High-Pressure XAFS Measurements of the Coordination Environments of Fe2+ and Fe3+ in Basaltic Glasses

Keisuke Ozawa[1], Kei Hirose[2], and Yoshio Takahashi[3]

[1]Department of Earth and Planetary Science, The University of Tokyo
[2]Tokyo Institute of Technology
[3]The University of Tokyo

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Abstract

We investigated pressure-induced changes in the coordination environments of Fe^{2+} and Fe^{3+} in basaltic glasses based on the Fe K-edge X-ray absorption fine structure (XAFS) analyses for both XANES and EXAFS regions. Upon compression from 1 bar to ˜15 GPa, the Fe^{2+}-O bond length remained similar, suggesting that the average coordination number of Fe^{2+} increased from ˜5 to 6. On the other hand, the Fe^{3+}-O bond was remarkably elongated, which indicates that Fe^{3+}changed from 4-fold to 6-fold coordination. Above 15 GPa, both Fe^{2+}-O and Fe^{3+}-O bond lengths decreased smoothly, suggesting minor changes in their coordination numbers. The data also showed that both Fe^{2+} and Fe^{3+} remained in the high-spin state up to 83 GPa and 60 GPa, respectively, in the basaltic glasses. These compression behaviors of the Fe^{2+}-O and Fe^{3+}-O bonds support that Fe^{2+} disproportionates into Fe^{3+} and metal Fe in a deep magma ocean.

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Keisuke Ozawa[1], Kei Hirose[1,2], and Yoshio Takahashi[1,3]

[1]Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

[2]Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan

[3]Institute of Materials Structure Science, High-Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan

Key Points

- We examined high-pressure coordination environments around Fe^{2+} and Fe^{3+} in basaltic glasses by X-ray absorption spectroscopy to 83 GPa.
- XANES and EXAFS analyses indicate that the coordination numbers of Fe^{2+} and Fe^{3+} increases with increasing pressure from 1 bar to ~15 GPa.
- Compression behaviors of the Fe-O bond lengths support the disproportionation of Fe^{2+} into Fe^{3+} and Fe^{0} in a deep magma ocean.

Abstract We investigated pressure-induced changes in the coordination environments of Fe^{2+} and Fe^{3+} in basaltic glasses based on the Fe K-edge X-ray absorption fine structure (XAFS) analyses for both XANES and EXAFS regions. Upon compression from 1 bar to ~15 GPa, the Fe^{2+}-O bond length remained similar, suggesting that the average coordination number of Fe^{2+} increased from ~5 to 6. On the other hand, the Fe^{3+}-O bond

was remarkably elongated, which indicates that Fe^{3+} changed from 4-fold to 6-fold coordination. Above 15 GPa, both Fe^{2+}-O and Fe^{3+}-O bond lengths decreased smoothly, suggesting minor changes in their coordination numbers. The data also showed that both Fe^{2+} and Fe^{3+} remained in the high-spin state up to 83 GPa and 60 GPa, respectively, in the basaltic glasses. These compression behaviors of the Fe^{2+}-O and Fe^{3+}-O bonds support that Fe^{2+} disproportionates into Fe^{3+} and metal Fe in a deep magma ocean.

Plain Language Summary The coordination environments around Fe^{2+} and Fe^{3+} in silicates are of great importance for their partial molar volumes, spin states, and partitioning. The local structures around Fe in silicate glasses were intensively studied at 1 bar by XAFS analyses, but their pressure-induced changes have not been examined. Here we conducted the XAFS measurements of Fe^{2+} in a reduced basaltic glass to 83 GPa and Fe^{3+} in an oxidized glass to 60 GPa. While the Fe-O bond is shortened by a simple compression effect, it is elongated due to an increase in the coordination number. The observed changes in the bond length showed that Fe^{2+} was ~5-fold coordinated at 1 bar and became 6-fold with compression to ~15 GPa. On the other hand, the coordination number of Fe^{3+} increased from 4 at ambient pressure to 6 at ~15 GPa. Both were 6-fold coordinated above 15 GPa. These bond lengths also suggest that both Fe^{2+} and Fe^{3+} remained high spin in our measurements. The difference between the Fe^{2+}-O and Fe^{3+}-O bond lengths support a previously-proposed negative volume change upon the disproportionation reaction of Fe^{2+} into Fe^{3+} and Fe^{0} above 10 GPa, which enhances such disproportionation in a deep magma ocean.

1. Introduction

Iron is the most abundant transition metal and exhibits multiple oxidation states in the Earth's mantle. The coordination environments and bond lengths of Fe^{2+}-O and Fe^{3+}-O in silicates change with increasing pressure. The spin states of Fe^{2+} and Fe^{3+} could also change not only in solid phases (Badro et al., 2003; Zhang & Oganov, 2006) but also in melts and glasses under high pressure (Nomura et al., 2011; Gu et al., 2012; Karki & Ghosh, 2018). The changes in the Fe^{2+}-O and Fe^{3+}-O bond lengths will tell their possible spin crossovers under lower-mantle pressures. It has been also suggested that Fe^{2+} disproportionates into Fe^{3+} and metal Fe in a deep magma ocean, depending on the partial molar volumes of FeO and $FeO_{1.5}$ and their compressibilities (O'Neill et al., 2006; Zhang et al., 2017; Armstrong et al., 2019). However, direct measurements of these properties are limited to 1 atm (Lange & Carmichael, 1987; Kress & Carmichael, 1991). They are dependent on the coordination environment of Fe ions, in particular their coordination number and the structure of silicate melts, both of which will change under high pressure (Sanloup et al., 2013a). However, the change in the coordination environment of iron in silicate melt has been experimentally investigated only up to 7.5 GPa by X-ray diffraction measurements (Sanloup et al., 2013b).

The XAFS spectrum is sensitive to the local structure of a specific element of interest including the bond length. It is therefore a useful tool for elucidating changes in the coordination environments and spin states of Fe^{2+} and Fe^{3+} under high pressure. However, the XAFS study of Fe^{2+} and Fe^{3+} in a silicate glass has been difficult at high pressures because diamond anvils absorb X-rays to a large extent at the Fe absorption edge energy (~7.1 keV), while the ambient-pressure XAFS measurements of Fe in silicate glasses have been intensively reported (Farges et al., 2004; Wilke et al., 2007).

70 Here we conducted the XAFS measurements of Fe^{2+} and Fe^{3+} in reduced and oxidized
71 basaltic glasses, respectively, at high pressures in the fluorescence yield mode (Ozawa et
72 al., 2021). The analyses of X-ray absorption near edge structure (XANES) including pre-
73 edge structure and extended X-ray absorption fine structure (EXAFS) demonstrate
74 changes in the Fe^{2+}-O and Fe^{3+}-O bond lengths with increasing pressure up to 83 GPa and
75 60 GPa, respectively, indicating their coordination environment and spin state under
76 pressure. Based on these results, we discuss the spin crossover of Fe^{2+} and Fe^{3+} in basaltic
77 glasses and the disproportionation of Fe^{2+} into Fe^{3+} and Fe^{0} in a deep magma ocean.

78 **2. Results**

79 We collected nine and eight XAFS (both XANES and EXAFS) spectra of reduced and
80 oxidized basaltic glasses with increasing pressure from 1 bar to 83.2 GPa and to 60.0 GPa,
81 respectively (see Experimental Methods in the Supporting Information). The Fe K-edge
82 XANES spectrum comprises three separate features relating to transitions of electrons to
83 different excited states: pre-edge (1s→3d), threshold energy (1s→4s), and white line
84 (1s→4p) (Waychunas et al., 1983) (Figure 1).

85 **2.1. Pre-edge Structure**

86 The pre-edge features were extracted from the normalized XANES spectra to emphasize
87 their characteristics (Figure 1). The calculated centroid position and integrated intensity
88 for the pre-edge absorbance are given for all the spectra in Table S2. The centroid energy
89 and intensity of the pre-edge absorbance at the Fe K-edge are sensitive to the oxidation
90 state and coordination environment of iron atoms in a sample, respectively (Figure 2).

The centroid position of the reduced basalt glass is 7111.92 eV at ambient pressure (Figure 2), indicating that almost all iron was Fe^{2+} in our reduced glass according to Wilke et al. (2005). Its pre-edge intensity observed at 1 bar is consistent with those for reduced basaltic glasses (Wilke et al., 2005) and reduced silicate melts (Alderman et al., 2017), which shows that the coordination number of Fe^{2+} is close to five. As pressure increased, the pre-edge intensity became closer to those of minerals with octahedrally coordinated ferrous iron (Figure 2). This observation suggests that the average coordination number of Fe^{2+} in our reduced glass increased with compression from ~5 at ambient pressure to 6 above 15 GPa.

On the other hand, the centroid position of the oxidized glass is 7113.40 eV at 1 bar (Figure 2), showing $Fe^{2+}/\Sigma Fe = 0.21$, which is consistent with the ratio expected for the condition where this glass was synthesized. Its pre-edge intensity suggests that Fe^{3+} is almost 4-fold at 1 bar. While Wilke et al. (2005) interpreted that Fe^{3+} in their oxidized glass was 5-fold, the pre-edge intensity itself is similar between this study and their measurements, and the discrepancy is attributed to the variation in the pre-edge intensity of reference minerals for tetrahedrally-coordinated Fe^{3+} (Boubnov et al., 2015). The change in the pre-edge intensity with increasing pressure also indicates that the average coordination number of Fe^{3+} increased upon compression from almost 4 at 1 bar to 6 above 15 GPa (Figure 2).

2.2. Absorption Edge Structure

The information on the valence state of Fe ion and the Fe-O bond length are included not only in the pre-edge feature but also in the absorption edge structure, in particular (i) the peak energy of the white line and (ii) the threshold energy, which is a structure around

114 the maximum of $d\mu_N/dE$ (μ_N, normalized absorbance; E, energy) (Figure 1 and Table S2).
115 It is known that both the white line peak energy and the threshold energy are higher for
116 Fe^{3+} than for Fe^{2+}.

117 In the case of the reduced glass, the while line peak energy significantly increased with
118 increasing pressure above 15 GPa (Figure 3a). Indeed, the increase in the peak energy is
119 well correlated to the shortening of the average Fe^{2+}-O bond length (see the next section)
120 (Figure S1). Previously Waychunas et al. (1983) reported similar observations in minerals.
121 In contrast, the threshold energy changed little with increasing pressure (Figure 3c).
122 While the first derivative spectrum at ambient pressure had a double-peaked shape (Berry
123 et al., 2003), it gradually became single-peak as pressure increased. The effect of silicate
124 glass composition may be important for the threshold energy; a reduced W-doped basaltic
125 glass exhibited a distinct value (Ozawa et al., 2021) (Figure S2). It contrasts the fact that
126 the compositional effect on the white line peak energy is quite small.

127 Our data on the oxidized glass demonstrate a negative correlation between the Fe^{3+}-O
128 bond length and the peak position of the white line for Fe^{3+}, similar to the case of Fe^{2+}
129 (Figure S1). The white line peak energy certainly decreased with increasing pressure from
130 1 bar to ~15 GPa and then increased at higher pressures (Figure 3b). It should be attributed
131 to the increase and subsequent decrease in the Fe^{3+}-O bond length in our oxidized glass
132 (see the next section). The first-derivative spectrum at 1 bar given in Figure 3d is similar
133 to that of an Fe^{3+}-rich silicate glass in Berry et al. (2003). The correlation between the
134 e^{3+}-O bond length and the threshold energy is not clear (Figure S2).

135 **2.3. EXAFS Spectra**

All of the present XAFS measurements include the EXAFS spectra that provide the Fe-O bond length quantitatively. The extracted k^3-weighted oscillations are shown in Figure S3. Considering that all Fe was Fe^{2+} in the reduced glass, we determined the Fe^{2+}-O bond length at each pressure from the EXAFS analyses (Figure 4 and Table S2).

We obtained the Fe^{2+}-O bond length r_{Fe2+-O} = 1.98 ± 0.02 Å at 1 bar for the reduced basaltic glass (Figure 4a). The r_{Fe2+-O} remained constant within errors up to 15.1 GPa, in which the bond length elongation because of an increase in the coordination number was compensated by shortening due to a simple compression effect. At higher pressures, the average Fe^{2+}-O bond length decreased continuously with increasing pressure up to 83.2 GPa. In this pressure range, the effect of the coordination number increase may be minor. The shortening per a given pressure increase above 15 GPa is found to be greater than that of the Si-O (Prescher et al., 2017) and Ge-O bonds (Hong et al., 2014) (Figure 4b).

The Fe^{3+}-O bond length in our oxidized glass was also determined at each pressure from the EXAFS analyses. At 1 bar, r_{Fe3+-O} is found to be 1.87 ± 0.02 Å (Figure 4a), consistent with the interatomic distance between four-fold Fe^{3+} and O in a peralkaline rhyolitic glass at ambient pressure (Giuli et al., 2012). The Fe^{3+}-O bond length increased with increasing pressure up to 16.2 GPa unlike the case of Fe^{2+}, indicating that the effect of the coordination number increase exceeded the simple bond length shortening by compression. With further compression from 16.2 GPa to 60.0 GPa, the Fe^{3+}- O bond length decreased constantly as for Fe^{2+}.

As described above, we found negative correlations between the Fe^{2+}-O/Fe^{3+}-O bond lengths and the white line peak energy (Figure S1), which indicates that the coordination number has little influence on the peak position of the white line. On the other hand, the

159 threshold energy also shows negative correlation with the Fe^{2+}-O bond length, but does
160 not have a clear correlation with the Fe^{3+}-O bond length (Figure S2). The white line peak
161 position in the XANES spectra can be a good indicator of the Fe^{2+}-O/Fe^{3+}-O bond lengths
162 in silicate melts and glasses when high-quality EXAFS data are not available.

163 ## 3. Discussion

164 ### 3.1. Compression Behaviors of Fe^{2+} and Fe^{3+} in Basaltic Glasses

165 The present pre-edge and EXAFS analyses showed that Fe^{3+} is almost 4-fold coordinated
166 in our basaltic glass sample at 1 bar, while Fe^{2+} is ~5-fold coordinated (Figure 2). The 4-
167 fold Fe^{3+} is considered to be a network former, polymerizing silicate melt/glass structures
168 and being accompanied with a charge compensator ion like Na^{+} and Ca^{2+}. In contrast, the
169 ~5-fold Fe^{2+} is a network modifier or plays an intermediate role (Alderman et al., 2017).

170 Below ~15 GPa, while the Fe^{2+}-O bond length remained similar, the Fe^{3+}-O bond was
171 elongated remarkably with compression (Figure 4a). Such difference is likely due to the
172 difference in their coordination number at 1 bar; the large increase in the Fe^{3+}-O bond
173 length below 15 GPa is attributed to an increase in the coordination number of ferric iron
174 from four to six, whereas the approximately uniform Fe^{2+}-O bond length is likely a
175 consequence of a small increase in its coordination number from about five to six. At the
176 higher pressure range, both the Fe^{2+}-O and Fe^{3+}-O bond lengths decreased similarly with
177 increasing pressure (Figure 4a), in which the effect of an increase in the coordination
178 number is likely to be minimal.

179 We compare the pressure-induced changes in the Fe^{2+}-O and Fe^{3+}-O bond lengths
180 observed in this study with those of Mg^{2+}-O (Ghosh & Karki, 2020), Ca^{2+}-O and Al^{3+}-O

(Ghosh & Karki, 2018), Si^{4+}-O (Prescher et al., 2017), Ge^{4+}-O (Hong et al., 2014), and W^{6+}-O (Ozawa et al., 2021) previously reported in silicate/germanate melt and glasses (Figure 4a, b). For both Mg^{2+} and Ca^{2+}, the bond lengths are almost constant from ambient pressure to 15 GPa, similar to the case of Fe^{2+}-O, indicating that the bond elongation by coordination number increase and the bond shortening by a simple compression effect are balanced. In contrast, the Al^{3+}-O bond length increases with pressure to 15 GPa as for Fe^{3+}, which indicates the role of Fe^{3+} in silicate glass structures is similar to that of Al^{3+} at such low pressure range. At higher pressures (>15 GPa for Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, and Fe^{3+}, >~20 GPa for Ge^{4+}, and >~30 GPa for Si^{4+} and W^{6+}), the bond lengths then decrease with compression (Figure 4a, b). The Fe^{2+}-O and Fe^{3+}-O bond lengths became shorter by -0.0015 Å/GPa and -0.0017 Å/GPa, respectively. They are equivalent to -0.0017 Å/GPa for Mg^{2+}-O in $(Mg,Fe)SiO_3$ melt at 3000 K (Ghosh & Karki, 2020) and -0.0024 Å/GPa for Ca^{2+}-O in $CaAl_2Si_2O_8$ glass (Ghosh & Karki, 2018). The similarity to the Mg^{2+}-O and Ca^{2+}-O bonds suggests that not only Fe^{2+} but also Fe^{3+} act as network modifiers under high pressures where they are predominantly six-fold coordinated. In contrast, for high field strength elements (with large valence/ionic-radius ratios), Si^{4+}-O in SiO_2 glass (-0.0006 Å/GPa), Ge^{4+}-O in GeO_2 glass (-0.0004 Å/GPa), W^{6+}-O in basaltic glass (-0.0001 Å/GPa), and Al^{3+}-O in $CaAl_2Si_2O_8$ glass (-0.0005 Å/GPa) exhibit more gradual changes (Prescher et al., 2017; Ozawa et al., 2021; Ghosh and Karki, 2018). These Si^{4+}, Ge^{4+}, W^{6+}, and Al^{3+} are the network forming cations with six-fold coordination at >~30 GPa. The gradual decrease in these bond lengths may be a result of the volume reduction by enhanced distortion of coordinated octahedra instead of isostructural compression (Spiekermann et al., 2019).

3.2. Spin Crossover of Iron in Silicate Glasses

Previous studies examined possible spin crossovers of ferrous and ferric iron in silicate glasses under high pressures based on X-ray emission spectroscopy (XES) and Mössbauer spectroscopy (Nomura et al., 2011; Gu et al., 2012; Murakami et al., 2014; Mao et al., 2014; Prescher et al., 2014; Dorfman et al., 2016; Solomatova et al., 2017). The Fe^{2+}-O and Fe^{3+}-O bond lengths obtained by XAFS measurements also show the spin state of ferrous and ferric iron at high pressures.

In Figure 4c, we compare the Fe^{2+}-O and Fe^{3+}-O bond lengths in our glass samples determined by the EXAFS analyses with those in Fe-bearing $MgSiO_3$ melt at 3000 K obtained by first principles molecular dynamics simulations (Ghosh & Karki, 2020). Although the bond lengths in the latter are longer partly because of thermal expansion, they exhibit similar pressure effects. The behavior of the Fe^{2+}-O bond length below 15 GPa is an exception; while it increased rapidly in the Fe-bearing $MgSiO_3$ melt, it changed little in our reduced glass. Such difference can be attributed to the difference in the coordination number of ferrous iron at ambient pressure; it was shown to be less than four in silicate (basaltic) melts by previous first principles simulations (Bajgain et al., 2015; Solomatova & Caracas, 2019; Ghosh & Karki, 2020), whereas it has been reported to be about five in glasses and melts by experimental studies including the present one (Alderman et al., 2017).

Upon compression from 15 to 83 GPa, the Fe^{2+}-O bond length in our basaltic glass decreased smoothly by ~0.1 Å (Figure 4c). Such shortening is similar to that calculated for the high-spin Fe^{2+} in $Mg_{0.75}Fe_{0.25}SiO_3$ melt (Ghosh & Karki, 2020). They also calculated for the low-spin Fe^{2+}, demonstrating much shorter bond lengths by ~0.2 Å

above 15 GPa (such difference is consistent with the difference in the ionic radius between six-fold high-spin and low-spin ferrous iron at 1 bar). The supposed low-spin Fe^{2+}-O bond length in a basaltic glass based on the calculations by Ghosh & Karki (2020) is substantially shorter than that of Fe^{2+}-O observed in this study.

Previous XES measurements of $Mg_{0.95}Fe_{0.05}SiO_3$ glass (Nomura et al., 2011) and $Mg_{0.8}Fe_{0.2}SiO_3$ and $Mg_{0.75}Fe_{0.20}Al_{0.05}SiO_3$ glasses (Gu et al., 2012) demonstrated a complete spin crossover of ferrous iron at 77 GPa and a partial loss of spin moment at >93 GPa, respectively. In addition, the Mössbauer measurements by Murakami et al. (2014) suggested a transition of Fe^{2+} to an intermediate-spin state in $(Mg_{0.8}Fe_{0.2})SiO_3$ glass. In contrast, Mao et al. (2014) analyzed the XES spectra taking the broadening effect into consideration and argued that all Fe remains in the high-spin state in an (Al, Fe)-bearing silicate glass up to 126 GPa. The Mössbauer study by Solomatova et al. (2017) argued that ferrous iron remains high-spin to ~100 GPa in a basaltic glass. The present data supports high-spin Fe^{2+} in basaltic glasses up to 83 GPa (Figure 4c). The apparent discrepancies among these studies may be attributed to the differences in glass composition.

The compression behavior of the Fe^{3+}-O bond length in our oxidized glass is similar to that theoretically calculated for the high-spin Fe^{3+} in $Mg_{0.875}Fe^{3+}_{0.25}Si_{0.875}O_3$ melt (Ghosh & Karki, 2020) (Figure 4c). Such similarity supports that Fe^{3+} remains high spin, at least to 60 GPa. The XES and Mössbauer measurements on $Fe_3Al_2Si_3O_{12}$ almandine glass by Dorfman et al. (2016) argued for the high-spin to low-spin crossover of Fe^{3+} between ambient pressure and 30 GPa. Such discrepancy may be also due to the difference in glass sample composition. Alternatively it is also possible that the Mössbauer observations by

250 Dorfman and others may be explained by the distortion of coordination polyhedron as
251 argued for an Fe^{3+}-rich sodium silicate glass (Prescher et al., 2014).

252 **3.3. Disproportionation of Fe^{2+} in a Deep Magma Ocean**

253 The earlier experiments performed by Armstrong et al. (2019) observed that the $Fe^{3+}/\Sigma Fe$
254 ratio in a silicate melt increased with increasing pressure above 10 GPa under a given
255 oxygen fugacity buffer, suggesting that Fe^{2+} disproportionates into Fe^{3+} and metal in a
256 deep magma ocean. They attributed it to the smaller partial molar volume of $FeO_{1.5}$ than
257 that of FeO in melt above 10 GPa. Indeed, the present study indicates that the coordination
258 number of Fe^{3+} increases rapidly from four at 1 atm to six at ~15 GPa (Figure 2). It causes
259 a remarkable reduction in the partial molar volume V of $FeO_{1.5}$ compared to that of FeO
260 in this pressure range. These support negative ΔV (= $V_{FeO1.5}$ - V_{FeO}) and resulting the
261 disproportionation of Fe^{2+} in the magma ocean above 10 GPa (Armstrong et al., 2019).
262 The recent first principles study by Deng et al. (2020) reported the positive ΔV even above
263 10 GPa, but it is likely due to an underestimation of the coordination number of Fe^{2+} at
264 ambient pressure, which leads to an overestimation of the compressibility of the partial
265 molar volume of FeO.

266 With increasing pressure above ~15 GPa, the Fe^{2+}-O bond length changed similarly to
267 that of Fe^{3+}-O (Figure 4c). This means that ΔV is almost unchanged upon compression in
268 this pressure range, at least to 60 GPa. If ΔV is negative at 10–25 GPa (Armstrong et al.,
269 2019), it stays negative and expands the stability of Fe^{3+} relative to Fe^{2+} in silicate melts
270 at higher pressures. It therefore supports that the disproportionation of FeO into $Fe_{1.5}O$
271 and metal Fe in a magma ocean is more enhanced with increasing pressure above 10 GPa
272 to lower-mantle conditions. Metal Fe produced by such disproportionation reaction may

have been segregated into the Earth's core, increasing the oxygen fugacity of the magma ocean, which changed the metal-silicate partitioning of siderophile elements (Wade & Wood, 2005) and the composition of early Earth atmosphere (Hirschmann, 2012).

4. Conclusions

Present *in-situ* high-pressure XAFS measurements elucidated the compression behavior of the coordination environments around Fe^{2+} and Fe^{3+} in basaltic glasses up to 83 GPa and 60 GPa, respectively. Pre-edge and EXAFS analyses demonstrated that between 1 atm and ~15 GPa, the coordination number of Fe^{2+} increased from ~5 to 6, while that of Fe^{3+} augmented from almost 4 to 6. At higher pressures, both Fe^{2+}-O and Fe^{3+}-O bond lengths decreased smoothly with increasing pressure, indicating minimal increase in their coordination number. In this pressure range, the observed compression behaviors of the Fe^{2+}-O and Fe^{3+}-O bonds are similar to those of earlier theoretical predictions of high-spin Fe^{2+} and Fe^{3+} in $Mg_{0.75}Fe^{2+}_{0.25}SiO_3$ and $Mg_{0.875}Fe^{3+}_{0.25}Si_{0.875}O_3$ melts, respectively, suggesting both Fe^{2+} and Fe^{3+} in the basaltic glasses remain high-spin at least to the maximum pressures explored here.

A larger change in the coordination number of Fe^{3+} than that of Fe^{2+} below 15 GPa suggests that the partial molar volume of $FeO_{1.5}$ is more compressible than that of FeO in this pressure range. It will lead to negative ΔV ($= V_{FeO1.5} - V_{FeO}$) above 10 GPa (Armstrong et al., 2019), which drives the disproportionation of Fe^{2+} into Fe^{3+} and metal Fe in a deep magma ocean. Our data showed that the both the Fe^{2+}-O and Fe^{3+}-O bond lengths decreased similarly with increasing pressure above 15 GPa. It suggests that ΔV would remain negative upon compression at least to 60 GPa, which accelerates the disproportionation reaction at deeper level of the magma ocean.

Open Research

Datasets for this research are found in Tables S1 and S2 available online (from https://doi.org/10.5281/zenodo.5749615).

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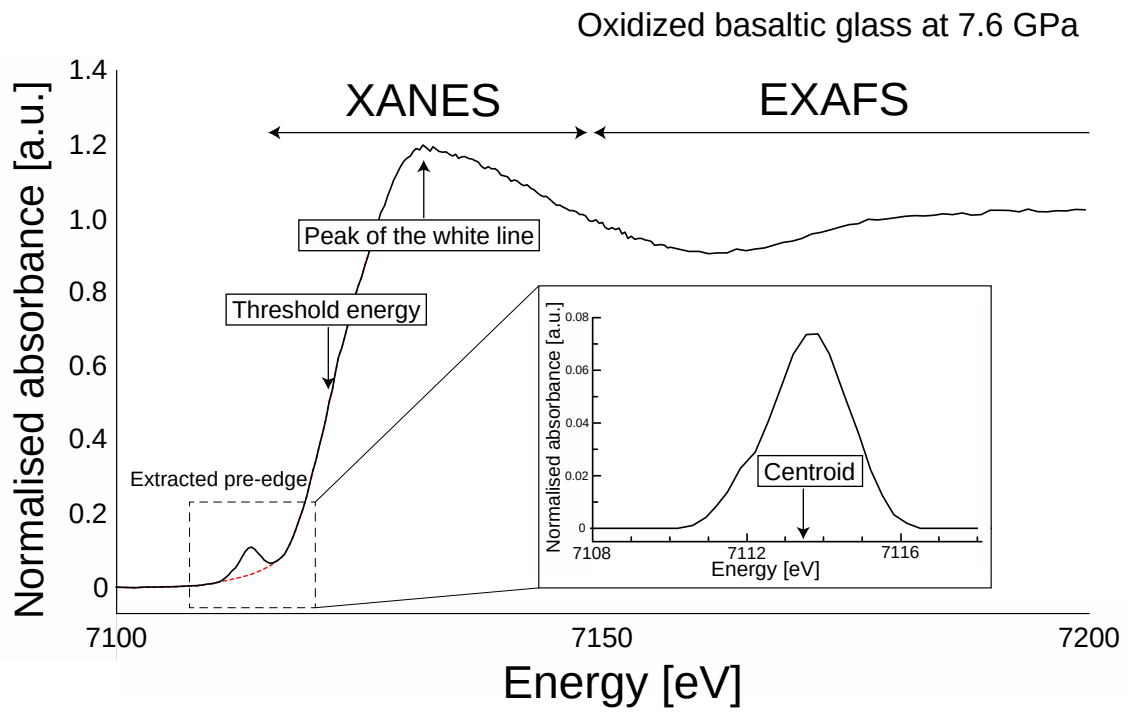

Figure 1. The μ-XAFS spectrum of oxidized basaltic glass in a DAC collected at 7.6 GPa, including the pre-edge features with centroid position, XANES with the threshold energy and the peak of the while line, and EXAFS oscillations. Red dashed line is a cubic spline function for the background of the pre-edge signals (Wilke et al., 2001).

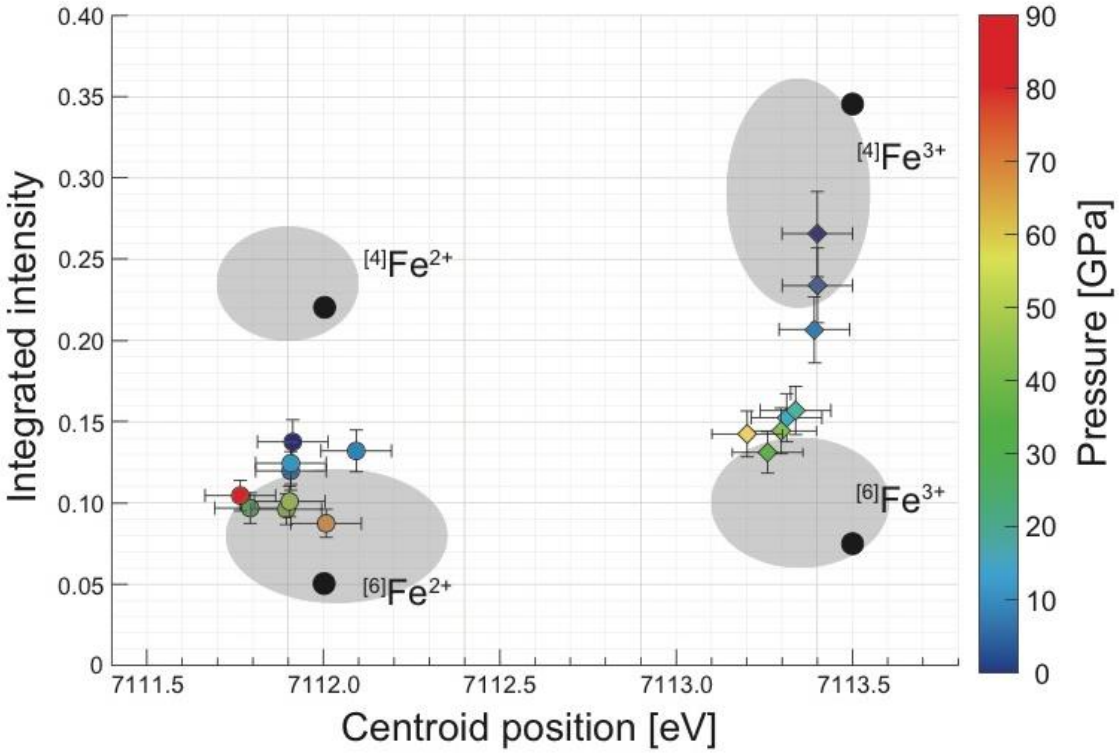

Figure 2. The pre-edge variogram of the centroid position vs. integrated intensity for reduced (circles) and oxidized basaltic glasses (diamonds) at high pressures. Pressure is given by color. Shaded areas indicate the ranges for ferrous and ferric iron with four- and six-fold coordination (Boubnov et al., 2015). Black circles represent the data for minerals with 4- and 6-fold ferrous/ferric iron given by Wilke et al. (2001).

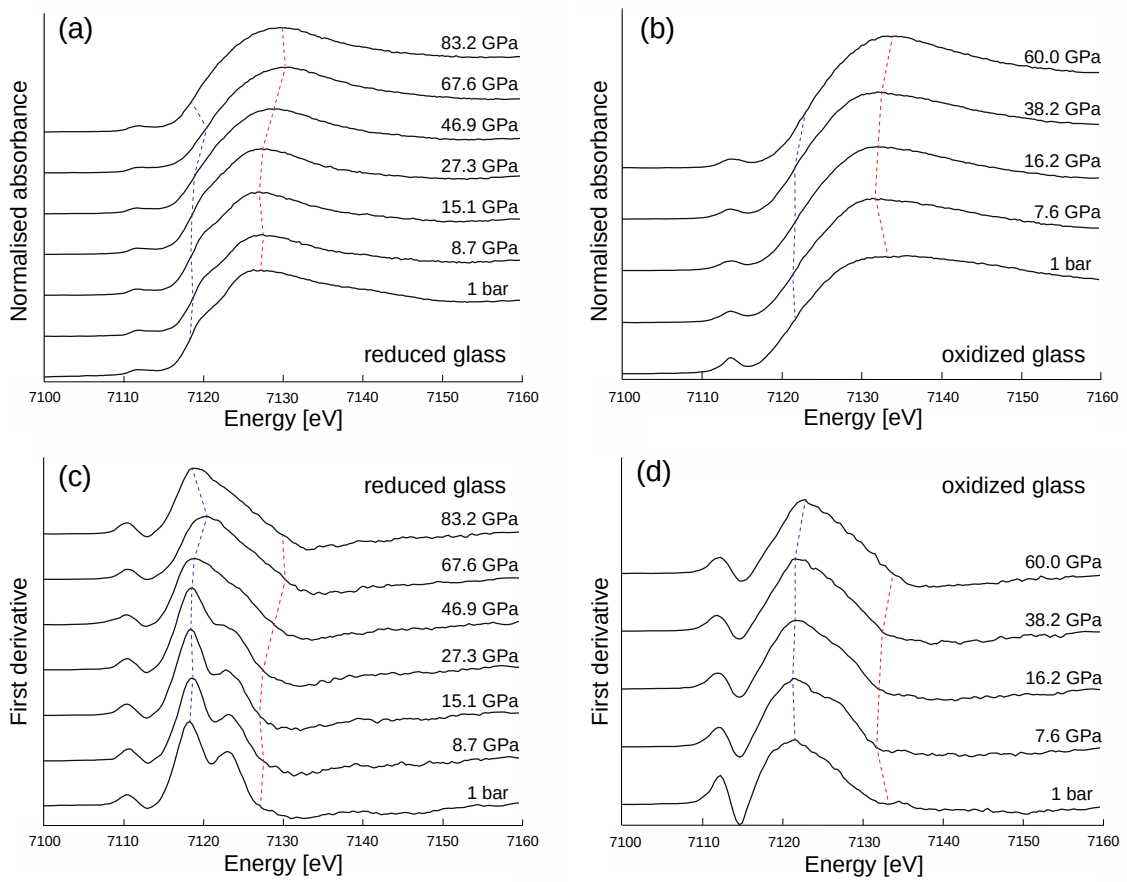

Figure 3. Fe K-edge XANES spectra and their first derivative spectra obtained by three-point moving average for reduced (a, c) and oxidized (b, d) basaltic glasses at high pressures. The spectrum of the reduced glass at 67.6 GPa is of a W-doped basaltic glass used in Ozawa et al. (2021). Red and blue dashed lines indicate pressure-evolutions of the peak energy of the white line and the threshold energy, respectively (see Figure 1).

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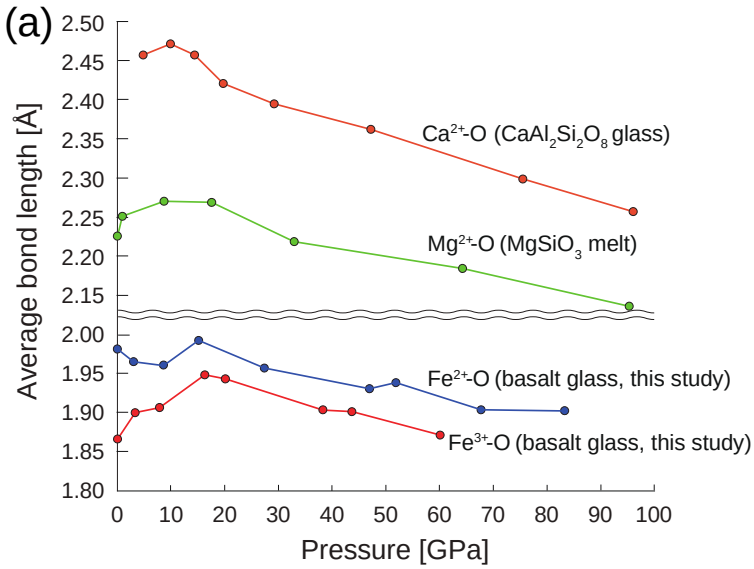
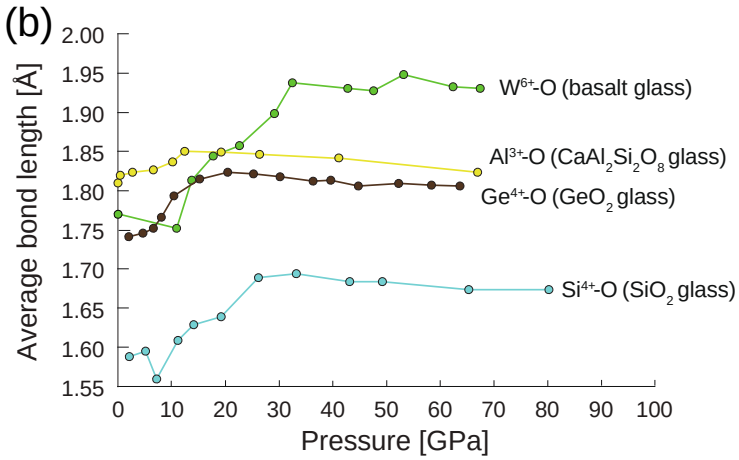
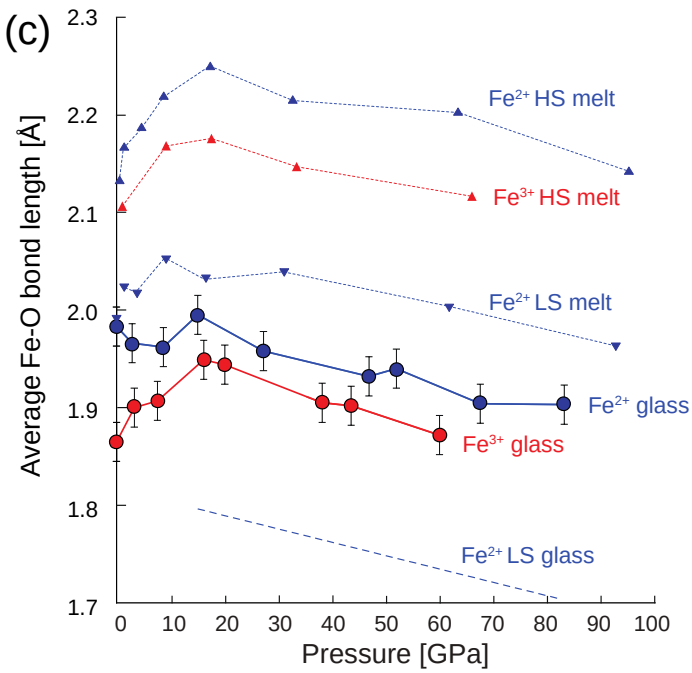

(a)
Average bond length [Å]
Pressure [GPa]
Ca2+-O (CaAl2Si2O8 glass)
Mg2+-O (MgSiO3 melt)
Fe2+-O (basalt glass, this study)
Fe3+-O (basalt glass, this study)


(b)
Average bond length [Å]
Pressure [GPa]
W6+-O (basalt glass)
Al3+-O (CaAl2Si2O8 glass)
Ge4+-O (GeO2 glass)
Si4+-O (SiO2 glass)


(c)
Average Fe-O bond length [Å]
Pressure [GPa]
Fe2+ HS melt
Fe3+ HS melt
Fe2+ LS melt
Fe2+ glass
Fe3+ glass
Fe2+ LS glass

478

Figure 4. (a, b) Interatomic distances between various cations and oxygen in silicate/germanate melt and glasses; Ca^{2+}-O and Al^{3+}-O (Ghosh & Karki, 2018), Mg^{2+}-O (Ghosh & Karki, 2020), $Fe^{2+/3+}$-O (this study), Si^{4+}-O (Prescher et al., 2017), Ge^{4+}-O (Hong et al., 2014), and W^{6+}-O (Ozawa et al., 2021). (c) Comparison of the Fe^{2+}-O (blue lines) and Fe^{3+}-O (red lines) bond lengths in our basaltic glasses with those in Fe-bearing $MgSiO_3$ melts (dotted lines) at 3000 K obtained by ab initio molecular dynamics simulations (Ghosh & Karki, 2020). The blue dashed line is for low-spin Fe^{2+} in the glass, estimated from a difference in the calculated Fe^{2+}-O bond length between high-spin and low-spin states.

Geophysical Research Letters

Supporting Information for

High-Pressure XAFS Measurements of the Coordination Environments of Fe^{2+} and Fe^{3+} in Basaltic Glasses

Keisuke Ozawa[1], Kei Hirose[1,2], and Yoshio Takahashi[1,3]

[1]Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

[2]Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan

[3]Institute of Materials Structure Science, High-Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan

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Experimental Methods

A couple of basaltic glasses were synthesized under reduced and oxidized conditions for the present XAFS measurements. Their chemical compositions and homogeneity were examined with an electron probe microanalyzer (FE-EPMA, JEOL JXA-8530F) (Table S1). They were prepared originally from gel and melted in reducing H_2-CO_2 gas atmosphere at 1473 K (three log units below the QFM buffer) and in air (oxidizing condition) at 1573 K, respectively, for 30 mins. Under the former reducing condition, ferrous iron should be predominant in the glass ($Fe^{2+}/\Sigma Fe = 0.985$) according to Berry et al. (2018). On the other hand, Fe in the latter oxidized glass should be dominated by ferric iron.

We collected both the XANES and EXAFS spectra of these basaltic glasses with increasing pressure at the beamline BL-4A, the Photon Factory, KEK with a beam focused to 5 μm × 5 μm area on a sample by using a K-B mirror system (Figure 1). The spectrum of Fe metal foil was also obtained in a similar manner at ambient condition to calibrate the X-ray energy based on the first inflection point of Fe metal foil at 7111.08 eV following Wilke et al. (2001). Basaltic glasses were compressed to high pressures in a diamond-anvil cell (DAC) using flat anvils with 200–600 μm culet size. In order to minimize X-ray absorption, we employed an X-ray transparent gasket (Merkel & Yagi, 2005) and collected the XAFS spectra under the experimental setting same as described in Ozawa et al. (2021). Measurements were performed near the K-edge of Fe in the fluorescence yield mode. Pressure was measured based on a Raman shift of a diamond anvil above 10 GPa (Akahama & Kawamura, 2004) and the ruby fluorescence method at lower pressures (Mao et al., 1978).

The XAFS scan was performed in an energy range of 7065–7450 eV with 0.3 eV steps for the pre-edge and XANES regions and > 0.9 eV steps for other regions. The spectra were normalized by the average absorbance at the 7200–7300 eV region. Then, the pre-edge feature was obtained by subtracting background that is estimated by using a cubic spline function (Wilke et al., 2001) (Figure 1). After the extraction, the centroid position (intensity-weighted pre-edge position) and the intensity of the pre-edge absorption were calculated (Table S2). We considered uncertainties to be ±10% in pre-edge intensity and ±0.1 eV in the centroid energy following Alderman et al. (2017). The pre-edge intensities at 1 bar for both reduced and oxidized basaltic glasses obtained here in the fluorescence yield mode are comparable to those measured in the transmission mode in Wilke et al. (2005). It indicates that the thickness effect on the pre-edge intensity is negligible compared to the uncertainty in the present measurements.

EXAFS spectra were analyzed by the REX2000 software (Rigaku Co. Ltd.) The k^3-weighted EXAFS oscillation was extracted from each spectrum, and Fourier transformed within the k-range of 2.6–8.4 $Å^{-1}$ to the radial structure functions. In order to extract information on the nearest neighbors of Fe atoms from the radial structural function, the first-neighbour shell EXAFS was filtered out using Hanning window function. The filtered radial structural functions were back-transformed to k-space using the backscattering amplitudes, and phase-shift functions of Fe-O were extracted by the FEFF 7.0 (Zabinsky et al., 1995) based on the structure of $FeSiO_3$ ferrosilite. Curve fitting analysis was performed for the first shell (Fe-O).

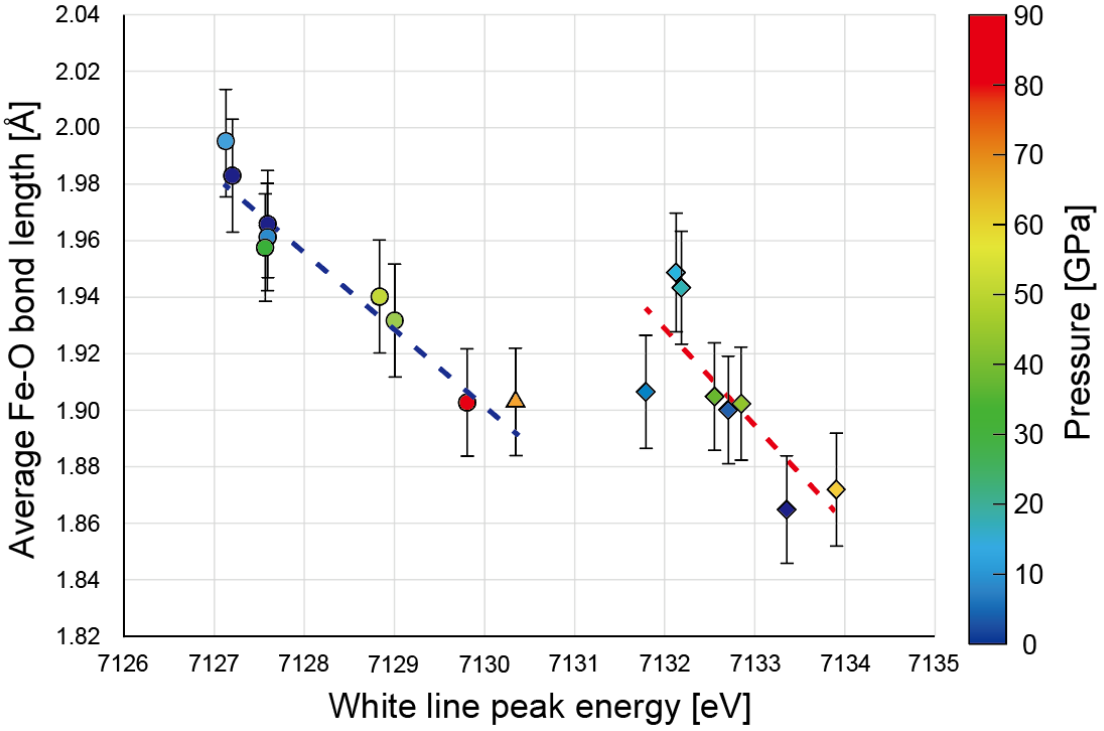

Figure S1. The peak energy of the white line vs. the average Fe^{2+}-O (circles, reduced glass; triangle, W-doped glass used in Ozawa et al., 2021) and Fe^{3+}-O bond lengths (diamonds, oxidized glass).

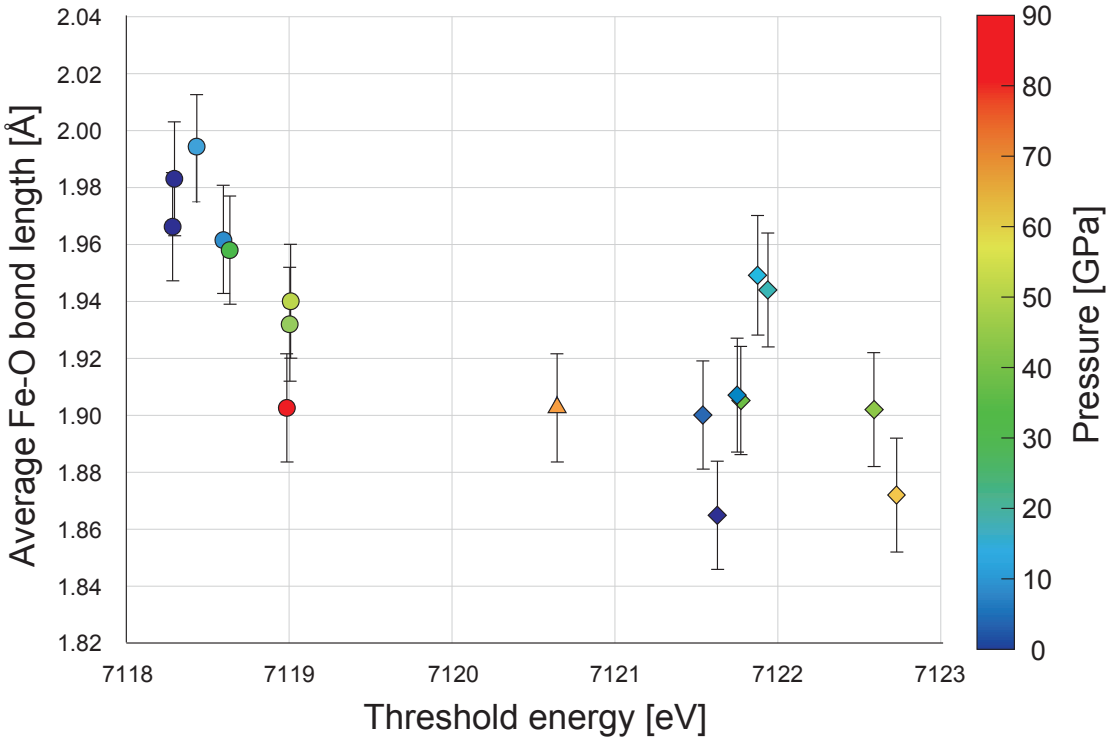

Figure S2. The threshold energy vs. the average Fe^{2+}-O and Fe^{3+}-O bond lengths. Symbols are the same as those in Figure S1.

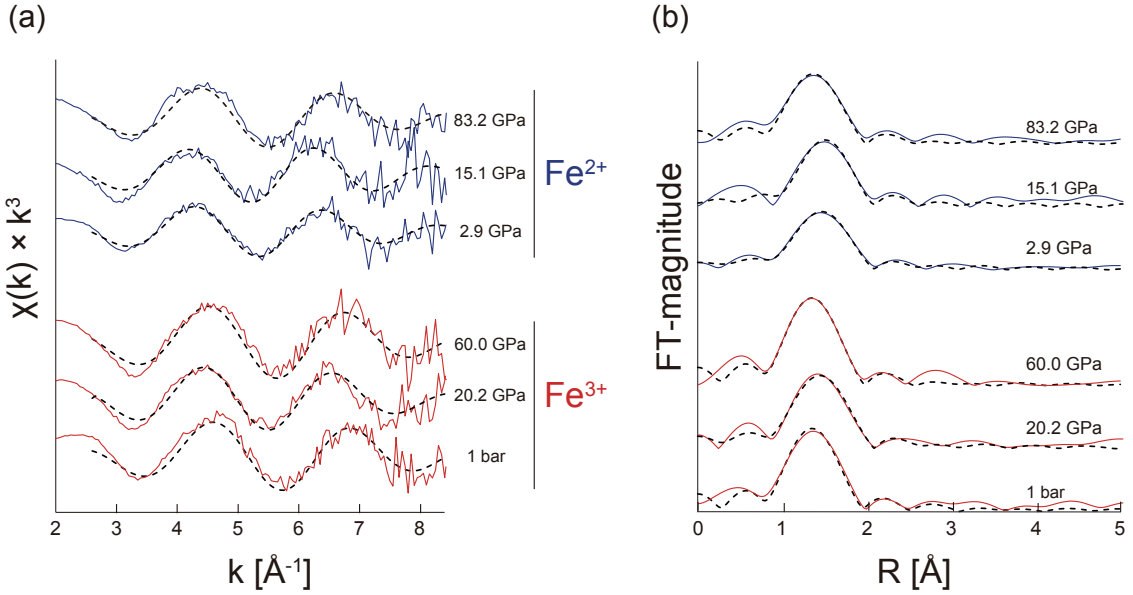

Figure S3. EXAFS oscillations and radial structure functions of Fe in the reduced (blue) and oxidized (red) basaltic glasses. (a) k^3-weighted oscillations, $\chi(k) \times k^3$, extracted from EXAFS spectra. (b) The radial structural function at the K-edge for Fe which was Fourie transformed (FT) from k^3-weighted EXAFS oscillations in (a). The black dashed curves in (a) and (b) show simulation data of EXAFS spectra using a parameter extracted by FEFF 7.0.

Table S1

Chemical Compositions of Reduced and Oxidized Basaltic Glasses

wt%	Reduced glass	Oxidized glass
SiO_2	49.50(35)	50.33(58)
TiO_2	1.09(5)	1.13(6)
Al_2O_3	14.68(11)	14.77(13)
FeO*	9.53(13)	10.39(12)
MgO	8.42(11)	8.45(9)
CaO	9.52(3)	9.36(11)
Na_2O	2.89(16)	3.39(7)
K_2O	0.12(2)	0.14(3)
Total	95.76	97.97

The values in parentheses represent one standard deviations in the last digits.

*total Fe as FeO.

Table S2

Pre-edge, XANES, and EXAFS Data for Reduced and Oxidized Basaltic Glasses

		Pre-edge		XANES		EXAFS	
	Pressure (GPa)	Centroid (eV)	Intensity	Threshold energy (eV)	Peak Energy (eV)	k range	Fe-O bond length (Å)
Reduced glass	1 bar	7111.92	0.1381	7118.30	7127.20	2.6–8.4	1.983 (20)
	2.9	7111.91	0.1200	7118.28	7127.58	2.6–8.4	1.966 (19)
	8.7	7112.09	0.1313	7118.60	7127.59	2.6–8.4	1.962 (19)
	15.1	7111.92	0.1248	7118.43	7127.13	2.6–8.4	1.995 (18)
	27.3	7111.79	0.0970	7118.64	7127.55	2.6–8.4	1.958 (19)
	46.9	7111.89	0.0968	7119.00	7128.99	2.6–8.4	1.932 (20)
	52.0	7111.91	0.1021	7119.01	7128.83	2.6–8.4	1.940 (20)
	67.6*	7112.01	0.0873	7120.64	7130.34	2.6–8.4	1.904 (19)
	83.2	7111.76	0.1044	7118.98	7129.81	2.6–8.4	1.903 (19)
Oxidized glass	1 bar	7113.40	0.2665	7121.63	7133.36	2.6–8.4	1.865 (19)
	3.3	7113.40	0.2332	7121.54	7132.70	2.6–8.4	1.900 (19)
	7.6	7113.39	0.2071	7121.75	7131.79	2.6–8.4	1.907 (20)
	16.2	7113.32	0.1514	7121.88	7132.13	2.6–8.4	1.949 (21)
	20.1	7113.34	0.1578	7121.94	7132.19	2.6–8.4	1.944 (20)
	38.2	7113.26	0.1312	7121.77	7132.56	2.6–8.4	1.905 (19)
	43.6	7113.30	0.1449	7122.59	7132.85	2.6–8.4	1.902 (20)
	60.0	7113.20	0.1420	7122.73	7133.91	2.6–8.4	1.872 (20)

The values in parentheses represent one standard deviations in the last digits. Uncertainties in the pre-edge intensity and the centroid energy are ±10% and ±0.1 eV, respectively.

*Reduced W-doped glass used in Ozawa et al. (2021).