during XANES analysis, which leads to an over-estimation of their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. Here, we determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in olivine-hosted melt inclusions from various arcs, MORB and OIB localities by Mössbauer and XANES spectroscopy. A careful evaluation of beam damage during XANES analysis was carried out with attentive investigation of XANES spectra and time series collected on hydrous basaltic and basanitic glasses using different radiation doses. Therefore, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained with these two methods on the same sample set allowed us to constrain the oxidation state of those magmas by avoiding the effect of beam-induced oxidation that may occur during XANES analysis.

Our results show that melt inclusions from MORBs, OIBs and arc basalts display mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.10 ± 0.05 ($n=5$), 0.13 ± 0.05 ($n=2$) and 0.25 ± 0.15 ($n=19$), respectively. Mount Etna melt inclusions display a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.26 ± 0.05 ($n=7$). Therefore, they confirm that arc magmas are more oxidized than those from hot spots and mid-ocean ridges. Furthermore, they suggest that the range in the oxidation state observed in our melt inclusion dataset may be linked to changes in the oxidation state of the mantle beneath arcs due to subduction processes.

1. Introduction

Many studies have demonstrated that arc basalts are more oxidized ($\sim \text{QFM}+1.5 \pm 1$; $f\text{O}_2$ given relatively to the quartz-fayalite-magnetite buffer; Gaillard et al. 2015 and references therein) than MORBs ($\text{QFM}-1.2$ to $\sim \text{QFM}$; e.g. Berry et al., 2018; Bézoz and Humler, 2005; Birner et al, 2018; Christie et al., 1986; Cottrell and Kelley, 2011, 2013; Mallmann and O'Neill, 2009; O'Neill et al., 2018; H. L. Zhang et al., 2018). However, the oxidation state of the sub-arc mantle is still debated. Kelley and Cottrell (2009, 2012) and Brounce et al. (2014, 2015) suggest that variations in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio measured in basaltic glasses and olivine-hosted

melt inclusions from mid-ocean ridges and arcs can be explained by the sub-arc mantle being more oxidized than the mantle beneath ridges. On the other hand, Mallmann and O'Neill (2009) and Lee et al. (2005, 2010) proposed the use of other $f\text{O}_2$ proxies, namely V/Sc and Zn/ ΣFe ratios in lavas and suggested that the oxidation state of the mantle wedge cannot be distinguished from that of the MORB mantle (see also Dauphas et al., 2009; Li and Lee, 2004).

Fe is an abundant multivalent 3d-transition element in silicate glasses, and its speciation is linked to the oxygen fugacity of the system (Kress and Carmichael, 1991). Many techniques allow measurements of the Fe oxidation state, such as wet chemistry (Bézos and Humler, 2005; Christie et al., 1986), Mössbauer spectroscopy (e.g. Jayasuriya et al., 2004; Mccammon, 2004; Partzsch et al., 2004; Zhang et al., 2018), the Flank method on the electron probe (e.g. Fialin et al., 2001; Zhang et al., 2018) and X-Ray absorption near-edge structure (XANES) spectroscopy. Micro-XANES has been widely used to provide $\text{Fe}^{3+}/\Sigma\text{Fe}$ in silicate glasses (e.g. Berry et al., 2003; Cottrell et al., 2009; Wilke et al., 2004). Its low detection limit and high spatial resolution of $\sim 1\text{-}5\text{ }\mu\text{m}$ makes it the ideal technique to analyze melt inclusions trapped in olivine (e.g. Brounce et al., 2014; Hartley et al., 2017; Kelley and Cottrell, 2009, 2012; Moussallam et al., 2016). Because magmas trapped as melt inclusions in primitive crystals are less affected by secondary processes such as degassing of volatiles and fractional crystallization than external magmas, they provide a unique window into the pre-eruptive conditions of magmas.

However, a recent study by Cottrell et al. (2018) showed that hydrous glasses can be affected by beam-induced oxidation during XANES analysis. According to this study, the iron oxidation state of glasses can be modified as a function of the radiation dose (which they defined as the total photons delivered per square micrometer) used to perform analyses, their water contents and their initial iron oxidation state. They found that the higher the radiation dose and

water content of glasses and the lower their initial $\text{Fe}^{3+}/\Sigma\text{Fe}$, the higher the over-estimation of their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.

In this study, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in olivine-hosted melt inclusions from various arcs, OIB and MORB localities were analyzed by μ -XANES spectroscopy after determination of the analytical conditions that allowed us to mitigate beam damage. In addition, for the first time, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of a subset of those melt inclusions were analyzed by synchrotron Mössbauer source spectroscopy. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained with these two methods on the same sample set allow us to constrain the oxidation state of iron in those magmas by avoiding the effect of beam-induced oxidation that may occur during XANES analysis. Then we were able to confirm that arc magmas are more oxidized than those from hot spots and mid-ocean ridges. Our results suggest that the variation in the oxidation state observed in our melt inclusion dataset may be linked to changes in the oxidation state of the mantle beneath arcs due to subduction processes.

2. Natural samples

Secondary processes such as magmatic differentiation and degassing of volatile species can affect magmas during their ascent to the surface and modify their chemical composition and their oxidation state (e.g. Cottrell and Kelley, 2011; Kelley and Cottrell, 2012; Moussallam et al., 2016). To investigate the oxidation state of primitive magmas, we selected melt inclusions trapped in high-Mg olivines (i.e., with a forsterite content $> 80\%$). We selected primary melt inclusions that were far from any crack, did not display daughter minerals or devitrification and therefore did not require re-homogenization. The 33 studied melt inclusions are larger than 30 μm and most of them contain a bubble that most likely formed after entrapment (Figure 1 of the Supplementary material).

We selected glassy melt inclusions from a picritic lapilli layer collected on the Torgil tuff ring and from the Red Cliff pyroclastic sequence (Ao15, Ao17, Ao2T-T, Ao-T; Sorbadere *et al.*, 2011) of Aoba volcano in the Vanuatu arc. Melt inclusions from Mont Etna were selected from the FS marker bed located on its eastern flank, and formed during a subplinian picritic eruption dated at 3930 ± 60 BP (SVP291c; Coltelli *et al.*, 2005; Kamenetsky *et al.*, 2007). We also selected melt inclusions from scoria samples from the ~50 000 year old La Sommata pyroclastic cone on Vulcano Island (Som; Rose-Koga *et al.*, 2012), and from a tephra layer located in a trench dug at 450 m a.s.l. on the northeastern flank of Stromboli volcano (St82p; Métrich *et al.*, 2001; Rosi *et al.*, 2000) in the Aeolian arc. Melt inclusions were selected from a Pleistocene-aged tephra layer from the mosaic ridge in the Mount Meager Volcanic Complex in the Garibaldi volcanic belt in the Cascades volcanic arc (Aw-15-185; Venugopal *et al.*, in prep). Previously studied melt inclusions from a picritic scoria sample from Piton de Caille on the Northwest rift-zone of Piton de la Fournaise, Reunion Island (CAI; Bureau *et al.*, 1998a; Bureau *et al.*, 1998b; Laubier, 2006) and from mid-ocean ridge basalts from the FAMOUS zone (Northern Mid-Atlantic Ridge; ARP73-10-03; Kamenetsky, 1996; Laubier *et al.*, 2007, 2012) and the Gakkel ridge are also part of our dataset.

3. Experimental samples

A series of 14 basaltic glasses were synthesized experimentally and used as reference material for XANES measurements. The starting composition was a MORB glass collected in the axial rift of the Pacific mid-ocean ridge (Searise 1 DR 04; Latitude 6.71, Longitude -114.30 and depth = 2800 m). The sample was ground under ethanol in an agate mortar to a homogeneous powder mixture.

Experiments under anhydrous conditions at 0.1 MPa (ML1 to 9) were performed at Laboratoire Magmas et Volcans (Clermont-Ferrand, France) in a vertical quenching furnace, with a CO₂–H₂ gas atmosphere. The oxygen fugacity was monitored using a ZrO₂–CaO oxygen cell calibrated against the Fe–FeO, Ni–NiO and Cu–Cu₂O buffers. In order to cover a range of redox conditions, experiments were performed at different fO_2 conditions ranging from -3,5 log units below the quartz–fayalite–magnetite buffer (QFM-3.5) to QFM+4. The sample material for these experiments consisted of ~ 50-70 mg of the mixture that had been mixed with polyvinyl alcohol and pressed into a pellet. This pellet was then sintered onto an iron–platinum alloy loop, which had been previously annealed with the starting composition in order to prevent Fe loss to the alloy during the experiment. The run temperature was continuously monitored using a Pt–Pt₉₀Rh₁₀ thermocouple. The thermocouple was placed in the hotspot of the furnace, where the thermal gradient is <1°C over the length of the sample. The sample was suspended alongside the thermocouple in order to minimize the difference between the temperature of the sample and the reading of the thermocouple. The reproducibility and measurement of this arrangement is better than 5°C. The experiments were run isothermally at 1350 °C at the run conditions and typically for 24h.

The BH hydrous glasses (BH1, BH3, BH6 BH7 and BH10) were synthesized at Laboratoire Magmas et Volcans in a piston-cylinder apparatus at 1 GPa and 1300 °C using a 1/2" assembly. The starting materials consisted of anhydrous glasses that were first synthesized by re-melting the starting material in a gas-mixing furnace at one bar, 1350 °C and three different fO_2 conditions of ~QFM, QFM+2 and QFM+4. The glasses were then ground under ethanol in an agate mortar to a homogeneous powder mixture. For the piston-cylinder experiments, we used a Pyrex–MgO assembly, a graphite heater, an outer NaCl sleeve, and Au₈₀–Pd₂₀ capsules (with a 4 mm outer diameter for 1/2" assemblies, 0.2 mm wall thickness, 4–5 mm length). To prepare the capsules, we first added deionized water at the bottom of the

capsule using a micro-syringe. After loading and compacting ~50 mg of glass powder, the capsule was welded shut. We checked for leaks during capsule preparation by weighing the welded capsules before and after ≥ 1 h heating at 120 °C in an oven. Before starting the experiments, the capsules were placed in an oven at 120 °C overnight to ensure homogenous distribution of the volatiles. During the experiments, the samples were held at 1300 °C and 1 GPa for only 15 min in order to minimize fO_2 re-equilibration and H_2O loss. The temperature was measured very close to the capsule by a $W_{95}Re_5$ - $W_{74}Re_{26}$ thermocouple. Quenching of the hydration experiments was done by switching off the heating power, which led to a cooling rate > 80 °C/s.

The glasses recovered from the experiments were polished on both sides for major element characterization by electron microprobe, H_2O concentration measurements by Raman spectroscopy (for hydrous glasses only) and XANES measurements. Fragments of the anhydrous glasses were also analyzed by conventional Mössbauer spectroscopy using a radioactive point source at the Bayerisches Geoinstitut. Details of the experimental conditions for each run, as well as their chemical compositions can be found in Table 1-2 of the Supplementary material.

Three basaltic and three basanitic experimental glasses from Magnien et al. (2004) and Schiavi et al. (2018), respectively, were added to our dataset to complete the range of $Fe^{3+}/\Sigma Fe$ ratios and water contents covered by our experimental glasses. Their chemical compositions can be found in Tables 1-2 of the Supplementary material.

4. Analytical methods

4.1. Electron microprobe analyzes

Melt inclusions and their host olivines were analyzed for major elements by electron microprobe at Laboratoire Magmas et Volcans with a CAMECA SX 100. All analyzes were performed with a 15 kV accelerating voltage. Olivines were measured with a 1 μm diameter focused beam and a 100 nA beam current. Counting times for each element were: Al (160-220 s), Si (20 s), Mg (30 s), Ca (160 s), Fe (40 s), Mn (60 s) and Ni (120 s). Analyzes of Si, Mg and Fe of olivines presenting a slightly tilted surface were performed in EDS mode using the electron microprobe to avoid bias on their stoichiometry. Counting time for these three elements using this analytical condition was 30 s. Melt inclusions were analyzed with a 10 μm diameter beam and two beam current conditions. The elements measured with a 8 nA beam and their respective counting times were: Na (10 s), Mg (30 s), Si (10 s), Al (20 s), Ca (10 s), Ti (30 s) and Fe (30 s). The elements measured at 50 nA and the respective counting times were: K (40 s), P (40 s) and Mn (80 s). Volatile elements were analyzed with a 10 μm diameter beam and a beam current of 40 nA. Respective counting times were: S (50 s), Cl (50 s) and F (300 s). Analytical uncertainties on glass data for major elements were obtained from replicate measurements on the natural glass Ve32 ($n = 23$). The total analytical 2σ error, which corresponds to the maximum value between the precision and accuracy of measurements, for the Ve32 basaltic glass was 1.4% rel. for SiO_2 , 4.1% for TiO_2 , 2.8% for Al_2O_3 , 4.8% for FeO^* , 11% for MnO , 3.4% for MgO , 3.2% for CaO , 9.2% for Na_2O , 9.9% for K_2O and 4.6% for P_2O_5 . The major and volatile element compositions of melt inclusions and the major element compositions of their host crystals are given in Table 3 of the Supplementary material. The values on the Ve32 standard are also reported in Table 3 of the Supplementary material.

4.2. Raman spectroscopy

Water content of 14 melt inclusions was determined by Raman spectroscopy. Spectra were collected at Laboratoire Magmas et Volcans using an InVia (Renishaw) confocal Raman micro-spectrometer. Analytical details can be found in Schiavi et al. (2018). The diode laser output power was 150 mW. Laser power on the sample was reduced by filters in order to operate at powers of ~ 1 mW. Laser power on the sample was periodically checked. The analytical conditions used result in lateral and axial spatial resolutions of ~ 1 and $3 \mu\text{m}$, respectively, near the sample surface. Daily calibration of the spectrometer was performed based on a Si 520.5 cm^{-1} peak. Analyzes were carried out at $2 \mu\text{m}$ depth on polished melt inclusions. The spectra were recorded in the wavenumber ranges from ~ 100 to 1350 cm^{-1} (alumino-silicate network domain) for 4 cycles of 30 s and from ~ 2900 to 3800 cm^{-1} (water domain) for 7 cycles of 30 s, using Wire 4.2 software. Basaltic, andesitic and rhyolitic glasses, with water content from 0 to $6.70 \pm 0.35 \text{ wt\%}$ were used as external reference standards (Médard and Grove, 2008; Schiavi et al., 2018) and analyzed several times during each analytical session at the same conditions as the samples, in order to correct for the dependence of band intensities on delivered energy. Analytical precision calculated based on repeated daily measurements of the reference glass 82-72f#9 was better than 16 % rel. Analyzes of host olivines were performed with the same conditions in order to correct melt inclusion spectra that suffered from signal contamination from the host crystal.

Absolute intensity areas of the water band and silicate band were determined after subtraction of a cubic and non-parametric baseline, respectively, using PeakFit© software. For determination of water content in glasses, we used both the external calibration procedure, which is based on the absolute intensities of the water band area, and an internal calibration procedure which normalizes the intensity of the water band area to the area of the silicate bands (Schiavi et al., 2018). The two methods often gave different results (up to $\sim 30\%$ rel.). As

demonstrated by Schiavi et al., (2018), the internal calibration is sensitive to matrix effects that are related to changes in glass density, the oxidation state or the presence of dissolved carbonate. For those reasons, we used an external calibration to determine the water content of our melt inclusions. The analytical uncertainty was calculated as the 2σ relative standard deviation (RSD) on replicate measurements. When melt inclusions could only be analyzed once, we report an analytical uncertainty that corresponds to the maximal 2σ RSD determined on replicate analyzes of other melt inclusions in the same session. Water contents of melt inclusions are given in Table 3 of the Supplementary material.

4.3.FTIR spectroscopy

The water contents of 16 melt inclusions were determined by Fourier Transform infrared spectroscopy. Analyzes were performed at LMV using a Bruker Vertex 70 spectrometer coupled with a Hyperion microscope. The spectrometer is equipped with a Globar light source, a KBr beamsplitter and a Mercury-Cadmium-Tellurium alloy (MCT) detector. Melt inclusions polished on both sides were placed on a CaF_2 window for the acquisition and the CaF_2 window was used for background correction. The beam size varied as a function of the melt inclusion size. Absorbance and background spectra were obtained by acquisition of 600 and 300 scans, respectively. The spectral resolution was 4 cm^{-1} . Spectra were collected in the wavenumber range from 7500 to 700 cm^{-1} . Spectra were corrected for atmospheric contamination using OPUS software. The water contents of melt inclusions were calculated using the Beer-Lambert law. Absorption was derived from the area of the 3550 cm^{-1} band after baseline subtraction using OPUS software. Sample thicknesses were measured as the vertical displacement of the optical microscope stage between the top of the sample and the sample holder using a focused Raman laser beam. The uncertainty on the thickness measurement was estimated to be $\sim 2\text{ }\mu\text{m}$. The density was calculated following Bouhifd et al. (2015). For basaltic glasses, we used a

molar absorption coefficient of $62.8 \pm 0.8 \text{ Lmol}^{-1}\text{cm}^{-1}$ as proposed by Mercier et al. (2010). For silicate under-saturated samples, we chose to use a molar absorption coefficient of $43.96 \pm 0.6 \text{ Lmol}^{-1}\text{cm}^{-1}$ (Mercier et al., 2010). The analytical uncertainty was calculated as the 2σ relative standard deviation (RSD) on replicate measurements. When melt inclusions could only be analyzed once, we report an analytical uncertainty that corresponds to the maximal 2σ RSD determined on replicate analyzes of other melt inclusions in the same session. Water contents of melt inclusions are given in Table 3 of the Supplementary material.

A few melt inclusions were both analyzed by Raman and FTIR spectroscopy. From the comparison between the two methods, we concluded that both methods gave consistent results, but that the uncertainties on the water contents derived from FTIR spectroscopy were larger due to the error on the thickness of melt inclusions and the uncertainty resulting from the range in the published values for the molar absorption coefficient. Therefore, when both types of data were available, the water contents derived from Raman spectroscopy were preferentially used.

4.4. Mössbauer analyzes

The iron speciation of the 12 anhydrous experimental glasses (Table 1 of the Supplementary material) was determined by conventional Mössbauer spectroscopy. Analyzes were carried out at the Bayerisches Geoinstitut, Bayreuth. Glasses were mounted between two pieces of plastic film and centered in a $1000 \mu\text{m}$ diameter hole drilled in a $25 \mu\text{m}$ thick Pb foil. Data were collected in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal $370 \text{ MBq } ^{57}\text{Co}$ point source in a $12 \mu\text{m}$ Rh matrix with active dimension of $500 \times 500 \mu\text{m}^2$. The velocity scale was calibrated with a $25 \mu\text{m}$ thick natural $\alpha\text{-Fe}$ foil. A line width of 0.36 mm/s for the outer lines was obtained for $\alpha\text{-Fe}$ at room temperature. Analyzes were performed at room temperature with measuring times from 7 hours to 5 days.

Fe³⁺/ΣFe in 14 olivine-hosted melt inclusions were determined using a synchrotron Mössbauer source (SMS; Potapkin et al., 2012; Smirnov et al., 1997). Analyzes were carried out at the Nuclear Resonance beamline ID18 (Rüffer and Chumakov, 1996) of the European Synchrotron Facility, Grenoble. Melt inclusions were polished on both sides to avoid signal contamination from their host crystal and were centered under a 20-30 μm hole drilled in a 25 μm-thick Re foil. Data were collected using a multi-bunch operating mode and a 10 × 15 μm² focalized beam for 4.5 to 9 hours at room temperature. The SMS provided ⁵⁷Fe resonant radiation with the energy of 14.4125 keV and the bandwidth of ~13 neV tunable in the energy range of about ± 0.3 μeV. The velocity scale was calibrated with a 25 μm-thick natural α-Fe foil and the source line width was checked after each analysis. Spectra were fitted using MossA software using a full transmission integral (Prescher et al., 2012).

The fitting methods applied to spectra collected using conventional Mössbauer and SMS spectroscopy are further described in the Results section.

4.5.XANES analyzes

Fe K-edge X-ray absorption near edge structure (XANES) were collected at the LUCIA (Vantelon et al., 2016) beamline of SOLEIL synchrotron, France, during five different sessions in 2014, 2015, 2017, 2018 and 2019. Data were collected in fluorescence mode between 7050 and 7300 eV, with 0.1 eV steps in the pre-edge region (7106–7120 eV). The excitation energy was selected using a Si(311) or a Si(111) double crystal monochromator depending on the analytical session, leading to a spectral energy resolution of 0.2 and 1 eV, respectively. The monochromator was calibrated by setting the first inflexion point of a Fe metallic foil to 7112 eV. The beam was focused using KB mirrors down to ~ 3 × 3 μm² (Table 4 of the Supplementary material). The fluorescence detector was a Bruker silicon drift diode mono-element with a total active area of 60 mm². The distance between the sample and the detector

was adjusted to ensure optimal counting rate for each sample. Samples were tilted at an angle of 5° with respect to the incident beam. X-ray fluorescence (XRF) chemical maps were used to select spots for XANES measurements. Spectra collected in anhydrous reference glasses during each session were used to refine the alignment of the spectra collected during the different sessions and to calibrate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained from the pre-edge region of XANES spectra collected on our unknown samples. For unknown samples, two consecutive XANES spectra were collected at the same location. More details on the analytical conditions are given in Tables 4-5 of the Supplementary material.

Cottrell et al. (2018) demonstrated that hydrous glasses can be affected by beam-induced oxidation depending on their H_2O content, their initial oxidation state and the radiation dose used to collect spectra. Therefore, during our 2019 session, we acquired XANES spectra on hydrous glasses using different radiation doses ranging from 7.9×10^5 to 2.4×10^8 photons/s/ μm^2 . This was done by changing the beam size from 3.7×3 to $35 \times 15 \mu\text{m}^2$ and/or attenuating the beam flux by placing a $60 \mu\text{m}$ thick Al foil along the beam path (Tables 4-5 of the Supplementary material). The radiation dose corresponds to the number of photons delivered to the sample per square micrometer. The sample area exposed to radiation was determined assuming that the beam had an elliptic shape. Melt inclusions were then analyzed during that 2019 session with a $4 \times 3 \mu\text{m}^2$ focused beam size using radiation doses of 3.7×10^7 photons/s/ μm^2 .

To better constrain conditions at which beam-induced oxidation occurs, we tested for a time dependent variation in the intensity of the pre-edge multiplets. Following Debret et al. (2015) and Cottrell et al. (2018), we measured the peak amplitude at two fixed energies that correspond to the energies of the Fe^{2+} and Fe^{3+} pre-edge peaks, respectively (7112.6 and 7114 eV), during 300 s. The duration of a time series acquisition corresponds to the time needed to

collect the pre-edge part of our XANES spectra. The time series were acquired at the same conditions as the XANES spectra (Tables 4-5 of the Supplementary material).

XANES spectra were normalized and corrected for self-absorption using Athena software (IFFEFIT suite; Ravel et Newville, 2005). Melt inclusion spectra were tested for potential contamination from the host olivine crystal by carrying out a comparison with spectra collected on synthetic glasses and using the principal component analysis procedure described in Hartley et al. (2017) and Shorttle et al. (2015). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of samples were derived by fitting the pre-edge region using PeakFit© software. The pre-edge region was fitted between 7108 and ~ 7118 eV with two Gaussian peaks, constrained to have the same width and line shape, simultaneously with the background, which was modeled as the tail of two other Gaussian functions. The pre-edge centroid energies, integrated areas and intensity ratios calculated as $I_{\text{Fe}^{3+}}/(I_{\text{Fe}^{3+}} + I_{\text{Fe}^{2+}})$ are reported in Table 6 of the Supplementary material. Intensities collected as a function of time at 7112.6 and 7114 eV in the same sample were normalized as $I[(\text{Fe}^{3+})/[(\text{Fe}^{3+})+I(\text{Fe}^{2+})]] = I(7114)/[I(7114)+I(7112.6)]$ in order to track the evolution of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios through time.

5. Results

5.1. Mössbauer spectroscopy

5.1.1. Independent characterization of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in reference glasses

Several methods were tested to fit the Mössbauer spectra (e.g. Berry et al., 2018; Cottrell et al., 2009) in order to define the best fitting method to apply to our data. The best fit as judged

by statistics and consistency of parameters across all spectra for reference glasses was obtained with three pseudo-Voigt doublets (Figure 1).

Figure 1: Results of the fitting procedure of four Mössbauer spectra collected for anhydrous basaltic reference glasses (Table 1 of the Supplementary material). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the glasses are given in brackets. The red dashed line corresponds to the linear baseline. The black line represents the modeled spectra. Blue, green and pink lines correspond to the three pseudo-Voigt doublets used to characterize iron environments. For the most reduced glasses (a) the three doublets are attributed to the Fe^{2+} environment. For reduced and oxidized glasses (b-c), the green pseudo-Voigt doublet was attributed to the Fe^{3+} environment whereas the two others were attributed to the Fe^{2+} environment. For the more oxidized sample (d), the pink pseudo-

Voigt doublet was attributed to the Fe^{2+} environment whereas the two others were attributed to the Fe^{3+} environment. Residuals obtained from the fitting procedure are given at the top of the spectra.

The values for the center shift (δ), quadrupole splitting (Δ) and the full width at half maximum (FWHM) for each doublet were set as free to vary at first. Then, the FWHMs of the three doublets were constrained to be equal when unrealistic values were obtained for hyperfine parameters. Reduced χ^2 values range from 0.95 to 1.93. Values obtained for hyperfine parameters are summarized in Table 7 of the Supplementary material. The values obtained for the hyperfine parameters indicate that two doublets are attributed to the Fe^{3+} environment, whereas one doublet is attributed to the Fe^{2+} environment in our most oxidized glass. In contrast, two doublets are attributed to the Fe^{2+} environment and one doublet is attributed to the Fe^{3+} environment in the less oxidized glasses. Three doublets are attributed to the Fe^{2+} environment in our most reduced glasses (e.g. Alberto et al., 1996; Berry et al., 2018; Cottrell et al., 2009; Zhang et al., 2018); Table 7 of the Supplementary material). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were obtained from the relative area of each doublet. Determination of the 2σ uncertainty is based on both the statistical uncertainty derived from the fit and the reproducibility given by results obtained from the several tested methods. The fit results are reported in Table 7 and Figure 1.

The values obtained for the hyperfine parameters in our most reduced glass standards suggest that no Fe^{3+} component is required. However, the doublets are characterized by broad lines and the hyperfine parameters show a systematic overlap of the Fe^{2+} components that suggests that a small amount of Fe^{3+} could be present in these reference glasses (Figure 1a). Therefore, we conclude that we are not able to determine the iron speciation accurately in glasses with $< 10\%$ $\text{Fe}^{3+}/\Sigma\text{Fe}$, and for that reason we decided not to use those in our XANES calibration (Table 1 of the Supplementary material).

5.1.2. Fe³⁺/ΣFe in melt inclusions

Due to a limited beamtime, synchrotron Mössbauer source spectra collected on melt inclusions have a lower signal to noise ratio than conventional Mössbauer spectra in the reference glasses (Figure 1-2). The consequence of this lower signal quality is that we were not able to apply the same fitting method for melt inclusions and reference glasses (Figure 2). However, in order to be as consistent as possible with the fitting procedure used for reference glasses, spectra collected on melt inclusions were fitted using two pseudo-Voigt doublets, where one doublet was attributed to the Fe²⁺ environment and the other one was attributed to the Fe³⁺ environment. As for reference glasses, hyperfine parameters (δ and Δ) and the FWHM of the doublets were first set as free to vary. Then, the FWHM of the doublets attributable to the Fe³⁺ environment was fixed to 0.4 mm/s when unrealistic values were obtained for hyperfine parameters. An asymmetric Lorentzian doublet with fixed hyperfine parameters was added to the fitting procedure (Figure 2) to correct the spectra for ⁵⁷Fe contamination from the Be lenses. Reduced χ^2 values range from 0.86 to 1.15. Hyperfine parameters are summarized in Table 8 of the Supplementary material.

Since the ⁵⁷Fe contamination due to the Be lenses is larger for spectra collected on iron-poor or thin melt inclusions, we tested for a correlation between the relative area of the Lorentzian doublet from the Be lenses and the Mössbauer thickness of the different samples (Table 9 and Figure 2 of the Supplementary material). The Mössbauer thickness is calculated from the density (g/cm³), porosity (%), thickness (μm) and total iron content (in wt% of element) of the sample (Long et al., 1983). The broad negative trend follows the expected behavior of the two parameters, i.e. the area of the Lorentzian doublet increases as either the iron content or the sample thickness decreases, confirming our approach to correct for ⁵⁷Fe contamination by the Be lenses.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were derived from the relative areas of each doublet and 2σ uncertainties were calculated from the statistical fitting uncertainties reported by the software. Results are shown in Table 3 of the Supplementary material.

Figure 2: Results of the fitting procedure applied to two room temperature Mössbauer spectra collected on melt inclusions using the synchrotron Mössbauer source. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of selected melt inclusions are given in brackets. The red dashed line corresponds to the quadratic baseline. The black line represents the modeled spectra. The grey line is the Lorentzian doublet used to correct spectra for ^{57}Fe contamination from the Be lenses. Blue and green lines are the pseudo-Voigt doublets attributed to the Fe^{2+} and Fe^{3+} environments, respectively. Residuals obtained after the fitting procedure are given at the top of the spectra.

5.2.XANES

5.2.1. Calibration of the XANES spectra

To derive $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from the pre-edge region of XANES spectra collected on unknown samples, these spectra have to be calibrated using XANES spectra collected on reference glasses with independently known $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (e.g. derived from Mössbauer spectroscopy). In previous studies, the XANES calibration uses either the pre-edge centroid energy (i.e., intensity-weighted energy) or the pre-edge intensity ratio (i.e., the ratio of the total area of the Fe^{3+} peak $[\text{I}(\text{Fe}^{3+})]$ to the sum of the areas of the Fe^{3+} peak $[\text{I}(\text{Fe}^{3+})]$ and the Fe^{2+} peak $[\text{I}(\text{Fe}^{2+})]$, or $\text{I}(\text{Fe}^{3+})/[\text{I}(\text{Fe}^{3+})+\text{I}(\text{Fe}^{2+})]$). Pre-edge centroid energy-based calibrations are less sensitive to changes in the coordination environment (Berry et al., 2003; Wilke et al., 2004), however they are more sensitive to energy shifts that can occur during and between analytical sessions (Cottrell et al., 2009). As spectra were collected on the same reference glasses during every session, we were able to correct our spectra for any shift in energy between sessions (no drift occurred within single sessions). Therefore, we applied the pre-edge centroid energy based calibration to estimate the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in the unknown samples.

Cottrell et al. (2009) also used a pre-edge centroid energy based calibration and found that the use of a second order polynomial fit to their most oxidized reference glasses was appropriate for their data. The use of this calibration leads to the determination of an average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.16 ± 0.01 for MORB glasses (Cottrell and Kelley, 2011). More recently, Berry et al. (2018) proposed that a linear calibration can be used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ of MORB glasses when only considering the appropriate $\text{Fe}^{3+}/\Sigma\text{Fe}$ range for MORBs ($\text{Fe}^{3+}/\Sigma\text{Fe} < 0.3$). They derived an average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.11 ± 0.02 for MORB glasses when they use the linear calibration and 0.10 ± 0.02 when they use the polynomial calibration. Results derived from these two calibrations are similar within error, which indicates that both calibrations can

be applied to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in the unknown samples. These authors have also proposed that the difference in the average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in MORB glasses arises from the method applied to fit the Mössbauer spectra of reference glasses. On the one hand, Cottrell et al. (2009) fitted their Mössbauer spectra using two 2D-gaussian doublets, with one doublet being attributed to the Fe^{2+} environment and the other one to the Fe^{3+} environment. On the other hand, Berry et al. (2018) have proposed that a third doublet has to be attributed to the Fe^{2+} environment, in particular in the case of reduced samples, otherwise their $\text{Fe}^{3+}/\Sigma\text{Fe}$ would be over-estimated. In the current study, we used three doublets to fit the Mössbauer spectra collected on our reference glasses and the third doublet was attributed to the Fe^{2+} environment in our most reduced samples, therefore we expect that our derived $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are not over-estimated.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from XANES spectra were determined for our natural glass samples from the centroid energy of the fitted pre-edge region using a polynomial calibration derived from seven basaltic reference glasses (Figure 3; Table 1 of the Supplementary material). As the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of our more reduced standards are below the detection limit of Mössbauer spectroscopy (<10 %), we did not use them in our calibration (Table 1 of the Supplementary material).

The XANES calibration is given by the equation:

$$E_{\text{centroid}} = -1.0540 (\text{Fe}^{3+}/\Sigma\text{Fe})_{\text{Mössbauer}}^2 + 2.6146 (\text{Fe}^{3+}/\Sigma\text{Fe})_{\text{Mössbauer}} + 7112.8004 \quad (1)$$

in which E_{centroid} corresponds to the centroid energy (in eV) and $(\text{Fe}^{3+}/\Sigma\text{Fe})_{\text{Mössbauer}}$ is the $\text{Fe}^{3+}/\Sigma\text{Fe}$ value obtained by Mössbauer spectroscopy. This calibration is applicable to samples with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios ranging between 0.10 and 0.90. The accuracy of the calibration was tested

by using one of our anhydrous experimental glasses (ML4; Table 1 of the Supplementary material) as an external standard. The mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.22 ± 0.02 ($n=6$) calculated for the ML4 glass using this calibration is in good agreement with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.21 ± 0.03 obtained by Mössbauer spectroscopy. This result demonstrates that our calibration can be used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of our unknown samples. The uncertainty on the ML4 glass is reported as the 2σ standard deviation of the replicate analyzes. This uncertainty will then be used as the 2σ error on the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of our unknown samples.

Figure 3: XANES calibration curve for the determination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt inclusions and glasses. The solid curve is the second order polynomial fit result. Averaged centroid energies and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from Mössbauer spectroscopy of anhydrous basaltic reference glasses are shown in Table 1 of the supplementary material. Error bars are reported as 2σ uncertainties (Table 1 of the supplementary material).

5.2.2. Time series in hydrous synthetic glasses

The measurement of the evolution of the pre-edge peak intensities with time at fixed energies gives us access to the evolution of the iron speciation of glasses during the time required to acquire the XANES pre-edge region, which, in our set-up, is about 5 minutes. The time series allows us to spot the occurrence of beam damage during acquisition. Time series

collected on hydrous experimental glasses with water contents ranging from 0.02 ± 0.002 to 2.86 ± 0.34 wt% and equilibrated at various fO_2 show no clear evidence of beam damage when using radiation doses lower than 1.2×10^8 photons/s/ μm^2 . When using higher doses, the time series collected on water-rich glasses ($\geq 2.48 \pm 0.20$ wt% H_2O) show a systematic increase in the intensity ratio $I(7114)/[I(7114)+I(7112.6)]$ (Figure 4). As time series are collected at fixed energies, the effect of beam-induced oxidation cannot be monitored using centroid positions. However, when considering a XANES spectrum, the use of the centroid position allows us to determine more accurate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.

At 2.4×10^8 photons/s/ μm^2 , time series collected on the BH1 glass (0.74 ± 0.02 wt% H_2O) also show an increase in its intensity. This suggests that beam damage can even occur for very low water contents when using such high radiation doses.

480

481 Figure 4: Time series of the intensity ratio $I(7114)/[I(7114)+I(7112.6)]$ collected over 300 s in
 482 the most hydrous experimental glass BSN101117 - 2 (Table 2 of the Supplementary material)
 483 using radiation doses from 7.9×10^5 to 2.4×10^8 photons/s/ μm^2 . No evidence of beam damage
 484 is visible when using radiation doses lower than 1.2×10^8 photons/s/ μm^2 . When using higher
 485 radiation doses ($\geq 1.2 \times 10^8$ photons/s/ μm^2) beam damage effects are recorded as an increase in
 486 the intensity through time. The overestimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ calculated from these time series
 487 is 10% rel. and 15% rel. using 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 respectively.

We converted the intensity of absorption recorded in the time series into $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios using a calibration based on non-normalized pre-edge peak intensity ratios in the reference glasses. Then we applied a linear regression through the variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ with time to calculate the over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ induced by beam damage. We find that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are over-estimated by 6 to 10 % rel. and 6 to 15 % rel. when using radiation doses of 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 , respectively. The percentage of over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios shows a poor positive correlation with the water content of glasses (Figure 5a) and no correlation with their original $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (i.e., as determined from the pre-edge centroid energy of a spectrum collected in non-damaging conditions (5.1×10^6 photons/s/ μm^2 ; Figure 5b). Cottrell et al. (2018) found that the beam damage susceptibility ϕ , which they define as the product of the water concentration and the ferrous/ferric oxide ratio on a molar basis, is positively correlated with the percentage of over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for hydrous glasses. Our data do not show such correlation (Figure 5c). The lack of correlation between these parameters implies that we were not able to quantify the over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for glasses analyzed using standard radiation doses ($\sim 10^8$ photons/s/ μm^2) and for which time series have not been collected.

Figure 5: Overestimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded by time series collected in hydrous glasses as a function of (a) their water content, (b) their 'initial' $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined in non-photo-oxidizing conditions (5.1×10^6 photons/s/ μm^2) and (c) the beam damage susceptibility ϕ ($\phi = \text{XHO}_{0.5} \times \text{XFeO}/\text{XFeO}_{1.5}$; Cottrell et al., 2018). Squares and triangles represent the overestimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for radiation doses of 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 , respectively. Errors given on water contents and 'initial' $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are expressed as 2σ errors (Table 2 of the Supplementary material).

5.2.3. XANES spectra in hydrous synthetic glasses

We first compared the pre-edge features of XANES spectra successively collected at the same location in our synthetic hydrous glasses to look for evidence for beam-induced oxidation between the two consecutive spectra (Figure 6). Changes in the pre-edge feature indicating that beam damage occurred during the acquisition were visible for water-rich glasses ($\geq 2.48 \pm 0.20$ wt% H₂O) that were analyzed with radiation doses of 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 . When we compared the Fe³⁺/ΣFe ratios obtained for these spectra, the over-estimation of the Fe³⁺/ΣFe ratios derived from the second spectrum is systematically contained in the 2σ uncertainty on these ratios. Similarly, we compared the Fe³⁺/ΣFe ratios obtained for these spectra with their original Fe³⁺/ΣFe ratios (i.e., as determined from the pre-edge centroid energy of a spectrum collected in non-damaging conditions of 5.1×10^6 photons/s/ μm^2). The over-estimation of Fe³⁺/ΣFe derived from XANES spectra that were affected by beam damage (as evidenced by time series and modification of the pre-edge region of XANES spectra) lies within the error except for BH7 at the highest radiation dose. We can also note that all the glasses that show changes in the pre-edge feature between two consecutive spectra also show evidence of beam induced oxidation in the time series. However, the inverse is not systematically observed (and this might indicate that the photo-oxidation has reached a plateau and/or that it is irreversible).

When no beam damage was detected either from the time series and/or the comparison of the pre-edge regions of the two consecutive spectra, we calculated a mean Fe³⁺/ΣFe from the two spectra collected at the same spot. 2σ uncertainties were calculated as the propagation of the 2σ uncertainty of the Fe³⁺/ΣFe ratios of both spectra. On the other hand, when there was evidence for oxidation from the difference in the two spectra, we discarded the value from the second spectrum and only kept the Fe³⁺/ΣFe ratio derived from the first spectrum.

536
 537 Figure 6: Pre-edge regions after baseline subtraction of two successive XANES spectra
 538 collected at the same spot. The spectra shown here were collected in hydrous glasses BH10 and
 539 BSN081117 - 2 (their water contents are given in brackets; Table 2 of the Supplementary
 540 material) with radiation doses of 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 , respectively. The first
 541 and second spectra are shown in red and black, respectively. The two spectra collected in the
 542 BH10 glass are identical. In contrast, the second spectrum collected in the BSN081117 - 2 glass
 543 shows a small decrease in its Fe^{2+} component and an increase in its Fe^{3+} component compared
 544 to the first spectrum, indicating beam damage.

545
 546 When using a radiation dose of about 10^7 photons/s/ μm^2 , we record no evidence of
 547 beam-induced oxidation from the time series and the two consecutive spectra. This indicates
 548 that decreasing the radiation dose of about one order of magnitude provides more accurate

Fe³⁺/ΣFe ratios while still keeping the small beam size that is required for melt inclusion analysis.

5.2.4. Determination of Fe³⁺/ΣFe in melt inclusions

Time series were collected using a radiation dose of 3.7×10^7 photons/s/μm² in melt inclusions that were large enough to accommodate several XANES spots. As we saw no evidence for beam-induced oxidation in the hydrous experimental glasses at the same beam conditions, we expected no beam damage in the melt inclusions. As expected, we found no evidence for beam damage in the time series of most melt inclusions except for three arc melt inclusions: the relative increase of the Fe³⁺/ΣFe ratio with time ranges from 6 to 63% rel. for water contents ranging from 2.31 to 4.14 wt% (Table 3 of the Supplementary material). The percentage of over-estimation of the Fe³⁺/ΣFe ratios does not, however, correlate with the water content in the melt inclusions. One should note that the largest amount of over-estimation of the Fe³⁺/ΣFe ratio (63% rel.) is comparable or sometimes lower than the 2σ uncertainties attributed to the Fe³⁺/ΣFe ratios calculated from Mössbauer spectra. However, we have demonstrated that the absolute Fe³⁺/ΣFe value calculated from the XANES spectrum is biased.

In addition to the time series, we also compared the pre-edge features of two spectra that were successively acquired at the same location. Beam damage affecting the second spectrum is clearly visible in eleven water-rich arc melt inclusions with water contents ranging from 2.31 to 4.59 wt%. Still, this effect is minimal and only one of them (inclusion SVP291c n4) shows an over-estimation of its Fe³⁺/ΣFe ratio that is larger than the 2σ uncertainty on the Fe³⁺/ΣFe ratio. Surprisingly this melt inclusion shows no clear evidence for beam damage in the time series, which suggests that the first spectrum has not been affected by beam damage and that the Fe³⁺/ΣFe ratio derived from it is reliable. In the end, more than half of the water-rich (> 1

wt% H₂O) melt inclusions did not show modification of the pre-edge feature between the two consecutive spectra.

When no sign of beam damage was recorded in the time series and/or in the comparison of the pre-edge regions of two spectra collected on the same spot, we calculated a mean Fe³⁺/ΣFe ratio from the two spectra. 2σ uncertainties were calculated as the propagation of the 2σ uncertainties of the Fe³⁺/ΣFe ratios of both spectra. When time series could not be collected for lack of space in the inclusion, we calculated a mean Fe³⁺/ΣFe ratio from the two spectra when their Fe³⁺/ΣFe ratios lie within the 2σ errors. Melt inclusions for which time series exhibit evidence of beam damage were removed from our dataset. When melt inclusions have been analyzed in different spots, mean Fe³⁺/ΣFe ratios were calculated using only the first spectra collected at each spot when the time series didn't record any beam damage. Results are given in Table 3 of the Supplementary material.

6. Discussion

6.1. The effect of beam-induced oxidation on the determination of Fe³⁺/ΣFe ratios in silicate glasses

The time series collected on hydrous experimental glasses by XANES indicate that beam damage systematically takes place at high water contents (≥ 2.5 wt% H₂O) for durations of 5 minutes and standard radiation doses (~10⁸ photons/s/μm²; Figure 4). At lower water contents (< 1 wt% H₂O), beam damage is not systematically observed. Beam induced oxidation recorded in the time series is usually, but not systematically, supported by changes in the pre-edge feature between the two XANES spectra collected successively at the same location (one spectrum acquisition lasts for 7 to 20 min; Figure 6), which suggests that the oxidation process

continues to occur during acquisition of the second spectrum. To explain the cases where time series showed oxidation through time, but no change was noticeable between the pre-edge features of the two spectra successively collected, we can make two hypotheses. The first hypothesis is that beam damage is “completed” after full acquisition of the pre-edge (Cottrell et al., 2018). The second hypothesis is that the modification due to beam damage is not systematically large enough to be visible given our spectral resolution. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios calculated for hydrous experimental glasses from their pre-edge centroid energies suggest that the effect of this process may be within the error associated with the calculation of these ratios. However, based on time series, an over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of about 15 % rel. may occur when using a radiation dose of 2.4×10^8 photons/s/ μm^2 . Thus, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt inclusions, and especially of arc melt inclusions that are usually water-rich, will likely be over-estimated when analyzing them with such doses.

A large number of melt inclusions have been analyzed with standard radiation doses ($\sim 10^8$ photons/s/ μm^2) during our first synchrotron sessions. At the time, as we did not realize how large the effects of beam damage could be, we did not systematically collect time series. The lack of or the poor correlation between the chemical composition of glasses (in particular their H_2O contents and/or initial $\text{Fe}^{3+}/\Sigma\text{Fe}$) and the over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded by time series collected on hydrous synthetic glasses (Figure 5) means that we are not able to quantify the over-estimation that potentially affected the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from XANES spectra collected on these melt inclusions using standard beam conditions. Therefore, we were not able to correct them and we decided not to use them.

Time series collected on hydrous experimental glasses using radiation doses lower than $\sim 10^8$ photons/s/ μm^2 do not show any evidence for oxidation. However, time series acquired in three hydrous melt inclusions using a radiation dose of 3.7×10^7 photon/s/ μm^2 show evidence of beam damage. Moreover, melt inclusions that exhibit an over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$

ratio derived from the second spectrum compared to the first one do not systematically display an evolution of the speciation through time in the time series. These observations corroborate the ones carried out by Cottrell et al. (2018) showing that lowering the radiation dose to about $\sim 10^7$ photons/s/ μm^2 allows us to mitigate but not definitively eliminate beam-induced oxidation during XANES analyzes. Using these more appropriate beam conditions, only three melt inclusions out of thirty show clear signs of beam damage during the acquisition of the first pre-edge spectrum.

6.2. $\text{Fe}^{3+}/\Sigma\text{Fe}$ inferred from Mössbauer vs. XANES spectroscopy

For the first time, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of olivine-hosted melt inclusions were determined by Mössbauer spectroscopy. Despite counting times of 4.5 to 9 h, the limited thickness of our melt inclusions resulted in much larger uncertainties in $\text{Fe}^{3+}/\Sigma\text{Fe}$ than the ones determined for reference glasses using conventional Mössbauer spectroscopy (Tables 1 and 3 of the Supplementary material). The difference can be explained by the lower signal to noise ratio of spectra collected on melt inclusions (Figure 1-2). Furthermore, these uncertainties are even larger for the most reduced melt inclusions ($\text{Fe}^{3+}/\Sigma\text{Fe} < 0.15$; Figure 3 of the Supplementary material). The increased uncertainties with decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio are explained by decreasing signal to noise ratio with decreasing Fe^{3+} content in the melt inclusions.

Figure 7 shows the comparison between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained by synchrotron Mössbauer source and XANES spectroscopy.

Figure 7: $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from Mössbauer spectroscopy compared to those from XANES spectroscopy. Here we report data from MORB and OIB melt inclusions from the Gakkel ridge (black triangles) and Piton de la Caille (Reunion island; grey squares), arc melt inclusions from Aoba (empty circles), Mount-Meager (squares), La Sommata (inverted triangles) and melt inclusions from Mount Etna (diamonds). Errors bars are reported as 2σ uncertainties (Table 3 of the Supplementary material).

The figure shows that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from these two methods mostly overlap within the 2σ uncertainties, with a distribution close to the 1:1 line. Nevertheless, we note that the absolute $\text{Fe}^{3+}/\Sigma\text{Fe}$ values calculated from Mössbauer spectra are generally lower than the ones obtained from XANES. Only two arc melt inclusions from Aoba (inclusions Ao17-D6 and Ao-T8) show significantly lower Mössbauer-derived $\text{Fe}^{3+}/\Sigma\text{Fe}$. The first hypothesis we can make is that these two melt inclusions were oxidized during XANES analysis. However, we see no evidence for beam-induced oxidation in the time series nor in the comparison of two consecutive spectra. A second hypothesis is that a small proportion of host olivine was sampled by the beam during Mössbauer analyses. The spectra collected in the Ao-T8 melt inclusion do not show evidences of signal contamination from the host olivine (Figure 2). Thus, it is more likely that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio obtained from Mössbauer spectroscopy in Ao-T8 is

underestimated because of the low signal to noise ratio and increased error. The poor signal to noise ratio of the spectra collected in the Ao17-D6 melt inclusion does not allow us to be as definitive as for the spectra collected in the Ao-T8 melt inclusion (Figure 4 in the supplementary material).

Generally, the comparison of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios inferred from these two methods seems to indicate that we managed to detect beam damage when it occurred during XANES analysis. However, the fact that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained by Mössbauer spectroscopy exhibit larger uncertainties because of the low spectral resolution indicates that we are not able to determine precise $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios using synchrotron Mössbauer yet, unless we increase counting times significantly.

6.3. The oxidation state of melt inclusions

In order to discuss further the oxygen fugacity at which melt inclusions equilibrate, their compositions have to be corrected for post-entrapment modification. Melt inclusions were corrected for host crystallization and/or ‘Fe loss’ using Petrolog3 software (Danyushevsky and Plechov, 2011). Details on the correction method used in this study are available in the Supplementary material. Corrected compositions and ‘original’ $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are reported in Table 3 of the Supplementary material.

Our results show that melt inclusions from MORB display a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.10 ± 0.05 ($n=5$). Melt inclusions from OIB and arcs display mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.13 ± 0.05 ($n=2$) and 0.25 ± 0.15 ($n=19$) respectively. Mount Etna is not classified as an arc volcano and has a more complex geodynamic setting than the other volcanoes presented in this study. Many authors suggested that Mount Etna has an OIB signature but for which the mantle is metasomatized by subduction-derived fluids. Nevertheless, the composition of the mantle beneath Mount Etna is still debated (e.g. Correale et al., 2014; Schiano et al., 2001; Schiavi et

al., 2015; Tonarini et al., 2001; Viccaro et Zuccarello, 2017). Our results show that melt inclusions collected in our Mount Etna sample display a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.26 ± 0.05 ($n=7$) that is closer to the mean value obtained for arc melt inclusions than the one obtained for OIB melt inclusions.

In Figure 8, we report the number of melt inclusions as a function of their geodynamic setting (melt inclusions from Mount Etna are reported here as arc melt inclusions) and their calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (light grey). Also reported are previously published data for melt inclusions in high-Mg olivines ($> \text{Fo}_{80}$; dark grey) and glasses (black) from MORBs (Berry et al., 2018; Birner et al., 2018; Cottrell and Kelley, 2011, 2013; Kelley and Cottrell, 2009; Zhang et al., 2018), OIBs (Brounce et al., 2017; De Moor et al., 2013; Hartley et al., 2017; Moussallam et al., 2016) and arcs (Brounce et al., 2014; Kelley and Cottrell, 2009, 2012). This figure shows that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in melt inclusions from MORBs are in good agreement with previous data and comparable to the ones obtained by Berry et al. (2018; 0.10 ± 0.02). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios calculated for melt inclusions from OIBs show similar or lower values than the previously published XANES data. This result may indicate beam-induced oxidation or that the range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for OIBs is larger than previously reported (Brounce et al., 2017; De Moor et al., 2013; Hartley et al., 2017; Moussallam et al., 2016). Melt inclusions from arcs from this study display a range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that is in good agreement with previous data (Brounce et al., 2014; Kelley and Cottrell, 2009, 2012). A few melt inclusions exhibit $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that are higher than literature data. This suggests that the range of oxidation state recorded in arc magmas may be larger than previously observed. Therefore, our results confirm that arc magmas are more oxidized than those from hot spots and mid-ocean ridges.

Figure 8: Number of melt inclusions and glasses as a function of their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and geological settings. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios plotted in this graph are mainly derived from XANES measurements at a radiation dose of 3.7×10^7 photons/s/ μm^2 (light grey; Table 3 of the Supplementary material). When XANES spectra showed evidence of beam damage, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from Mössbauer spectroscopy instead (6 melt inclusions). Also reported are literature data for glasses (black) and melt inclusions from high-Mg olivines ($> \text{Fo}_{80}$) from arc basalts, OIBs and MORB for comparison (dark grey; Berry et al., 2018; Birner et al., 2018; Brounce et al., 2014, 2017; Cottrell and Kelley, 2011, 2013; De Moor et al., 2013; Hartley et al., 2017; Kelley and Cottrell, 2009, 2012; Moussallam et al., 2016; Zhang et al., 2018).

Similarly observations by Kelley and Cottrell (2009), $\text{Fe}^{3+}/\Sigma\text{Fe}$ correlates positively with the H_2O content in melt inclusions (Figure 9). These authors suggested that the positive correlation between these two parameters most likely reflects changes in the oxidation state of the mantle beneath arcs because of subduction processes.

Figure 9: $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt inclusions as a function of their water content. $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios reported in this graph are mainly derived from XANES measurements at a radiation dose of 3.7×10^7 photons/s/ μm^2 (light grey; Table 3 of the Supplementary material). When XANES spectra showed evidence of beam damage, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from Mössbauer spectroscopy instead (6 melt inclusions). Data from this study are represented by black symbols. Error bars are 2σ (Table 3 of the Supplementary material). Previous data (grey symbols) from Brounce et al. (2014, 2017), Cottrell and Kelley (2011), Kelley and Cottrell (2009, 2012), Moussallam et al. (2016) and Zhang et al. (2018) collected in glasses and melt inclusions from high-Mg olivines ($> \text{Fo}_{80}$) are also reported.

$f\text{O}_2$ values of our melt inclusions were calculated relative to the QFM buffer using the algorithm of Kress and Carmichael (1991) and are reported in Table 3 of the Supplementary material and in Figure 9. The QFM values reported in Figure 10 show that melt inclusions from arc basalts are generally more oxidized (QFM +0.1 to +2.8) than those from MORBs (QFM -1.9 to -0.1) and OIBs (QFM -0.8 and +0.3).

Figure 10: Number of melt inclusions as a function of their fO_2 calculated relative to the QFM buffer using the Kress and Carmichael (1991) algorithm (Table 3 of the Supplementary material). $Fe^{3+}/\Sigma Fe$ ratios plotted in this graph are mainly derived from XANES measurements at a radiation dose of 3.7×10^7 photons/s/ μm^2 (light grey; Table 3 of the Supplementary material). When XANES spectra showed evidence of beam damage, we report $Fe^{3+}/\Sigma Fe$ ratios derived from Mössbauer spectroscopy instead (6 melt inclusions).

Within our population of melt inclusions from arc basalts, we see a range in fO_2 values. Melt inclusions from Stromboli (Eolian arc) and Mount Meager (Cascades) are the least oxidized with mean fO_2 values of QFM +0.1 and QFM +0.6 (n=6), respectively. Melt inclusions from La Sommata (Vulcano island, Eolian arc) are the most oxidized with a mean fO_2 of QFM +2.1 (n=4). Melt inclusions from Aoba volcano (Vanuatu arc) display a mean fO_2 value that is intermediate (QFM +1.3, n=8). Furthermore, we note that melt inclusions from Aoba display the largest range in fO_2 , overlapping nearly the entire range in fO_2 in all the arc melt inclusions from this study. Melt inclusions from Mount Etna display a mean fO_2 value of QFM +1.2 (n=7). This fO_2 value is closer to arc values than the OIB values determined in this study.

7. Conclusions

We used XANES and Mössbauer spectroscopy to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of primitive olivine-hosted melt inclusions from basaltic samples from various volcanic arcs, mid-ocean ridges and hot spots.

First, a careful evaluation of beam damage effects during XANES analysis was carried out by monitoring changes in the pre-edge feature of XANES spectra and intensities variations of time series. Beam induced oxidation recorded in the time series collected in hydrous experimental glasses using standard radiation doses ($\sim 10^8$ photons/s/ μm^2) is usually, but not systematically, supported by changes in the pre-edge feature between the two XANES spectra collected successively at the same location. This suggests that the oxidation process continues to occur during acquisition of the second spectrum and may be “completed” after full acquisition of the pre-edge (Cottrell et al., 2018). Our results show that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in water-rich glasses (≥ 2.5 w% H_2O) are likely to be over-estimated when derived from XANES spectra collected using standard radiation doses ($\sim 10^8$ photons/s/ μm^2). The amount of over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded by the time series does not or poorly correlates with the water content, the ‘initial’ $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio or the beam damage susceptibility ϕ of glasses as defined by Cottrell et al. (2018). Therefore, it is difficult to assess beam damage effects in melt inclusions that were analyzed using standard radiation doses when time series have not been collected. When a lower radiation dose is used ($\leq 3.7 \times 10^7$ photons/s/ μm^2), we record no evidence of beam damage in hydrous synthetic glasses. However, time series acquired in three hydrous melt inclusions using a radiation dose of 3.7×10^7 photon/s/ μm^2 show evidence of beam damage. Moreover, melt inclusions that exhibit an over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio derived from the second spectrum compared to the first one do not systematically display an evolution of the speciation through time in the time series. Therefore, decreasing the radiation

dose allowed us to mitigate but not definitively avoid beam damage in all melt inclusions. For that reason, systematic acquisition of time series is recommended even at low radiation doses in order to assess beam damage in glasses.

The iron speciation in a subset of melt inclusions was also analyzed using a Mössbauer synchrotron source. The comparison of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios inferred from these two methods suggests that we successfully identified the melt inclusions that suffered from beam damage. However, $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained by Mössbauer spectroscopy exhibit large uncertainties because of low signal to noise ratio. A significant increase of counting times (in the order of a day) would lead to a better resolution, but it would decrease the number of samples that can be analyzed during a synchrotron session.

The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt inclusions derived from XANES spectroscopy using a low radiation dose are in good agreement with previously published data. Our results confirm that primitive arc magmas are more oxidized than those from hot spots and mid-ocean ridges. A positive correlation between the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios calculated for melt inclusions and their water contents suggests that the oxidation recorded in primitive arc magmas is likely linked to changes in the oxidation state of the mantle beneath arcs because of subduction processes (Kelley and Cottrell, 2009). The calculation of the $f\text{O}_2$ relative to the QFM buffer confirms that arc melt inclusions and Mount Etna melt inclusions are more oxidized than MORB and OIB melt inclusions. The results also indicate that the range of oxidation state recorded in arc melt inclusions varies from one subduction zone to another.

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