in the
[Na/(Na+K)] ratio both at HT and LT.
Extended X-ray Absorption fine structure (EXAFS) data of the two end-member synthesized in air indicate that Fe$^{3+}$ is in tetrahedral coordination with $<\text{Fe-O}> = 1.88 \pm 0.02$ Å. This value is in agreement with previous studies on phonolitic and peralkaline rhyolitic glasses (Giuli et al. 2011, 2012a). The glasses synthesized at HT and reducing conditions (FMQ, FMQ-2, IW) show similar reducing patterns, independently of the $[\text{Na}/(\text{Na+K})]$ ratio, which is in agreement with the EXAFS results, suggesting that the local environments slightly change as a function of the Na/K content.

Our experimental data demonstrate that models (i.e. Optical basicity; Duffy and Ingram 1976; Ottonello et al. 2001) are not able to fully reproduce the magnitude of the variations of the Fe$^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio by changing relevant parameters, such as T and $[\text{Na}/(\text{Na+K})]$ ratio. This study thereby confirms that further experimental data will be required to improve the much-needed theoretical models developed to date.

Acknowledgments

We acknowledge the European Synchrotron Radiation Facility (Grenoble, F) for provision of synchrotron radiation facilities and the authors would like to thank A. Trapananti for assistance in using beamline BM08. The authors thank R. Moretti and M.R. Carroll for useful discussions. The authors are grateful to the anonymous reviewers for critically reviewing and correcting the manuscript.

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References cited


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TABLE 1 – Chemical compositions of the five phonolitic glasses synthesized in air (wt %)

<table>
<thead>
<tr>
<th></th>
<th>Ph1 LT*</th>
<th>Ph0.75 LT</th>
<th>Ph0.5 LT</th>
<th>Ph0.25 MT*§</th>
<th>Ph0 HT*§</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>50.60</td>
<td>48.95</td>
<td>47.88</td>
<td>49.24</td>
<td>46.77</td>
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<tr>
<td>TiO₂</td>
<td>1.42</td>
<td>1.36</td>
<td>1.33</td>
<td>1.36</td>
<td>1.38</td>
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<tr>
<td>Al₂O₃</td>
<td>19.68</td>
<td>20.95</td>
<td>18.61</td>
<td>16.58</td>
<td>18.31</td>
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<td>FeO</td>
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<td>7.17</td>
<td>7.14</td>
<td>7.67</td>
<td>7.34</td>
</tr>
<tr>
<td>MgO</td>
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<td>1.16</td>
<td>1.21</td>
<td>1.21</td>
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<tr>
<td>CaO</td>
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<td>6.44</td>
<td>6.15</td>
<td>6.06</td>
<td>6.91</td>
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<tr>
<td>Na₂O</td>
<td>11.45</td>
<td>8.37</td>
<td>6.75</td>
<td>3.24</td>
<td>0.05</td>
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<tr>
<td>K₂O</td>
<td>0.07</td>
<td>4.85</td>
<td>9.33</td>
<td>13.65</td>
<td>17.50</td>
</tr>
<tr>
<td>Total</td>
<td>99.16</td>
<td>99.30</td>
<td>98.35</td>
<td>99.01</td>
<td>99.48</td>
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<tr>
<td>[Na/(Na+K)]</td>
<td>1.0</td>
<td>0.74</td>
<td>0.52</td>
<td>0.27</td>
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</tbody>
</table>

* LT = low temperature 1250°C; MT = intermediate temperature 1325°C; HT = high temperature 1400°C; § Minimum temperatures for which no crystalline phases were detected.
TABLE 2 – Run conditions of each experiment and Fe$^{3+}$/(Fe$^{2+}$+Fe$^{3+}$) determinations from XANES data analysis.

<table>
<thead>
<tr>
<th>Label</th>
<th>T (°C)</th>
<th>Dwell time (h)</th>
<th>-log(fO2)</th>
<th>Centroid (eV) ±0.03 *</th>
<th>Integrated Intensity ±0.05</th>
<th>Fe$^{3+}$/(Fe$^{2+}$+Fe$^{3+}$) % ±5</th>
<th>notes</th>
</tr>
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<td>Ph1_air</td>
<td>1250</td>
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<td>0.68</td>
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<td>1.72</td>
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<td>0.14</td>
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<td>4</td>
<td>11.26</td>
<td>1.92</td>
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<td>44.0</td>
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<td>12</td>
<td>11.26</td>
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<td>0.16</td>
<td>27.5</td>
<td>31.4</td>
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<td>24</td>
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<td>1.64</td>
<td>0.16</td>
<td>31.0</td>
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<td>Ph1_IW36§</td>
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<td>36</td>
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<td>0.15</td>
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<td>Ph1_IW48§</td>
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<td>6.30</td>
<td>1.19</td>
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<td>10.0</td>
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<td>8.20</td>
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<td>1250</td>
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</tr>
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<td>Ph0.75_FMQ</td>
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<td>0.68</td>
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<td>1.40</td>
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<td>89.0</td>
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<td>31.0</td>
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<tr>
<td>Ph0.5_FMQ-2 HT</td>
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<td>24</td>
<td>8.20</td>
<td>1.30</td>
<td>0.14</td>
<td>14.5</td>
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<tr>
<td>Ph0.5_IW HT</td>
<td>1400</td>
<td>24</td>
<td>9.60</td>
<td>1.07</td>
<td>0.12</td>
<td>6.0</td>
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<tr>
<td>Ph0.25_air MT</td>
<td>1325</td>
<td>24</td>
<td>0.68</td>
<td>2.27</td>
<td>0.26</td>
<td>82.0</td>
<td>86.7</td>
</tr>
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<td>0.68</td>
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<td>0.26</td>
<td>82.0</td>
<td>Lc</td>
</tr>
<tr>
<td>Ph0.25_FMQ HT</td>
<td>1400</td>
<td>24</td>
<td>6.33</td>
<td>1.58</td>
<td>0.16</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
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<td>1400</td>
<td>24</td>
<td>8.18</td>
<td>1.29</td>
<td>0.15</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>Ph0.25_IW HT</td>
<td>1400</td>
<td>24</td>
<td>9.60</td>
<td>1.23</td>
<td>0.14</td>
<td>10.0</td>
<td>Lc</td>
</tr>
<tr>
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<td>80.0</td>
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<td>Ph0_FMQ-2 HT</td>
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<td>24</td>
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<td>1.48</td>
<td>0.14</td>
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<tr>
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<td>1400</td>
<td>36</td>
<td>9.60</td>
<td>1.71</td>
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<td>35.0</td>
<td>Lc, I</td>
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<tr>
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<td>9.60</td>
<td>1.56</td>
<td>0.15</td>
<td>27.0</td>
<td>Lc, I</td>
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</table>

* Centroid = Pre-edge peak centroid energy - 7112.0 eV (metallic foil energy);
§ kinetic experiments
Lc: traces of leucite; I: inhomogeneous sample.
TABLE 3 – Essential parameters of the EXAFS fits for the end-member glasses, synthesized in air (HT).

<table>
<thead>
<tr>
<th>parameters</th>
<th>glasses</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Ph1_air</td>
<td>Ph0_air</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;-O&lt;sup&gt;-&lt;/sup&gt; (Å)</td>
<td>1.88 ± 0.02 (4x)</td>
<td>1.88 ± 0.02 (4x)</td>
<td></td>
</tr>
<tr>
<td>* σ&lt;sup&gt;2&lt;/sup&gt; Fe&lt;sup&gt;3+&lt;/sup&gt; (Å&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>0.005</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>theta (degree)</td>
<td>109.85</td>
<td>112.20</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;-O&lt;sup&gt;-&lt;/sup&gt; (Å)</td>
<td>2.22 (2x)</td>
<td>2.28 (1x)</td>
<td></td>
</tr>
<tr>
<td>* σ&lt;sup&gt;2&lt;/sup&gt; Fe&lt;sup&gt;2+&lt;/sup&gt; (Å&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>0.019</td>
<td>0.009</td>
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<tr>
<td>E&lt;sub&gt;0&lt;/sub&gt; (eV)</td>
<td>7123.53</td>
<td>7125.27</td>
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</tr>
<tr>
<td>E&lt;sub&gt;0&lt;/sub&gt;&lt;sup&gt;f&lt;/sup&gt; (eV)</td>
<td>7123.69</td>
<td>7126.29</td>
<td></td>
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<tr>
<td># S&lt;sub&gt;0&lt;/sub&gt;&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.83</td>
<td>0.83</td>
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</tr>
<tr>
<td>* R&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.49E-06</td>
<td>0.12E-05</td>
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</tr>
<tr>
<td>* CN [Fe&lt;sup&gt;3+&lt;/sup&gt;]</td>
<td>4 ± 0.5</td>
<td>4 ± 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Note: Number in brackets corresponds to the multiplicity of each distance.

* σ<sup>2</sup> = Debye-Waller factor; E<sub>0</sub> = experimental energy; E<sub>0</sub><sup>f</sup> = EXAFS refined energy edge; R<sup>d</sup> = disagreement index; CN [Fe<sup>3+</sup>] = Fe<sup>3+</sup> refined coordination number (Filipponi and Di Cicco, 2000).

# see text.
TABLE 4 – Parameters relative to the linear regression equations for Ph samples synthetised at HT and LT.

<table>
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<tr>
<th>sample</th>
<th>HT</th>
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<th>LT</th>
</tr>
</thead>
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<td></td>
<td>m</td>
<td>b</td>
<td>R² #</td>
</tr>
<tr>
<td>Ph1</td>
<td>0.227 (0.03)</td>
<td>-0.389 (0.21)</td>
<td>0.97</td>
</tr>
<tr>
<td>Ph0.75</td>
<td>0.231 (0.03)</td>
<td>-0.57 (0.24)</td>
<td>0.96</td>
</tr>
<tr>
<td>Ph0.5</td>
<td>0.179 (0.02)</td>
<td>-0.631 (0.11)</td>
<td>0.98</td>
</tr>
<tr>
<td>Ph0.25</td>
<td>0.186 (0.01)</td>
<td>-0.759 (0.07)</td>
<td>0.99</td>
</tr>
<tr>
<td>Ph0</td>
<td>0.136 (0.04)</td>
<td>-0.743 (0.25)</td>
<td>0.91</td>
</tr>
</tbody>
</table>

* calculated on two points;
# R values are reported as a measure of goodness-of-fit of linear regressions.
Figure 1 – a) XAS spectra of the 5 glasses synthesized in air at higher temperature (1400 °C). In the XANES region is evident a shift toward lower energies of the signals corresponding to the increase of the [Na/(Na+K)] ratio, with the exception of sample Ph0.25. In the inset a magnification of the pre-edge peak region. b) Plot of the pre-edge peak integrated intensity vs. centroid energy position. Black squares refer to the phonolitic glasses, synthesized in air (HT), whereas the small cross symbols joined by the dotted lines represent the mixing lines between the pre-edge peaks, calculated mixing between $^{[5]}$Fe$^{2+}$ with $^{[4]}$Fe$^{3+}$. There is a clear trend with the increase of the amount of divalent Fe by increasing the [Na/(Na+K)] ratio (sample Ph0.25 - down triangle - is the only exception).

Figure 2 – (a-b) Normalized XANES spectra of the phonolitic glass Ph1 ([Na/(Na+K)] = 1). Each spectrum corresponds to various lengths of time at reducing conditions (IW), at 1400 °C (HT - a) and at 1250 °C (LT - b). The spectra of the glasses synthesized in air are reported for comparison. c) Plot of the pre-edge peak integrated intensity vs. centroid energy position for the kinetic experiments of glass Ph1 done at higher and lower temperatures (HT and LT, respectively). Bold labels refer to the Ph1 HT samples. d) Time dependence of redox ratios as determined from XANES for glass composition Ph1, both at HT and LT. The curves and the $\tau$ values are obtained from Magnien et al. (2006) equation (see text).

Figure 3 - Plot of the pre-edge peak integrated area vs. centroid energy position for all the glasses synthesized at HT and at different redox conditions (air, FMQ, FMQ-2 and IW). At constant oxygen fugacity, the [Na/(Na+K)] ratio has a strong effect on the Fe$^{3+}$(Fe$^{2+}$+Fe$^{3+}$) ratio. Please refer to the colour online version.

Figure 4 – a) Experimental (empty circles), and model (solid lines) EXAFS signals of the Ph0 and Ph1 glasses, synthesized at HT, in air. b) Fourier transforms for the analyzed signals. The disagreement indices (Rd), and the parameters obtained from the EXAFS signals data analysis are reported in Table 3.
Figure 5 - Centroid energy positions of each pre-edge peak vs. the alkali ratio of samples synthesized in air, both at HT and LT. The two series seem to have distinct directions. The equations for the two straight solid lines are reported. The dotted line represents only the continuation of the straight line calculated on three points for the LT samples.

Figure 6 - log[Fe\textsuperscript{2+}/Fe\textsuperscript{3+}] as a function of oxygen fugacity (f\textsubscript{O\textsubscript{2}}) for the five compositions synthetised at HT. The equations of straight lines (y = mx+b) are reported. Ph1 composition has a slope value close to the ideal one (0.25), and gradually, by substituting K for Na, the slope decreases. Please refer to the colour online version.

Figure 7 – log[Fe\textsuperscript{2+}/Fe\textsuperscript{3+}] vs. the [Na/(Na+K)] ratio for samples synthetised at HT at oxidizind (air) and reducing conditions (IW). By increasing the K content in the glasses, both at oxidizing and reducing conditions, there is an increase of ferric iron.

Figure 8 – a) log(Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) calculated from [1] Duffy (1993) and [2] Ottonello et al. (2001) models and from [3] XANES data in this study vs. the [Na/(Na+K)] ratio. Solid lines refer to samples synthesized in air at HT, whereas the dashed lines to those synthesized at LT. At HT models and experimental data agree: there is a decrease of the Fe\textsuperscript{3+} with increasing sodium, although there are differences in the magnitude of the changes between the models and the experimental data. If we compare the data obtained with the Ottonello model for synthesis in HT and LT, no big differences can be detected. Instead, the experimental data for LT synthesis (empty triangles) show that the trend is completely different. b) The drop of the optical basicity for glasses synthesized both at HT and LT (calculated from the basicity moderating parameters) by increasing the content of sodium.
Figure 1

(a) Normalized Absorption (arb. units)

Energy (eV)

(b) Pre-edge peak integrated area vs. E-E_0^{Fe} (eV)

Fe^{2+} Fe^{3+}

References:
Figure 2
Figure 3

[Graph showing pre-edge peak integrated area vs. E-E_{0}^{Fe} (eV) for different iron states and conditions, with symbols representing various conditions and data points distributed across the graph.]
Figure 4
Figure 5

![Graph showing pre-edge peak centroid (eV) vs. [Na/(Na+K)] for 1250 °C and 1400 °C.]

- HT: $y = 2.26 + 0.08x$, $R^2 = 0.92$
- LT: $y = 2.29 - 0.204x$, $R^2 = 0.88$
Figure 6
Figure 7

![Graph showing log([Fe$^{2+}$/Fe$^{3+}$]) vs. [Na/(Na+K)] for 1400°C and air conditions. The graph compares IW and air treatments.](image-url)
Figure 8

(a) 

\[ \log \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \right) \]

- [1] Duffy 1993
- [3] This study

(b) 

Optical Basicity (\(\Lambda\))

- HT
- LT

\(Na\) (mol%) vs. \(Na/(Na+K)\)