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Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of olivine-hosted melt inclusions using Mössbauer and XANES spectroscopy

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1 Fe³⁺/ΣFe of olivine-hosted melt inclusions inferred from Mössbauer and XANES
2 spectroscopy

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16
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19
20 Iron speciation is linked to the oxygen fugacity of the system; hence determining the
21 Fe³⁺/ΣFe ratio of glasses can allow us to determine their oxidation state. Using X-ray
22 Absorption Near Edge Structure (XANES) spectroscopy in silicate glasses and olivine-hosted
23 melt inclusions, previous studies have shown that arc basalts are more oxidized than mid-
24 oceanic ridge basalts (MORB) and oceanic island basalts (OIB). However, Cottrell et al. (2018)
25 have recently demonstrated that hydrous glasses can be affected by beam-induced oxidation

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

34 Our results show that melt inclusions from MORBs, OIBs and arc basalts display mean
35 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.10 ± 0.05 (n=5), 0.13 ± 0.05 (n=2) and 0.25 ± 0.15 (n=19), respectively.
36 Mount Etna melt inclusions display a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.26 ± 0.05 (n=7). Therefore, they
37 confirm that arc magmas are more oxidized than those from hot spots and mid-ocean ridges.
38 Furthermore, they suggest that the range in the oxidation state observed in our melt inclusion
39 dataset may be linked to changes in the oxidation state of the mantle beneath arcs due to
40 subduction processes.

41 **1. Introduction**

42 Many studies have demonstrated that arc basalts are more oxidized ($\sim \text{QFM}+1.5 \pm 1$;
43 $f\text{O}_2$ given relatively to the quartz-fayalite-magnetite buffer; Gaillard et al. 2015 and references
44 therein) than MORBs (QFM-1.2 to $\sim \text{QFM}$; e.g. Berry et al., 2018; Bézoz and Humler, 2005;
45 Birner et al, 2018; Christie et al., 1986; Cottrell and Kelley, 2011, 2013; Mallmann and O'Neill,
46 2009; O'Neill et al., 2018; H. L. Zhang et al., 2018). However, the oxidation state of the sub-
47 arc mantle is still debated. Kelley and Cottrell (2009, 2012) and Brounce et al. (2014, 2015)
48 suggest that variations in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio measured in basaltic glasses and olivine-hosted

49 melt inclusions from mid-ocean ridges and arcs can be explained by the sub-arc mantle being
50 more oxidized than the mantle beneath ridges. On the other hand, Mallmann and O'Neill (2009)
51 and Lee et al. (2005, 2010) proposed the use of other fO_2 proxies, namely V/Sc and Zn/ Σ Fe
52 ratios in lavas and suggested that the oxidation state of the mantle wedge cannot be
53 distinguished from that of the MORB mantle (see also Dauphas et al., 2009; Li and Lee, 2004).

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

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

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

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

86 **2. Natural samples**

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

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

112 **3. Experimental samples**

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

118 Experiments under anhydrous conditions at 0.1 MPa (ML1 to 9) were performed at
119 Laboratoire Magmas et Volcans (Clermont-Ferrand, France) in a vertical quenching furnace,
120 with a CO₂-H₂ gas atmosphere. The oxygen fugacity was monitored using a ZrO₂-CaO oxygen
121 cell calibrated against the Fe-FeO, Ni-NiO and Cu-Cu₂O buffers. In order to cover a range of
122 redox conditions, experiments were performed at different fO_2 conditions ranging from -3,5 log
123 units below the quartz-fayalite-magnetite buffer (QFM-3.5) to QFM+4. The sample material
124 for these experiments consisted of ~ 50-70 mg of the mixture that had been mixed with
125 polyvinyl alcohol and pressed into a pellet. This pellet was then sintered onto an iron-platinum
126 alloy loop, which had been previously annealed with the starting composition in order to
127 prevent Fe loss to the alloy during the experiment. The run temperature was continuously
128 monitored using a Pt-Pt₉₀Rh₁₀ thermocouple. The thermocouple was placed in the hotspot of
129 the furnace, where the thermal gradient is <1°C over the length of the sample. The sample was
130 suspended alongside the thermocouple in order to minimize the difference between the
131 temperature of the sample and the reading of the thermocouple. The reproducibility and
132 measurement of this arrangement is better than 5°C. The experiments were run isothermally at
133 1350 °C at the run conditions and typically for 24h.

134 The BH hydrous glasses (BH1, BH3, BH6 BH7 and BH10) were synthesized at
135 Laboratoire Magmas et Volcans in a piston-cylinder apparatus at 1 GPa and 1300 °C using a
136 1/2" assembly. The starting materials consisted of anhydrous glasses that were first synthesized
137 by re-melting the starting material in a gas-mixing furnace at one bar, 1350 °C and three
138 different fO_2 conditions of ~QFM, QFM+2 and QFM+4. The glasses were then ground under
139 ethanol in an agate mortar to a homogeneous powder mixture. For the piston-cylinder
140 experiments, we used a Pyrex-MgO assembly, a graphite heater, an outer NaCl sleeve, and
141 Au₈₀-Pd₂₀ capsules (with a 4 mm outer diameter for 1/2" assemblies, 0.2 mm wall thickness, 4–
142 5 mm length). To prepare the capsules, we first added deionized water at the bottom of the

143 capsule using a micro-syringe. After loading and compacting ~50 mg of glass powder, the
144 capsule was welded shut. We checked for leaks during capsule preparation by weighing the
145 welded capsules before and after ≥ 1 h heating at 120 °C in an oven. Before starting the
146 experiments, the capsules were placed in an oven at 120 °C overnight to ensure homogenous
147 distribution of the volatiles. During the experiments, the samples were held at 1300 °C and 1
148 GPa for only 15 min in order to minimize fO_2 re-equilibration and H₂O loss. The temperature
149 was measured very close to the capsule by a W₉₅Re₅-W₇₄Re₂₆ thermocouple. Quenching of the
150 hydration experiments was done by switching off the heating power, which led to a cooling
151 rate > 80 °C/s.

152 The glasses recovered from the experiments were polished on both sides for major
153 element characterization by electron microprobe, H₂O concentration measurements by Raman
154 spectroscopy (for hydrous glasses only) and XANES measurements. Fragments of the
155 anhydrous glasses were also analyzed by conventional Mössbauer spectroscopy using a
156 radioactive point source at the Bayerisches Geoinstitut. Details of the experimental conditions
157 for each run, as well as their chemical compositions can be found in Table 1-2 of the
158 Supplementary material.

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

163 **4. Analytical methods**

164 **4.1. Electron microprobe analyzes**

165 Melt inclusions and their host olivines were analyzed for major elements by electron
166 microprobe at Laboratoire Magmas et Volcans with a CAMECA SX 100. All analyzes were
167 performed with a 15 kV accelerating voltage. Olivines were measured with a 1 μm diameter
168 focused beam and a 100 nA beam current. Counting times for each element were: Al (160-220
169 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
170 Fe of olivines presenting a slightly tilted surface were performed in EDS mode using the
171 electron microprobe to avoid bias on their stoichiometry. Counting time for these three elements
172 using this analytical condition was 30 s. Melt inclusions were analyzed with a 10 μm diameter
173 beam and two beam current conditions. The elements measured with a 8 nA beam and their
174 respective counting times were: Na (10 s), Mg (30 s), Si (10 s), Al (20 s), Ca (10 s), Ti (30 s)
175 and Fe (30 s). The elements measured at 50 nA and the respective counting times were: K (40
176 s), P (40 s) and Mn (80 s). Volatile elements were analyzed with a 10 μm diameter beam and a
177 beam current of 40 nA. Respective counting times were: S (50 s), Cl (50 s) and F (300 s).
178 Analytical uncertainties on glass data for major elements were obtained from replicate
179 measurements on the natural glass Ve32 ($n = 23$). The total analytical 2σ error, which
180 corresponds to the maximum value between the precision and accuracy of measurements, for
181 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^* ,
182 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 .
183 The major and volatile element compositions of melt inclusions and the major element
184 compositions of their host crystals are given in Table 3 of the Supplementary material. The
185 values on the Ve32 standard are also reported in Table 3 of the Supplementary material.

186 **4.2.Raman spectroscopy**

187 Water content of 14 melt inclusions was determined by Raman spectroscopy. Spectra
188 were collected at Laboratoire Magmas et Volcans using an InVia (Renishaw) confocal Raman
189 micro-spectrometer. Analytical details can be found in Schiavi et al. (2018). The diode laser
190 output power was 150 mW. Laser power on the sample was reduced by filters in order to operate
191 at powers of ~ 1 mW. Laser power on the sample was periodically checked. The analytical
192 conditions used result in lateral and axial spatial resolutions of ~ 1 and $3 \mu\text{m}$, respectively, near
193 the sample surface. Daily calibration of the spectrometer was performed based on a Si 520.5
194 cm^{-1} peak. Analyzes were carried out at $2 \mu\text{m}$ depth on polished melt inclusions. The spectra
195 were recorded in the wavenumber ranges from ~ 100 to 1350 cm^{-1} (alumino-silicate network
196 domain) for 4 cycles of 30 s and from ~ 2900 to 3800 cm^{-1} (water domain) for 7 cycles of 30 s,
197 using Wire 4.2 software. Basaltic, andesitic and rhyolitic glasses, with water content from 0 to
198 $6.70 \pm 0.35 \text{ wt\%}$ were used as external reference standards (Médard and Grove, 2008; Schiavi
199 et al., 2018) and analyzed several times during each analytical session at the same conditions
200 as the samples, in order to correct for the dependence of band intensities on delivered energy.
201 Analytical precision calculated based on repeated daily measurements of the reference glass
202 82-72f#9 was better than 16 % rel. Analyzes of host olivines were performed with the same
203 conditions in order to correct melt inclusion spectra that suffered from signal contamination
204 from the host crystal.

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

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

219 **4.3.FTIR spectroscopy**

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

235 molar absorption coefficient of $62.8 \pm 0.8 \text{ Lmol}^{-1}\text{cm}^{-1}$ as proposed by Mercier et al. (2010). For
236 silicate under-saturated samples, we chose to use a molar absorption coefficient of 43.96 ± 0.6
237 $\text{Lmol}^{-1}\text{cm}^{-1}$ (Mercier et al., 2010). The analytical uncertainty was calculated as the 2σ relative
238 standard deviation (RSD) on replicate measurements. When melt inclusions could only be
239 analyzed once, we report an analytical uncertainty that corresponds to the maximal 2σ RSD
240 determined on replicate analyzes of other melt inclusions in the same session. Water contents
241 of melt inclusions are given in Table 3 of the Supplementary material.

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

248 **4.4. Mössbauer analyzes**

249 The iron speciation of the 12 anhydrous experimental glasses (Table 1 of the
250 Supplementary material) was determined by conventional Mössbauer spectroscopy. Analyzes
251 were carried out at the Bayerisches Geoinstitut, Bayreuth. Glasses were mounted between two
252 pieces of plastic film and centered in a $1000 \mu\text{m}$ diameter hole drilled in a $25 \mu\text{m}$ thick Pb foil.
253 Data were collected in transmission mode on a constant acceleration Mössbauer spectrometer
254 with a nominal $370 \text{ MBq } ^{57}\text{Co}$ point source in a $12 \mu\text{m}$ Rh matrix with active dimension of
255 $500 \times 500 \mu\text{m}^2$. The velocity scale was calibrated with a $25 \mu\text{m}$ thick natural $\alpha\text{-Fe}$ foil. A line
256 width of 0.36 mm/s for the outer lines was obtained for $\alpha\text{-Fe}$ at room temperature. Analyzes
257 were performed at room temperature with measuring times from 7 hours to 5 days.

258 $\text{Fe}^{3+}/\Sigma\text{Fe}$ in 14 olivine-hosted melt inclusions were determined using a synchrotron
259 Mössbauer source (SMS; Potapkin et al., 2012; Smirnov et al., 1997). Analyzes were carried
260 out at the Nuclear Resonance beamline ID18 (Rüffer and Chumakov, 1996) of the European
261 Synchrotron Facility, Grenoble. Melt inclusions were polished on both sides to avoid signal
262 contamination from their host crystal and were centered under a 20-30 μm hole drilled in a 25
263 μm -thick Re foil. Data were collected using a multi-bunch operating mode and a $10 \times 15 \mu\text{m}^2$
264 focalized beam for 4.5 to 9 hours at room temperature. The SMS provided ^{57}Fe resonant
265 radiation with the energy of 14.4125 keV and the bandwidth of ~ 13 neV tunable in the energy
266 range of about $\pm 0.3 \mu\text{eV}$. The velocity scale was calibrated with a 25 μm -thick natural $\alpha\text{-Fe}$
267 foil and the source line width was checked after each analysis. Spectra were fitted using MossA
268 software using a full transmission integral (Prescher et al., 2012).

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

271 **4.5.XANES analyzes**

272 Fe K-edge X-ray absorption near edge structure (XANES) were collected at the LUCIA
273 (Vantelon et al., 2016) beamline of SOLEIL synchrotron, France, during five different sessions
274 in 2014, 2015, 2017, 2018 and 2019. Data were collected in fluorescence mode between 7050
275 and 7300 eV, with 0.1 eV steps in the pre-edge region (7106–7120 eV). The excitation energy
276 was selected using a Si(311) or a Si(111) double crystal monochromator depending on the
277 analytical session, leading to a spectral energy resolution of 0.2 and 1 eV, respectively. The
278 monochromator was calibrated by setting the first inflexion point of a Fe metallic foil to
279 7112 eV. The beam was focused using KB mirrors down to $\sim 3 \times 3 \mu\text{m}^2$ (Table 4 of the
280 Supplementary material). The fluorescence detector was a Bruker silicon drift diode mono-
281 element with a total active area of 60 mm^2 . The distance between the sample and the detector

282 was adjusted to ensure optimal counting rate for each sample. Samples were tilted at an angle
283 of 5° with respect to the incident beam. X-ray fluorescence (XRF) chemical maps were used to
284 select spots for XANES measurements. Spectra collected in anhydrous reference glasses during
285 each session were used to refine the alignment of the spectra collected during the different
286 sessions and to calibrate $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios obtained from the pre-edge region of XANES spectra
287 collected on our unknown samples. For unknown samples, two consecutive XANES spectra
288 were collected at the same location. More details on the analytical conditions are given in Tables
289 4-5 of the Supplementary material.

290 Cottrell et al. (2018) demonstrated that hydrous glasses can be affected by beam-induced
291 oxidation depending on their H_2O content, their initial oxidation state and the radiation dose
292 used to collect spectra. Therefore, during our 2019 session, we acquired XANES spectra on
293 hydrous glasses using different radiation doses ranging from 7.9×10^5 to 2.4×10^8
294 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
295 attenuating the beam flux by placing a $60 \mu\text{m}$ thick Al foil along the beam path (Tables 4-5 of
296 the Supplementary material). The radiation dose corresponds to the number of photons
297 delivered to the sample per square micrometer. The sample area exposed to radiation was
298 determined assuming that the beam had an elliptic shape. Melt inclusions were then analyzed
299 during that 2019 session with a $4 \times 3 \mu\text{m}^2$ focused beam size using radiation doses of 3.7×10^7
300 photons/s/ μm^2 .

301 To better constrain conditions at which beam-induced oxidation occurs, we tested for a
302 time dependent variation in the intensity of the pre-edge multiplets. Following Debret et al.
303 (2015) and Cottrell et al. (2018), we measured the peak amplitude at two fixed energies that
304 correspond to the energies of the Fe^{2+} and Fe^{3+} pre-edge peaks, respectively (7112.6 and 7114
305 eV), during 300 s. The duration of a time series acquisition corresponds to the time needed to

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

308 XANES spectra were normalized and corrected for self-absorption using Athena
309 software (IFFEFIT suite; Ravel et Newville, 2005). Melt inclusion spectra were tested for
310 potential contamination from the host olivine crystal by carrying out a comparison with spectra
311 collected on synthetic glasses and using the principal component analysis procedure described
312 in Hartley et al. (2017) and Shorttle et al. (2015). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of samples were derived
313 by fitting the pre-edge region using PeakFit© software. The pre-edge region was fitted between
314 7108 and ~ 7118 eV with two Gaussian peaks, constrained to have the same width and line
315 shape, simultaneously with the background, which was modeled as the tail of two other
316 Gaussian functions. The pre-edge centroid energies, integrated areas and intensity ratios
317 calculated as $I_{\text{Fe}^{3+}}/(I_{\text{Fe}^{3+}} + I_{\text{Fe}^{2+}})$ are reported in Table 6 of the Supplementary material.
318 Intensities collected as a function of time at 7112.6 and 7114 eV in the same sample were
319 normalized as $I[(\text{Fe}^{3+})]/[I(\text{Fe}^{3+})+I(\text{Fe}^{2+})] = I(7114)/[I(7114)+I(7112.6)]$ in order to track the
320 evolution of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios through time.

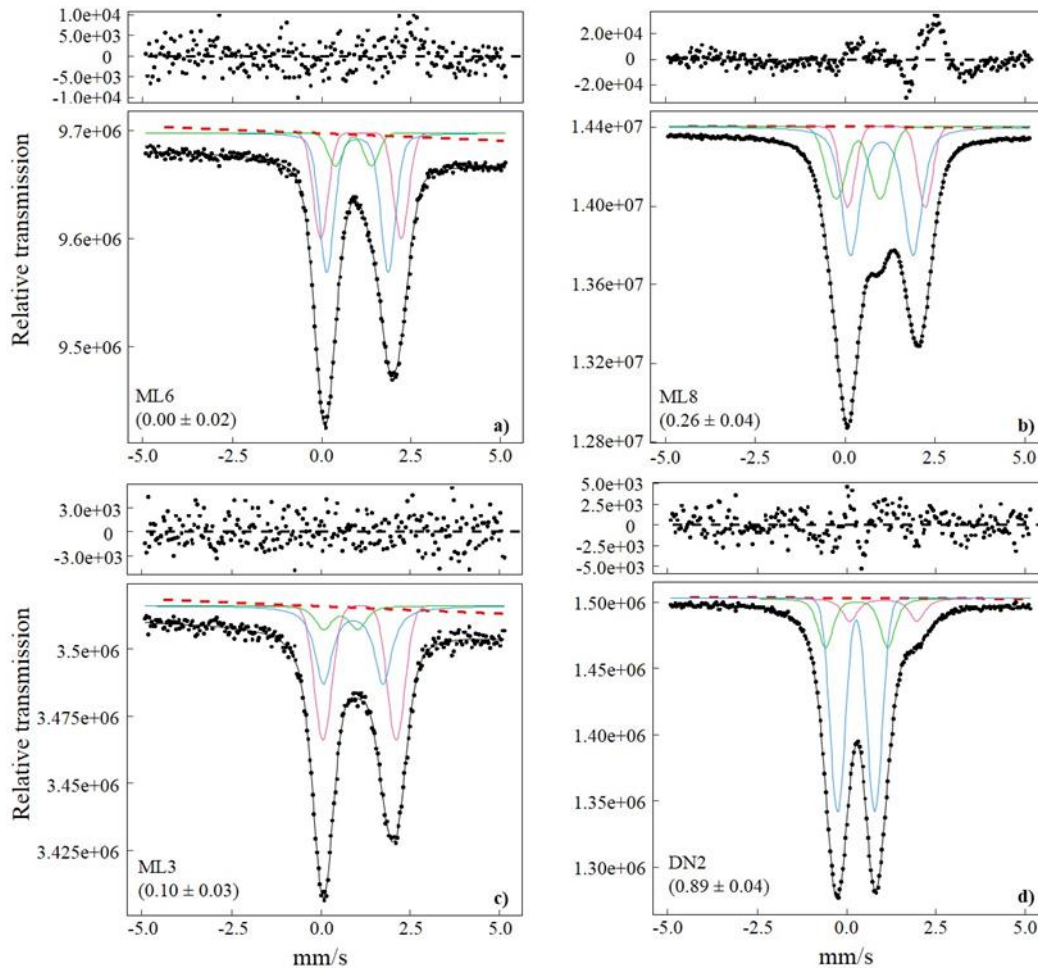
321 **5. Results**

322 **5.1. Mössbauer spectroscopy**

323 **5.1.1. Independent characterization of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in reference** 324 **glasses**

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

327 by statistics and consistency of parameters across all spectra for reference glasses was obtained
 328 with three pseudo-Voigt doublets (Figure 1).
 329



330
 331 Figure 1: Results of the fitting procedure of four Mössbauer spectra collected for anhydrous
 332 basaltic reference glasses (Table 1 of the Supplementary material). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of the
 333 glasses are given in brackets. The red dashed line corresponds to the linear baseline. The black
 334 line represents the modeled spectra. Blue, green and pink lines correspond to the three pseudo-
 335 Voigt doublets used to characterize iron environments. For the most reduced glasses (a) the
 336 three doublets are attributed to the Fe^{2+} environment. For reduced and oxidized glasses (b-c),
 337 the green pseudo-Voigt doublet was attributed to the Fe^{3+} environment whereas the two others
 338 were attributed to the Fe^{2+} environment. For the more oxidized sample (d), the pink pseudo-

339 Voigt doublet was attributed to the Fe²⁺ environment whereas the two others were attributed to
340 the Fe³⁺ environment. Residuals obtained from the fitting procedure are given at the top of the
341 spectra.

342

343 The values for the center shift (δ), quadrupole splitting (Δ) and the full width at half
344 maximum (FWHM) for each doublet were set as free to vary at first. Then, the FWHMs of the
345 three doublets were constrained to be equal when unrealistic values were obtained for hyperfine
346 parameters. Reduced χ^2 values range from 0.95 to 1.93. Values obtained for hyperfine
347 parameters are summarized in Table 7 of the Supplementary material. The values obtained for
348 the hyperfine parameters indicate that two doublets are attributed to the Fe³⁺ environment,
349 whereas one doublet is attributed to the Fe²⁺ environment in our most oxidized glass. In contrast,
350 two doublets are attributed to the Fe²⁺ environment and one doublet is attributed to the Fe³⁺
351 environment in the less oxidized glasses. Three doublets are attributed to the Fe²⁺ environment
352 in our most reduced glasses (e.g. Alberto et al., 1996; Berry et al., 2018; Cottrell et al., 2009;
353 Zhang et al., 2018); Table 7 of the Supplementary material). Fe³⁺/ Σ Fe ratios were obtained from
354 the relative area of each doublet. Determination of the 2 σ uncertainty is based on both the
355 statistical uncertainty derived from the fit and the reproducibility given by results obtained from
356 the several tested methods. The fit results are reported in Table 7 and Figure 1.

357 The values obtained for the hyperfine parameters in our most reduced glass standards
358 suggest that no Fe³⁺ component is required. However, the doublets are characterized by broad
359 lines and the hyperfine parameters show a systematic overlap of the Fe²⁺ components that
360 suggests that a small amount of Fe³⁺ could be present in these reference glasses (Figure 1a).
361 Therefore, we conclude that we are not able to determine the iron speciation accurately in
362 glasses with < 10 % Fe³⁺/ Σ Fe, and for that reason we decided not to use those in our XANES
363 calibration (Table 1 of the Supplementary material).

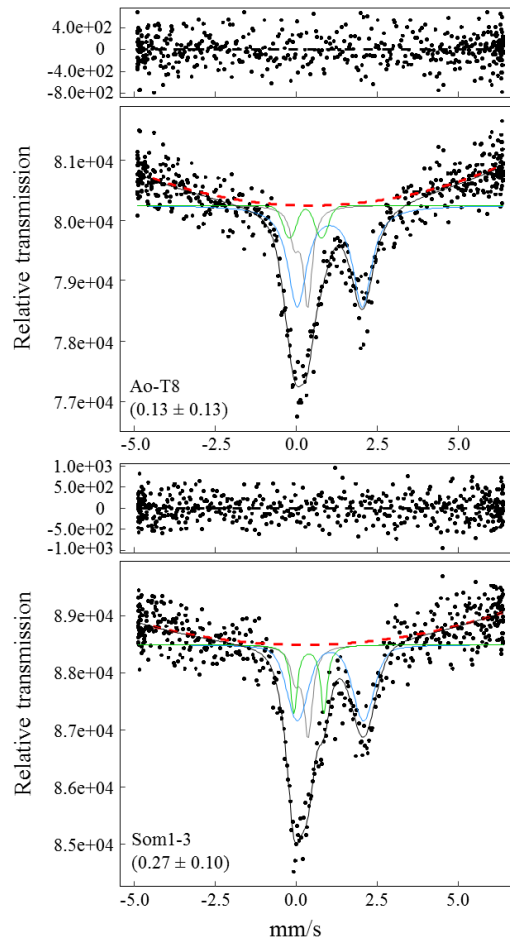
364 **5.1.2. Fe³⁺/ΣFe in melt inclusions**

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

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

388 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were derived from the relative areas of each doublet and 2σ uncertainties
389 were calculated from the statistical fitting uncertainties reported by the software. Results are
390 shown in Table 3 of the Supplementary material.

391



392

393

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

401 5.2.XANES

402 5.2.1. Calibration of the XANES spectra

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

416 Cottrell et al. (2009) also used a pre-edge centroid energy based calibration and found
417 that the use of a second order polynomial fit to their most oxidized reference glasses was
418 appropriate for their data. The use of this calibration leads to the determination of an average
419 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.16 ± 0.01 for MORB glasses (Cottrell and Kelley, 2011). More recently,
420 Berry et al. (2018) proposed that a linear calibration can be used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ of
421 MORB glasses when only considering the appropriate $\text{Fe}^{3+}/\Sigma\text{Fe}$ range for MORBs ($\text{Fe}^{3+}/\Sigma\text{Fe} <$
422 0.3). They derived an average $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of 0.11 ± 0.02 for MORB glasses when they use
423 the linear calibration and 0.10 ± 0.02 when they use the polynomial calibration. Results derived
424 from these two calibrations are similar within error, which indicates that both calibrations can

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

436 $Fe^{3+}/\Sigma Fe$ ratios derived from XANES spectra were determined for our natural glass
 437 samples from the centroid energy of the fitted pre-edge region using a polynomial calibration
 438 derived from seven basaltic reference glasses (Figure 3; Table 1 of the Supplementary material).
 439 As the $Fe^{3+}/\Sigma Fe$ ratios of our more reduced standards are below the detection limit of Mössbauer
 440 spectroscopy (<10 %), we did not use them in our calibration (Table 1 of the Supplementary
 441 material).

442 The XANES calibration is given by the equation:

$$443$$

$$444 \quad E_{centroid} = -1.0540 (Fe^{3+}/\Sigma Fe)_{Mössbauer}^2 + 2.6146 (Fe^{3+}/\Sigma Fe)_{Mössbauer} +$$

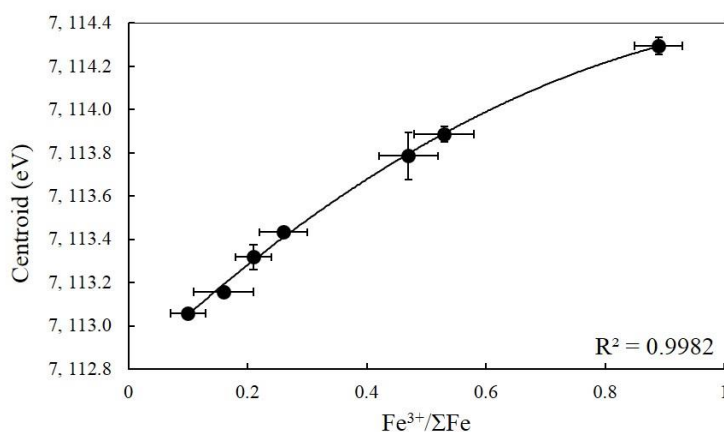
$$445 \quad 7112.8004 \quad (1)$$

446

447 in which $E_{centroid}$ corresponds to the centroid energy (in eV) and $(Fe^{3+}/\Sigma Fe)_{Mössbauer}$ is the
 448 $Fe^{3+}/\Sigma Fe$ value obtained by Mössbauer spectroscopy. This calibration is applicable to samples
 449 with $Fe^{3+}/\Sigma Fe$ ratios ranging between 0.10 and 0.90. The accuracy of the calibration was tested

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

457



458

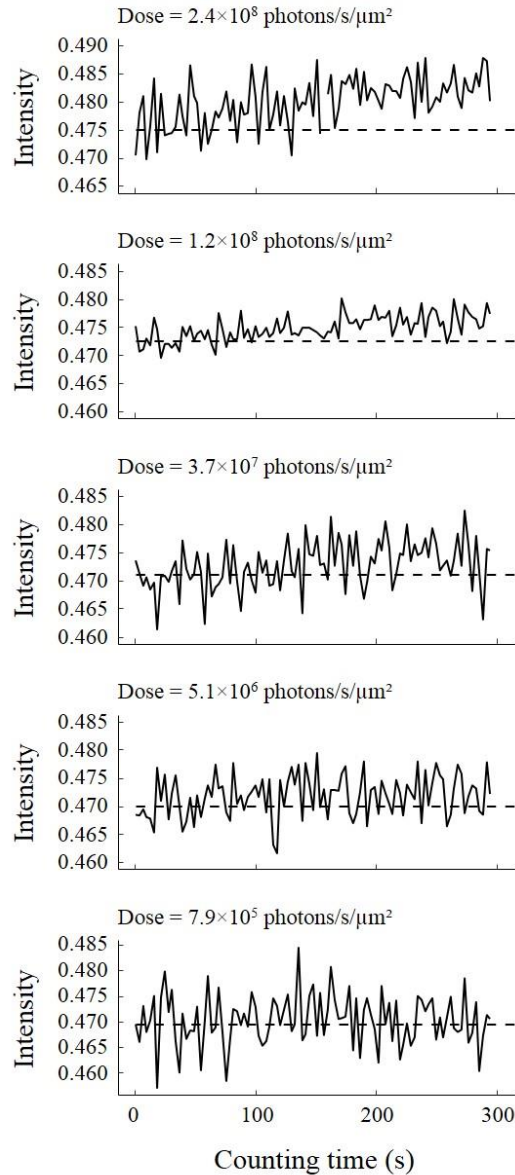
459 Figure 3: XANES calibration curve for the determination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of melt
460 inclusions and glasses. The solid curve is the second order polynomial fit result. Averaged
461 centroid energies and $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios from Mössbauer spectroscopy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

464 **5.2.2. Time series in hydrous synthetic glasses**

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

469 collected on hydrous experimental glasses with water contents ranging from 0.02 ± 0.002 to
470 2.86 ± 0.34 wt% and equilibrated at various fO_2 show no clear evidence of beam damage when
471 using radiation doses lower than 1.2×10^8 photons/s/ μm^2 . When using higher doses, the time
472 series collected on water-rich glasses ($\geq 2.48 \pm 0.20$ wt% H₂O) show a systematic increase in
473 the intensity ratio $I(7114)/[I(7114)+I(7112.6)]$ (Figure 4). As time series are collected at fixed
474 energies, the effect of beam-induced oxidation cannot be monitored using centroid positions.
475 However, when considering a XANES spectrum, the use of the centroid position allows us to
476 determine more accurate $Fe^{3+}/\Sigma Fe$ ratios.

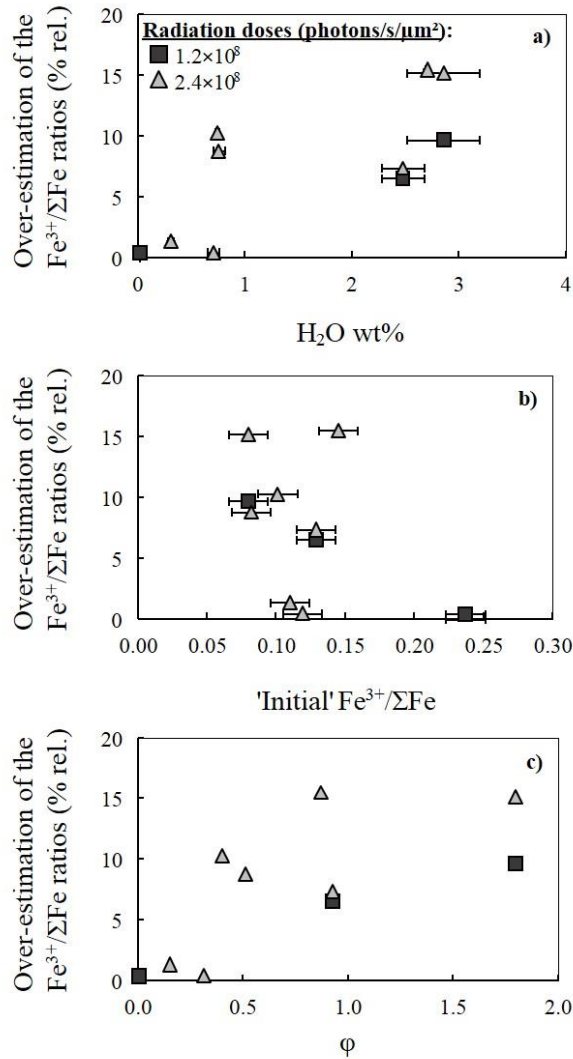
477 At 2.4×10^8 photons/s/ μm^2 , time series collected on the BH1 glass (0.74 ± 0.02 wt%
478 H₂O) also show an increase in its intensity. This suggests that beam damage can even occur for
479 very low water contents when using such high radiation doses.



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.

488 We converted the intensity of absorption recorded in the time series into $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
489 using a calibration based on non-normalized pre-edge peak intensity ratios in the reference
490 glasses. Then we applied a linear regression through the variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ with time to
491 calculate the over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ induced by beam damage. We find that $\text{Fe}^{3+}/\Sigma\text{Fe}$
492 ratios are over-estimated by 6 to 10 % rel. and 6 to 15 % rel. when using radiation doses of
493 1.2×10^8 and 2.4×10^8 photons/s/ μm^2 , respectively. The percentage of over-estimation of the
494 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios shows a poor positive correlation with the water content of glasses (Figure 5a)
495 and no correlation with their original $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (i.e., as determined from the pre-edge
496 centroid energy of a spectrum collected in non-damaging conditions (5.1×10^6 photons/s/ μm^2 ;
497 Figure 5b). Cottrell et al. (2018) found that the beam damage susceptibility ϕ , which they define
498 as the product of the water concentration and the ferrous/ferric oxide ratio on a molar basis, is
499 positively correlated with the percentage of over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for
500 hydrous glasses. Our data do not show such correlation (Figure 5c). The lack of correlation
501 between these parameters implies that we were not able to quantify the over-estimation of
502 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios for glasses analyzed using standard radiation doses ($\sim 10^8$ photons/s/ μm^2) and
503 for which time series have not been collected.



504

505 Figure 5: Overestimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded by time series collected in hydrous

506 glasses as a function of (a) their water content, (b) their 'initial' $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios determined in

507 non-photo-oxidizing conditions (5.1×10^6 photons/s/ μm^2) and (c) the beam damage

508 susceptibility ϕ ($\phi = \text{XHO}_{0.5} \times \text{XFeO}/\text{XFeO}_{1.5}$; Cottrell et al., 2018). Squares and triangles

509 represent the overestimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for radiation doses of 1.2×10^8 and

510 2.4×10^8 photons/s/ μm^2 , respectively. Errors given on water contents and 'initial' $\text{Fe}^{3+}/\Sigma\text{Fe}$

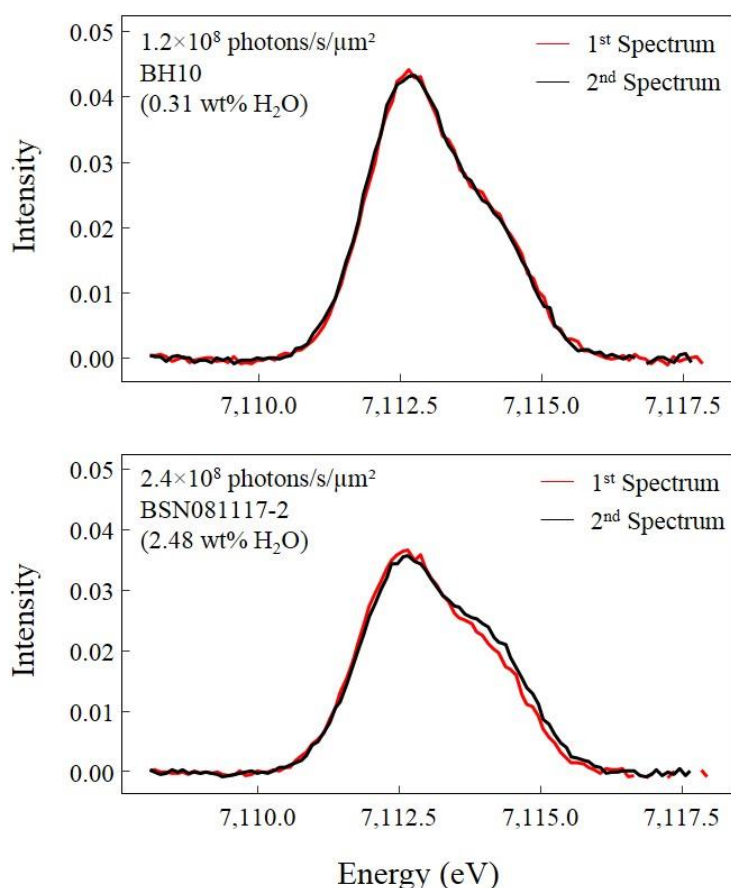
511 ratios are expressed as 2σ errors (Table 2 of the Supplementary material).

5.2.3. XANES spectra in hydrous synthetic glasses

512

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

530 When no beam damage was detected either from the time series and/or the comparison
531 of the pre-edge regions of the two consecutive spectra, we calculated a mean Fe³⁺/ΣFe from the
532 two spectra collected at the same spot. 2σ uncertainties were calculated as the propagation of
533 the 2σ uncertainty of the Fe³⁺/ΣFe ratios of both spectra. On the other hand, when there was
534 evidence for oxidation from the difference in the two spectra, we discarded the value from the
535 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

549 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios while still keeping the small beam size that is required for melt inclusion
550 analysis.

551 **5.2.4. Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in melt inclusions**

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

564 In addition to the time series, we also compared the pre-edge features of two spectra that
565 were successively acquired at the same location. Beam damage affecting the second spectrum
566 is clearly visible in eleven water-rich arc melt inclusions with water contents ranging from 2.31
567 to 4.59 wt%. Still, this effect is minimal and only one of them (inclusion SVP291c n4) shows
568 an over-estimation of its $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio that is larger than the 2σ uncertainty on the $\text{Fe}^{3+}/\Sigma\text{Fe}$
569 ratio. Surprisingly this melt inclusion shows no clear evidence for beam damage in the time
570 series, which suggests that the first spectrum has not been affected by beam damage and that
571 the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio derived from it is reliable. In the end, more than half of the water-rich (> 1

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

574 When no sign of beam damage was recorded in the time series and/or in the comparison
575 of the pre-edge regions of two spectra collected on the same spot, we calculated a mean
576 Fe³⁺/ΣFe ratio from the two spectra. 2σ uncertainties were calculated as the propagation of the
577 2σ uncertainties of the Fe³⁺/ΣFe ratios of both spectra. When time series could not be collected
578 for lack of space in the inclusion, we calculated a mean Fe³⁺/ΣFe ratio from the two spectra
579 when their Fe³⁺/ΣFe ratios lie within the 2σ errors. Melt inclusions for which time series exhibit
580 evidence of beam damage were removed from our dataset. When melt inclusions have been
581 analyzed in different spots, mean Fe³⁺/ΣFe ratios were calculated using only the first spectra
582 collected at each spot when the time series didn't record any beam damage. Results are given
583 in Table 3 of the Supplementary material.

584 **6. Discussion**

585 **6.1. The effect of beam-induced oxidation on the determination of** 586 **Fe³⁺/ΣFe ratios in silicate glasses**

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

594 continues to occur during acquisition of the second spectrum. To explain the cases where time
595 series showed oxidation through time, but no change was noticeable between the pre-edge
596 features of the two spectra successively collected, we can make two hypotheses. The first
597 hypothesis is that beam damage is “completed” after full acquisition of the pre-edge (Cottrell
598 et al., 2018). The second hypothesis is that the modification due to beam damage is not
599 systematically large enough to be visible given our spectral resolution. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
600 calculated for hydrous experimental glasses from their pre-edge centroid energies suggest that
601 the effect of this process may be within the error associated with the calculation of these ratios.
602 However, based on time series, an over-estimation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of about 15 % rel. may occur
603 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
604 inclusions, and especially of arc melt inclusions that are usually water-rich, will likely be over-
605 estimated when analyzing them with such doses.

606 A large number of melt inclusions have been analyzed with standard radiation doses
607 ($\sim 10^8$ photons/s/ μm^2) during our first synchrotron sessions. At the time, as we did not realize
608 how large the effects of beam damage could be, we did not systematically collect time series.
609 The lack of or the poor correlation between the chemical composition of glasses (in particular
610 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
611 recorded by time series collected on hydrous synthetic glasses (Figure 5) means that we are not
612 able to quantify the over-estimation that potentially affected the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios derived from
613 XANES spectra collected on these melt inclusions using standard beam conditions. Therefore,
614 we were not able to correct them and we decided not to use them.

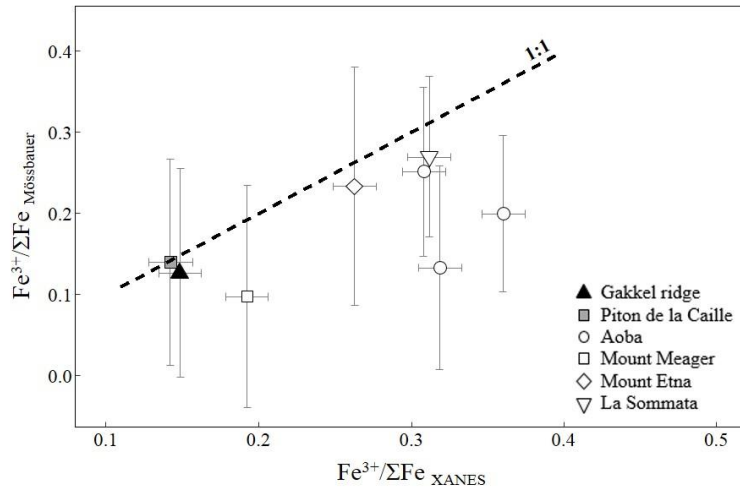
615 Time series collected on hydrous experimental glasses using radiation doses lower than
616 $\sim 10^8$ photons/s/ μm^2 do not show any evidence for oxidation. However, time series acquired in
617 three hydrous melt inclusions using a radiation dose of 3.7×10^7 photon/s/ μm^2 show evidence
618 of beam damage. Moreover, melt inclusions that exhibit an over-estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$

619 ratio derived from the second spectrum compared to the first one do not systematically display
620 an evolution of the speciation through time in the time series. These observations corroborate
621 the ones carried out by Cottrell et al. (2018) showing that lowering the radiation dose to about
622 $\sim 10^7$ photons/s/ μm^2 allows us to mitigate but not definitively eliminate beam-induced oxidation
623 during XANES analyzes. Using these more appropriate beam conditions, only three melt
624 inclusions out of thirty show clear signs of beam damage during the acquisition of the first pre-
625 edge spectrum.

626 **6.2. $\text{Fe}^{3+}/\Sigma\text{Fe}$ inferred from Mössbauer vs. XANES spectroscopy**

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

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



638

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

645

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

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

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

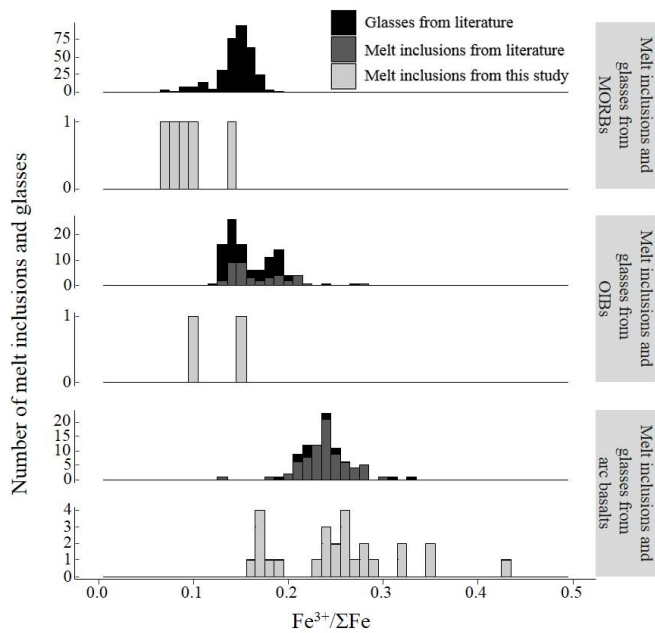
667 **6.3. The oxidation state of melt inclusions**

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

674 Our results show that melt inclusions from MORB display a mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of
675 0.10 ± 0.05 (n=5). Melt inclusions from OIB and arcs display mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of
676 0.13 ± 0.05 (n=2) and 0.25 ± 0.15 (n=19) respectively. Mount Etna is not classified as an arc
677 volcano and has a more complex geodynamic setting than the other volcanoes presented in this
678 study. Many authors suggested that Mount Etna has an OIB signature but for which the mantle
679 is metasomatized by subduction-derived fluids. Nevertheless, the composition of the mantle
680 beneath Mount Etna is still debated (e.g. Correale et al., 2014; Schiano et al., 2001; Schiavi et

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

685 In Figure 8, we report the number of melt inclusions as a function of their geodynamic
686 setting (melt inclusions from Mount Etna are reported here as arc melt inclusions) and their
687 calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (light grey). Also reported are previously published data for melt
688 inclusions in high-Mg olivines ($> \text{Fo}_{80}$; dark grey) and glasses (black) from MORBs (Berry et
689 al., 2018; Birner et al., 2018; Cottrell and Kelley, 2011, 2013; Kelley and Cottrell, 2009; Zhang
690 et al., 2018), OIBs (Brounce et al., 2017; De Moor et al., 2013; Hartley et al., 2017; Moussallam
691 et al., 2016) and arcs (Brounce et al., 2014; Kelley and Cottrell, 2009, 2012). This figure shows
692 that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in melt inclusions from MORBs are in good agreement with previous
693 data and comparable to the ones obtained by Berry et al. (2018; 0.10 ± 0.02). $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
694 calculated for melt inclusions from OIBs show similar or lower values than the previously
695 published XANES data. This result may indicate beam-induced oxidation or that the range of
696 $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios recorded for OIBs is larger than previously reported (Brounce et al., 2017; De
697 Moor et al., 2013; Hartley et al., 2017; Moussallam et al., 2016). Melt inclusions from arcs from
698 this study display a range in $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios that is in good agreement with previous data
699 (Brounce et al., 2014; Kelley and Cottrell, 2009, 2012). A few melt inclusions exhibit $\text{Fe}^{3+}/\Sigma\text{Fe}$
700 ratios that are higher than literature data. This suggests that the range of oxidation state recorded
701 in arc magmas may be larger than previously observed. Therefore, our results confirm that arc
702 magmas are more oxidized than those from hot spots and mid-ocean ridges.

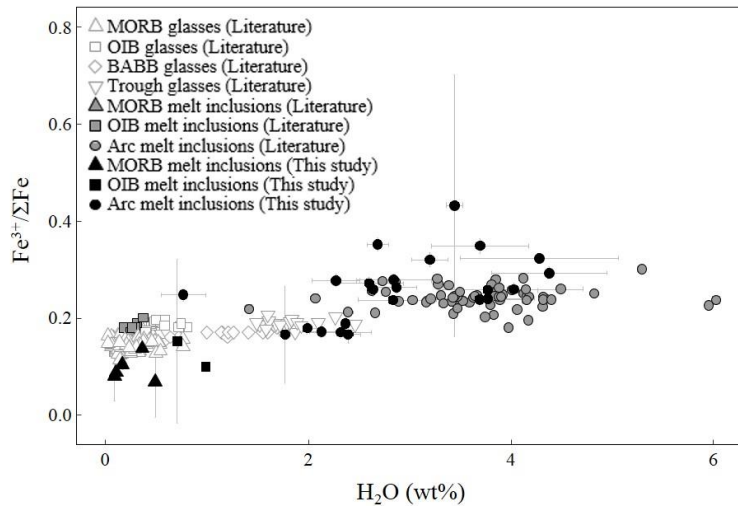


703

704 Figure 8: Number of melt inclusions and glasses as a function of their $Fe^{3+}/\Sigma Fe$ ratios and
 705 geological settings. $Fe^{3+}/\Sigma Fe$ ratios plotted in this graph are mainly derived from XANES
 706 measurements at a radiation dose of 3.7×10^7 photons/s/ μm^2 (light grey; Table 3 of the
 707 Supplementary material). When XANES spectra showed evidence of beam damage, we report
 708 $Fe^{3+}/\Sigma Fe$ ratios, we report $Fe^{3+}/\Sigma Fe$ ratios derived from Mössbauer spectroscopy instead (6 melt
 709 inclusions). Also reported are literature data for glasses (black) and melt inclusions from high-
 710 Mg olivines ($> Fo_{80}$) from arc basalts, OIBs and MORB for comparison (dark grey; Berry et
 711 al., 2018; Birner et al., 2018; Brounce et al., 2014, 2017; Cottrell and Kelley, 2011, 2013; De
 712 Moor et al., 2013; Hartley et al., 2017; Kelley and Cottrell, 2009, 2012; Moussallam et al.,
 713 2016; Zhang et al., 2018).

714

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

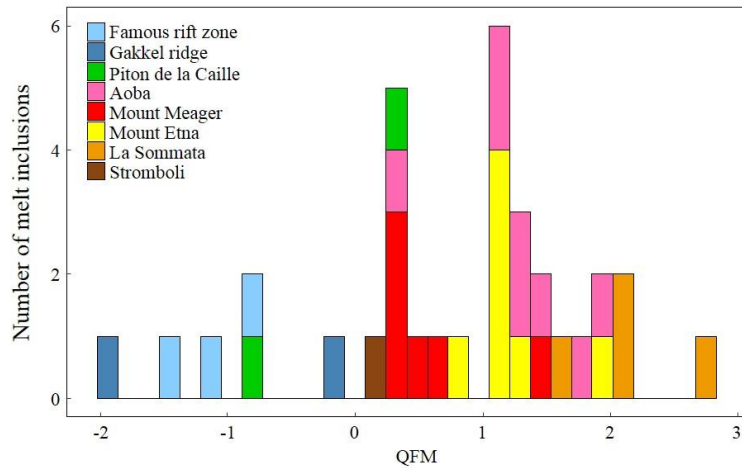


719

720 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
 721 reported in this graph are mainly derived from XANES measurements at a radiation dose of
 722 3.7×10^7 photons/s/ μm^2 (light grey; Table 3 of the Supplementary material). When XANES
 723 spectra showed evidence of beam damage, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios, we report $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios
 724 derived from Mössbauer spectroscopy instead (6 melt inclusions). Data from this study are
 725 represented by black symbols. Error bars are 2σ (Table 3 of the Supplementary material).
 726 Previous data (grey symbols) from Brounce et al. (2014, 2017), Cottrell and Kelley (2011),
 727 Kelley and Cottrell (2009, 2012), Moussallam et al. (2016) and Zhang et al. (2018) collected in
 728 glasses and melt inclusions from high-Mg olivines ($> \text{Fo}_{80}$) are also reported.

729

730 $f\text{O}_2$ values of our melt inclusions were calculated relative to the QFM buffer using the
 731 algorithm of Kress and Carmichael (1991) and are reported in Table 3 of the Supplementary
 732 material and in Figure 9. The QFM values reported in Figure 10 show that melt inclusions from
 733 arc basalts are generally more oxidized (QFM +0.1 to +2.8) than those from MORBs (QFM -
 734 1.9 to -0.1) and OIBs (QFM -0.8 and +0.3).



735

736

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

743

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

753 **7. Conclusions**

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

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

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

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

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

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