

1 Coupled interactions between volatile activity and Fe oxidation state
2 during arc crustal processes

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20 **ABSTRACT**

21 Arc magmas erupted at the earth's surface are commonly more oxidised than
22 those produced at mid-ocean ridges. Possible explanations for this high oxidation
23 state are that the transfer of fluids during the subduction process results in
24 direct oxidation of the sub-arc mantle wedge; or that oxidation is caused by the
25 effect of later crustal processes, including protracted fractionation and degassing
26 of volatile-rich magmas. This study sets out to investigate the effect of
27 disequilibrium crustal processes that may involve coupled changes in H₂O
28 content and Fe oxidation state, by examining the degassing and hydration of
29 sulphur-free rhyolites. We show that experimentally hydrated melts record
30 strong increases in Fe³⁺/ΣFe with increasing H₂O concentration as a result of
31 changes in water activity. This is relevant for the passage of H₂O-undersaturated
32 melts from the deep crust towards shallow crustal storage regions, and raises the
33 possibility that vertical variations in *f*O₂ might develop within arc crust.

34 Conversely, degassing experiments produce an increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ with
35 decreasing H_2O concentration. In this case the oxidation is explained by loss of H_2
36 as well as H_2O into bubbles during decompression, consistent with
37 thermodynamic modelling, and is relevant for magmas undergoing shallow
38 degassing *en route* to the surface. We discuss these results in the context of the
39 possible controls on $f\text{O}_2$ during the generation, storage and ascent of magmas in
40 natural arc settings, in particular considering the timescales of equilibration
41 relative to observation as this affects the quality of the petrologic record of
42 magmatic $f\text{O}_2$.

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44

45 INTRODUCTION

46 A fundamental question in earth sciences concerns the distribution of oxygen
47 within the solid Earth, its cycling through subduction zones and, through
48 volcanic degassing, its effects on the atmosphere. In particular, the controls on
49 the oxidation state of melts as they pass through the mantle and crust are
50 challenging to constrain. It is clear that transfer of hydrous fluids from the
51 subducting slab into the mantle is crucial for generating some of the typical
52 geochemical signatures of subduction zone magmas, such as enrichment in large
53 ion lithophile elements (LILE) and volatiles. Comparison of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in lavas
54 arriving at the Earth's surface shows that arc lavas also tend to be more oxidised
55 than those produced at mid-ocean ridges or in other settings (e.g. Carmichael
56 1991; Ballhaus 1993; Lee et al. 2010; Evans et al. 2012). Mantle xenoliths
57 entrained by arc magmas also appear to be more oxidised than those in other
58 tectonic environments (e.g. Wood et al. 1990; Brandon & Draper 1996;
59 Parkinson & Arculus 1999; Frost & McCammon 2008).

60 It is commonly suggested that increased $f\text{O}_2$ in arc systems compared with
61 other tectonic environments is a primary feature related to mass transfer from
62 the subducting slab to the mantle wedge (e.g. Brandon & Draper 1996; Parkinson
63 & Arculus 1999; Kelley & Cottrell 2009), either directly through addition of
64 volatiles, or indirectly if hydrous fluids carry dissolved Fe^{3+} or sulphate (Kelley &

65 Cottrell 2009). However, subduction zone magmatism is also characterised by
66 complex crustal processes that could be expected to exert significant controls on
67 oxidation state. These processes include magma fractionation, decompression,
68 degassing and eruption. Arc magmas tend to be volatile rich and may be more
69 prone to stalling and storage in the crust during ascent; this may increase the
70 importance of fractionation and degassing in particular. Arc magmas also tend to
71 crystallise magnetite early during differentiation, and studies based on the
72 partitioning of redox-sensitive incompatible elements suggest that magmatic
73 differentiation could be one reason for the higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ of arc lavas (e.g.
74 Mallman & O'Neill 2009; Lee et al. 2010). Other studies suggest that the influence
75 of volatiles on $f\text{O}_2$ could be significant, particularly during crustal processes such
76 as the degassing of C-O-H-S volatile species during shallow magmatic ascent (e.g.
77 Sato 1978; Mathez 1984; Candela 1986; Burgisser & Scaillet 2007; Burgisser et
78 al. 2008; Fiege et al. 2014).

79 Understanding the relationship between volatiles and the oxidation state
80 of magmas involves untangling two distinct problems. The first problem is the
81 fundamental effect of dissolved volatiles, as chemical constituents of the melt, in
82 determining Fe oxidation state. This is at the heart of whether H_2O can itself be
83 an important oxidising agent, or whether the observed link between H_2O and
84 $\text{Fe}^{3+}/\Sigma\text{Fe}$ is possible only by association with oxidised components in slab fluids
85 (e.g. Lecuyer & Ricard 1996; Parkinson & Arculus 1999). The second problem is
86 to understand the ways in which crustal processes may affect both melt volatile
87 concentrations and melt oxidation state. These effects include (i) variations in
88 *equilibrium* volatile speciation and Fe redox state with pressure and
89 temperature, and (ii) factors related to processes such as magmatic degassing;
90 these factors could be truly *disequilibrium* (i.e., kinetically inhibited over the
91 time- and length-scale of interest) or *open system* (for example, involving
92 segregation of melt and vapour).

93 In Part I of this study we present a brief review of literature evidence
94 relating to the first problem, that of chemical mechanisms linking volatile
95 dissolution with melt oxidation state, to consider whether volatiles can
96 fundamentally affect oxidation state *via* melt chemistry. In Part II, we tackle the

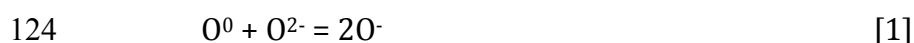
97 second problem, presenting new data to explore the effect of disequilibrium or
98 open system changes in H₂O content on the oxidation state of sulphur-free
99 rhyolite melts and glasses, using a new series of coupled H₂O and Fe³⁺/ΣFe
100 measurements from existing hydration and decompression experiments. We
101 discuss the implications of our results for processes operating in natural
102 magmas, highlighting the need to consider kinetics in these arc systems where
103 there is ample evidence of disequilibrium at a variety of temporal and spatial
104 scales.

105

106 **PART I: A REVIEW OF THE EVIDENCE LINKING VOLATILES, MELT** 107 **CHEMISTRY AND OXIDATION STATE**

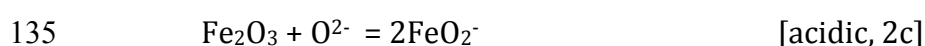
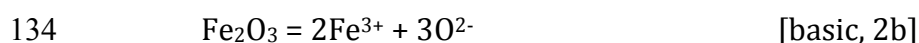
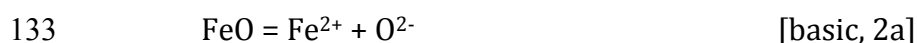
108 The effects of variations in anhydrous melt composition on ferric-ferrous ratios
109 at constant fO_2 are well known (e.g. Paul & Douglas 1965; Sack et al. 1980; Kress
110 & Carmichael 1991; Toplis 2005), but there has been considerable debate over
111 the effect of H₂O, as a chemical component of the melt, on Fe³⁺/ΣFe. In particular,
112 it has been suggested that the same process that causes oxidation when alkalis
113 are added into silicate melts at constant fO_2 (e.g. Paul & Douglas 1965) should
114 also operate during dissolution of volatile species (Fraser 2005; Moretti 2005;
115 Toplis 2005), by altering the relative activity coefficients of Fe²⁺ and Fe³⁺ species
116 within the melt.

117 This relies on the quasi-chemical theory defined by the Lux-Flood
118 'basicity' of different oxide components. This considers equilibrium between
119 bridging oxygens (O⁰), non-bridging oxygens (O⁻) and 'free oxide' anions that are
120 not bonded to the tetrahedral silicate polymer network (O²⁻, Toop & Samis
121 1962). In this model, the melt is a molten ionic solution dominated by oxide ions
122 (Flood & Förland 1947; Fraser 1975; Duffy 1993; Ottonello et al 2001; Moretti
123 2005; Fraser 2005). Interaction between oxygen in different structural positions:



125 defines the basicity of the solution. Basic oxides such as alkalis (Na₂O or K₂O)
126 dissociate to supply O²⁻ to the system and hence drive depolymerisation
127 (breaking of oxo-bridges; equilibrium [1] moves to the RHS) while acidic oxides

128 (such as SiO₂) react with O²⁻ to form polymer chains. Amphoteric oxides,
129 including Fe₂O₃, Al₂O₃, H₂O and CO₂ (Fraser 1977), can act as an acid or a base
130 depending on the composition of the silicate solution (Kushiro 1975). Fe oxide
131 components in the silicate melt therefore have the following possible reactions
132 (neglecting acidic behaviour of FeO, Fraser 1975; 2005):



136 where FeO₂⁻ is part of the structural network, analogous to AlO₄⁻.

137 Some evidence suggests that the dissolution of H₂O in polymerised silicate
138 melts occurs by a depolymerisation reaction with the tetrahedral network by
139 breaking of T-O-T bridges to form shorter polymer chains terminated by -OH
140 (e.g. Stolper 1982; Xue & Kanzaki 2006; Malfait et al. 2014; though also see Kohn
141 2000), as well as by incorporation of unreacted molecular H₂O (e.g. Burnham
142 1975; Stolper 1982). This suggests that in these cases, dissolved H₂O should also
143 show basic behaviour, similar to K₂O or Na₂O (in addition to the incorporation of
144 unreacted, molecular water):



146 In strongly basic melts, it was predicted that H₂O could also behave as an acidic
147 oxide (Yokokawa 1986; Fraser 1977; Fraser 2005; Moretti 2005):



149 where OH⁻ is “free hydroxyl” that is not bound to the silicate network but
150 complexed with metal cations. This is supported by ¹H NMR experiments (Xue &
151 Kanzaki 2004) and may contribute to variations in solubility with silicate melt
152 composition (Yokokawa 1986). Similar reactions are suggested for dissolution of
153 CO₂, and this is supported by variations in carbon speciation with melt basicity
154 (Brooker et al. 1999) as well as NMR and Raman spectroscopy studies (Mysen et
155 al. 2011).

156

157 **Linking H₂O solubility, melt basicity and oxidation state**

158 In silicate melts, the ratios of multi-valent ions such as $\text{Eu}^{3+}/\text{Eu}^{2+}$ increase with
159 increasing melt basicity ($a\text{O}^{2-}$) at constant $f\text{O}_2$ (Morris & Haskin 1974; Tilquin et
160 al. 1997). This is consistent with thermodynamic constraints if amphoteric
161 behaviour of Fe oxide components is considered (reactions 2a-c, Fraser 1975),
162 and explains the observed increase of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with increasing alkali (or basic
163 oxide) content of the melt (e.g. Paul & Douglas 1965; Sack et al. 1980; Kress &
164 Carmichael 1991; Toplis 2005). Increasing the availability of free oxide (O^{2-})
165 leads to an overall net decrease of $a\text{Fe}_2\text{O}_3(\text{m})$ from reactions 2b and 2c while
166 simultaneously increasing $a\text{FeO}(\text{m})$ from reaction 2a. This produces an overall
167 increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ at constant $f\text{O}_2$, and should also polymerise the melt
168 structure, because of the contribution of FeO_2^- to the melt framework (Fraser
169 1977; Ottonello et al. 2001; Fraser 2005; Moretti 2005).

170 For volatiles, the same approach predicts that (basic) reaction of H_2O with
171 the silicate melt to form dissolved $-\text{OH}$ [3b] should result in a net increase in $a\text{O}^{2-}$
172 (and hence increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$) whereas (acidic) formation of free hydroxyl in
173 very basic melts [3a] results in a net decrease in $a\text{O}^{2-}$ (and hence decreased
174 $\text{Fe}^{3+}/\Sigma\text{Fe}$). Similarly, dissolution of carbon dioxide in basic melts should result in
175 net decrease in $a\text{O}^{2-}$, and thus decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$. This provides a testable link
176 between volatile solution mechanisms and melt oxidation state, which we review
177 below.

178

179 **Previous work on $\text{Fe}^{3+}/\text{Fe}^{2+}$ in hydrous melts**

180 Several previous studies have attempted to discern differences in redox state
181 between equivalent hydrous and anhydrous melt compositions, with somewhat
182 equivocal results. Moore et al. (1995) found no effect of H_2O on the Fe oxidation
183 state of hydrous peralkaline rhyolites, supporting an earlier study (Sisson &
184 Grove 1993) that compared $\text{Fe}^{3+}/\Sigma\text{Fe}$ in hydrous basalts with the anhydrous
185 predictions of the Kress & Carmichael (1991) model. Botcharnikov et al. (2005)
186 concluded that $\text{Fe}^{3+}/\Sigma\text{Fe}$ in hydrous ferrobalt was mainly controlled
187 experimentally by $a\text{H}_2\text{O}$ (and hence $f\text{O}_2$) and was within the range predicted by
188 existing anhydrous models.

189 In contrast, Gaillard et al. (2001) showed that addition of up to 6 wt% H₂O
190 has an oxidising effect on metaluminous rhyolite relative to Kress & Carmichael
191 (1991), but only at lower fO_2 conditions ($<NNO+1$). Gaillard et al. (2003a) also
192 observed higher $Fe^{3+}/\Sigma Fe$ in hydrous vs anhydrous rhyolite and ascribed this to
193 a decrease in the ratio of activity coefficients ($\gamma_{Fe_2O_3^L}/\gamma_{FeO^L}$) in hydrous melts, or
194 decreasing $a_{Fe_2O_3^L}$ for a given $X_{Fe_2O_3}$ and increasing a_{FeO^L} for a given X_{FeO} . This
195 is essentially the same effect as predicted by acid-base theory (as described
196 above). Schuessler et al. (2008) found that $Fe^{3+}/\Sigma Fe$ increased with H₂O content
197 at constant fO_2 in hydrous phonotephrites, which they attributed to the effects of
198 melt basicity as described by Ottonello et al. (2001) and Moretti (2005). These
199 principles are also supported by observations of differences in olivine-melt
200 K_D^{Fe-Mg} in hydrous and anhydrous melts (Toplis 2005).

201 Thus, while the results are still unclear, it does seem possible that H₂O has
202 a resolvable effect on melt $Fe^{3+}/\Sigma Fe$ through behaviour that is similar to the
203 basic metal oxides (e.g. K₂O). Such an effect is probably minor, but would be most
204 important in relatively polymerised melts and at high pressures where
205 variations in oxidation state could affect the compositions of minerals that could
206 fractionate Fe^{2+} from Fe^{3+} . This would appear to justify further work in the
207 context of hydrous subduction zone melts. Finally, the basicity approach
208 highlights that oxidation state should be considered alongside an understanding
209 of melt chemical species and melt structure.

210

211

212 **PART II: EFFECT OF VARYING VOLATILE CONTENTS ON OXIDATION STATE**

213 The second part of this paper specifically addresses how variations in melt
214 volatile concentrations during crustal processes may affect melt $Fe^{3+}/\Sigma Fe$. We
215 seek to explore two key processes in particular: (i) dehydration or degassing of
216 volatiles during decompression, and (ii) hydration, due to H₂O-undersaturated
217 magma ascent from high pressures. We present new XANES $Fe^{3+}/\Sigma Fe$ analysis
218 for two sets of existing experimental samples to investigate these processes: a
219 set of decompression experiments from the study of Mangan & Sisson (2000),

220 and a set of partial hydration experiments from Humphreys et al. (2008). A brief
221 description of the experimental procedures is included below.

222

223 **Decompression and H₂O degassing experiments**

224 Samples of the experimentally degassed Panum Crater Dome obsidian were
225 taken from the study of Mangan & Sisson (2000; table 1). The starting materials
226 for these experiments were slabs of obsidian, loaded into Pt capsules together
227 with excess H₂O. The samples were superheated at 1000 °C for several hours in
228 Hf-Zr-Mo cold-seal pressure vessels at 200 MPa, pressurised using Ar gas, then
229 equilibrated at 900 °C for three days, and finally decompressed isothermally at
230 0.025 MPa/s to variable final pressure (P_f) and immediately quenched.
231 Decompression runs lasted 17 to 117 minutes. There was no attempt to buffer
232 fO_2 but rapid H₂ diffusion through the Pt capsule would have equilibrated the
233 samples at a high fO_2 during the initial 3-day heating. Any observed covariance
234 between H₂O loss and $Fe^{3+}/\Sigma Fe$ over short lengthscales in the samples must
235 therefore be related to the short decompression phase of the experiment. The
236 resulting glasses are variably vesicular, with bubbles nucleating throughout the
237 capsule in some runs, but only at the margins of the capsule in others (table 1;
238 Mangan & Sisson 2000). Most of the samples analysed by XANES contained
239 primarily marginal bubbles. H₂O contents and vesicularity data clearly
240 demonstrate that bubble nucleation was delayed and did not occur at
241 equilibrium (Mangan & Sisson 2000), yielding a suite of glasses with
242 heterogeneous H₂O contents over short lengthscales. The anhydrous
243 composition of the glass is constant within analytical uncertainty (table 2),
244 indicating that no other compositional changes to the melt occurred during
245 degassing.

246

247 **Partial hydration experiments**

248 To compare the mechanisms of hydration and H₂O degassing, we analysed
249 partially hydrated Lipari obsidian cores as reported in Humphreys et al. (2008).
250 The starting materials for these experiments were cylinders of homogeneous

251 Lipari obsidian, which were loaded into gold capsules with excess H₂O, along
252 with a small amount of finely ground obsidian powder to prevent dissolution of
253 the glass during the experiment. The capsules were then held at super-liquidus
254 conditions, 150-200 MPa and 855-905 °C in cold-seal pressure vessel apparatus
255 pressurised by water. Run times were short (20-80 minutes) and achieved
256 partial hydration of the glass cylinders (table 1; Humphreys et al. 2008). No
257 double capsule oxygen buffer control was used during the experiments but the
258 short run times, low temperatures and use of Au capsules effectively ensure
259 impermeability to H₂ during the experiments (Chou 1986). The anhydrous
260 composition of the glass is constant within analytical uncertainty (table 2),
261 indicating that hydration is not associated with any other compositional changes
262 to the melt.

263

264

265 **ANALYTICAL METHODS**

266 **X-ray Absorption Near Edge Structure (XANES)**

267 Fe³⁺/ΣFe of experimental glasses were measured using Fe K-edge micro X-ray
268 Absorption Near Edge Structure (μXANES) spectroscopy on the I18 (Microfocus
269 Spectroscopy) beamline at the Diamond Light Source, UK. Spectra were recorded
270 in fluorescence mode and the beam size at the sample was approximately 3 x 5
271 μm. The beamline uses a Si(111) crystal monochromator which gives an energy
272 resolution ($\Delta E/E$) of 1.4×10^{-4} (approximately 1 eV at the Fe K-edge); the energy
273 stability of the beamline is ± 0.05 eV per day. Fluorescence X-rays were
274 normalised to the incident beam flux and collected using a 9-element solid state
275 detector. The energy was calibrated by defining the first peak of the first
276 derivative of Fe foil to be at 7112 eV (or 7111.1 eV for comparison with older
277 published literature data, e.g. Wilke et al. 2001). Spectra were recorded from
278 7028 eV to 7400 eV using a 0.086 eV step over the pre-edge region (7098-7123
279 eV), 0.259 eV step across the edge (7123-7158 eV) and ~5 eV step to define both
280 the baseline (7028-7098 eV) and the post-edge region. Initial spectra were
281 collected up to 7340 eV but this was extended out to 7400 eV in later runs to aid

282 the normalisation procedure (see below). Counting times were 2000 msec on all
283 points. The locations of all points analysed were recorded carefully with
284 reference to reflected light images of the samples to enable accurate relocation
285 for later SIMS analyses of the same points.

286 $\text{Fe}^{3+}/\Sigma\text{Fe}$ measurements were quantified by referencing the centroid
287 energy of the pre-edge feature to a linear calibration (Figure 1a) constructed
288 using a suite of anhydrous rhyolite glass standards that were synthesised at 1
289 atm and a range of $f\text{O}_2$ (FMQ+0.8 to +6) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ from 0.238 to 0.806
290 (Cottrell et al. 2009; table 3). The raw spectra were normalised by fitting a
291 straight line to both the low-energy baseline and the post-edge region, using the
292 *Athena* software package (Ravel & Newville 2005). The pre-edge feature in Fe
293 spectra typically shows two overlapping peaks whose centroid energy is
294 quantitatively proportional to redox state (e.g. Wilke et al. 2001; Berry et al.
295 2003; Cottrell et al. 2009). The pre-edge regions of the normalised spectra were
296 fitted between 7106 and ~ 7118 eV, using a cubic baseline plus a Gaussian to
297 define the rising background towards the main K-edge, and two additional
298 Gaussian peaks to define the pre-edge region (following Berry et al. 2003;
299 Cottrell et al. 2009).

300

301 **SIMS and EPMA**

302 Glasses were analysed for $^1\text{H}^+$, $^7\text{Li}^+$, $^{12}\text{C}^+$, $^{25}\text{Mg}^+/2$, $^{16}\text{O}^1\text{H}^+$, $^{19}\text{F}^+$, $^{23}\text{Na}^+$, $^{26}\text{Mg}^+$, $^{30}\text{Si}^+$,
303 $^{35}\text{Cl}^+$ and $^{29}\text{K}^+$ using the CAMECA ims 4f secondary ion mass spectrometer at the
304 University of Edinburgh. NIST SRM610 was used as the primary calibration
305 standard; $^{30}\text{Si}^+$ was the internal standard. Mass 0.7 was used to monitor the
306 background count rate of the electron multiplier detector. A 10 kV, 2 nA, 0-
307 primary beam was accelerated onto the sample with a net impact energy of 14.5
308 kV. Secondary ions were extracted at +4.5 eV using a 75 V offset. A pre-sputter
309 period of approximately 2 minutes, with a nominal 15 μm rastered beam, was
310 used to clean the sample surface, during which time the mass spectrometer was
311 calibrated for the secondary ions. For quantitative analysis, the focused beam
312 was reduced to ~ 10 μm using a field aperture. H_2O contents of the glass were
313 derived using a daily working curve (figure 1b) of measured $^1\text{H}^+/^{30}\text{Si}^+$ vs. H_2O in

314 well-calibrated hydrous glass standards, following the methods of Blundy &
315 Cashman (2005). Typical errors in determining H₂O are ~8-12% relative. Where
316 possible, the same points analysed by XANES were targeted for SIMS
317 measurements. Major element glass compositions were analysed using a 5-
318 spectrometer Cameca SX-100 electron microprobe at the University of
319 Cambridge, with a defocused (15 µm), 15 kV, 4 nA electron beam for major
320 elements and a 10 nA beam for minor elements. Other analytical conditions were
321 equivalent to those of Humphreys et al. (2006a).

322

323

324 RESULTS

325 All the samples studied (including XANES standards) are rhyolite glasses with
326 FeO_T ranging from 1.0-5.7 wt%. The resulting XANES spectra show a sharp, clear
327 pre-edge feature, with a well defined post-edge peak at ~7130 eV, followed by a
328 deep trough at ~7160 eV and broad, shallow oscillations in the EXAFS region
329 (figure 2). In common with Berry et al. (2003) and Wilke et al. (2005) we
330 observe systematic changes to the shape of the spectra with increasing Fe
331 oxidation state of the standard glasses (figure 2), including: (i) changes to the
332 shape of the pre-edge feature, (ii) an increase in the energy of the main edge, (iii)
333 an increase in the height and breadth (and in detail, a change in the shape) of the
334 post-edge peak, and (iv) a slight increase in the energy of the post-edge trough.
335 The change in energy of the post-edge trough has the potential to introduce
336 errors into the dataset during processing if the region ~7160-7260 eV is used to
337 normalise the spectra. We therefore normalised the spectra to the average
338 intensity of the far post-edge region (up to 7400 eV), which avoids any of these
339 uncertainties. Only the shape of the pre-edge feature was used to make
340 quantitative inferences about the Fe oxidation state of the unknown samples.

341 The shape of the pre-edge feature is generally quantified by calculating
342 the *centroid energy*, C , i.e. the area-weighted average energy of the pre-edge
343 feature:

$$344 \quad C = E_1 \frac{A_1}{A_1+A_2} + E_2 \frac{A_2}{A_1+A_2} \quad [4]$$

345 where E_i is the peak energy of component i , and A_i is the total area (or integrated
346 intensity) of component i . Average precision on the centroid energy from
347 uncertainties in the fitting parameters is extremely good, ± 0.008 eV and far
348 better than the accuracy, which relies on calibration of the centroid energy with
349 $\text{Fe}^{3+}/\Sigma\text{Fe}$. Fully propagated uncertainty for our analyses gave an 80% confidence
350 interval of ~ 0.067 for $\text{Fe}^{3+}/\Sigma\text{Fe}$, but with very high precision. This translates to
351 $\Delta f\text{O}_2$ of approximately ± 0.6 log units. This method assumes similar Fe
352 coordination in the calibration standards and the unknowns because the
353 intensities of the pre-edge components can vary with both $\text{Fe}^{3+}/\Sigma\text{Fe}$ and iron
354 coordination (Wilke et al. 2001). All our samples have similar total pre-edge
355 intensity (figure 3), which suggests no significant change in Fe environment and
356 indicates an average Fe-coordination number of approximately [5], consistent
357 with a stable mixture of [4] and [6] environments (Wilke et al. 2001) for both
358 Fe^{2+} and Fe^{3+} . The most oxidised reference glasses plot at slightly higher total
359 intensity than the unknowns, which may be a result of slight self-absorption
360 effects (which has negligible effect on the centroid position, Bajt et al. 1994).

361

362 **H₂O degassing**

363 The experimentally degassed samples show a range of H₂O contents as measured
364 by ion probe and inferred from greyscale variations (figure 4). Water contents
365 range from 2.3 to 6.4 wt% H₂O, with one measurement at 7.2 wt% H₂O (figure
366 4c; table 4). These values are higher than the volatile contents as measured by
367 FTIR (1.8 – 5.4 wt% H₂O, Mangan & Sisson 2000) but span a similar range. The
368 cause of the discrepancy between the SIMS and FTIR data is unclear; however
369 the key point for this study is that the glasses show clear relative variations of
370 H₂O with $\text{Fe}^{3+}/\Sigma\text{Fe}$. Back-scattered SEM images of individual samples typically
371 show clear increases in greyscale intensity that correlate well with decreasing
372 H₂O concentration (figure 4b) from the core to the rim of samples with only
373 marginal bubbles. This indicates progressive diffusive loss of H₂O to the margins
374 of the sample to feed the growing marginal bubbles. Those samples with more
375 vesicular interiors did not show any clear variations of BSE intensity and
376 typically showed more limited H₂O variation.

377 XANES spectra for these samples have a relatively small range in pre-edge
378 centroid energy from 7114.05 to 7114.15 eV (table 4). Total pre-edge intensity
379 increases with increasing centroid energy (figure 3), consistent with previous
380 observations for silicate glasses (Wilke et al. 2005). The pre-edge centroid
381 energies for these samples correspond to an overall iron oxidation state,
382 $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.52 to 0.64. Although this variation is small compared to the fully
383 propagated measurement uncertainty, there are clear relative variations both
384 between and within samples. There is a correlation between H_2O concentration
385 and oxidation state, consistent with an increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ due to degassing of
386 H_2O from the melt.

387

388 **Hydration**

389 The margins of the Lipari obsidian samples are strongly hydrated, with water
390 contents approaching the equilibrium values calculated for the experimental run
391 conditions (4.8-5.6 wt%, Humphreys et al. 2008), while the interiors remain un-
392 hydrated and record the initial volatile content of the Lipari obsidian starting
393 material (~ 0.2 wt% H_2O ; table 5). The variation in H_2O contents is clearly visible
394 as a strong outward decrease in back-scattered SEM intensity (e.g. figure 5a;
395 Humphreys et al. 2008). The influx of water into the samples was previously
396 modelled successfully based on established concentration-dependent H_2O
397 diffusivity data (Nowak & Behrens 1997; Zhang & Behrens 2000) and is
398 consistent with H_2O diffusion into the samples over the timescale of the
399 experiments (Humphreys et al 2008).

400 XANES spectra for the high-temperature hydrated samples show strong
401 changes in pre-edge centroid energy from 7113.65 to 7114.1 eV, with one outlier
402 at 7113.60 eV (table 5), corresponding to $\text{Fe}^{3+}/\Sigma\text{Fe}$ values from 0.04 to 0.60
403 (figure 5b). In marked contrast to the degassed samples, H_2O concentration
404 correlates positively with oxidation state, indicating increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ linked
405 to diffusion of H_2O into the sample. This is further demonstrated by the close
406 correspondence in the shapes of the compositional profiles with distance from
407 the margin of each chip (Figure 6). These spatial profiles also highlight a small

408 but apparently significant (in that it is present in each sample) negative
409 deviation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ at low H_2O contents ($\sim 0.5\text{-}1.5$ wt% H_2O).

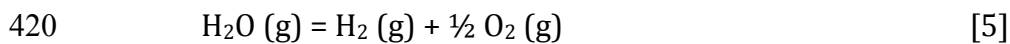
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411

412 INTERPRETATION

413 Oxidation due to melt hydration

414 The hydrated samples show clearly that increasing H_2O content causes an
415 increase in the Fe oxidation state (figures 5 and 6). This observation is very
416 similar to the results of an earlier equilibrium study (Botcharnikov et al. 2005),
417 which used long run times and an AuPd capsule that is permeable to H_2 to
418 control $f\text{O}_2$ in the experiments, according to the equilibrium constant for the
419 dissociation reaction:



$$421 \quad K_{\text{eq}}^{\text{fl}} = (f\text{H}_2 \cdot f\text{O}_2^{1/2}) / f\text{H}_2\text{O}^{\text{fl}} \quad [6]$$

422 Although $f\text{H}_2$ of the fluid was fixed (*via* a Shaw membrane), variations of $\text{XH}_2\text{O}^{\text{fl}}$
423 between capsules introduced differences in equilibrium $f\text{O}_2$ in different
424 experimental runs (Botcharnikov et al. 2005), because $f\text{H}_2\text{O} = a\text{H}_2\text{O} * f^{\text{H}_2\text{O}}$ (and
425 assuming ideal behaviour, $a\text{H}_2\text{O} \sim \text{XH}_2\text{O}$). The actual $f\text{O}_2$ experienced was
426 calculated from the imposed $f\text{O}_2$ and XH_2O (Botcharnikov et al. 2005):

$$427 \quad \log f\text{O}_2 \text{ (actual)} = \log f\text{O}_2 \text{ (imposed)} + 2 \log \text{XH}_2\text{O} \quad [7]$$

428 In our experiments, we assume that the use of an Au capsule (minimally
429 permeable to H_2 at our experimental temperatures, Chou 1986) and very short
430 run times (20-80 minutes) resulted in approximately constant $f\text{H}_2$ fluid inside
431 the experiments (see later). Our experiments were not equilibrated, and
432 diffusion of H_2O from the fluid into the melt resulted in wide variations of XH_2O
433 within each quenched glass chip, from water-saturated at the hydrated margin
434 (~ 5.5 to 6 wt% H_2O) to highly undersaturated in the unhydrated core (~ 0.2 wt%
435 H_2O). We can write equivalent reactions to [5-6] that apply for the melt phase,
436 even though equilibration was incomplete. We therefore calculated the apparent
437 change in $\log f\text{O}_2$ (melt) following the approach of Botcharnikov et al. (2005). We

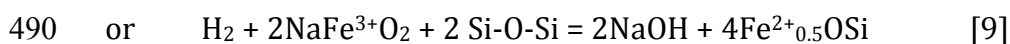
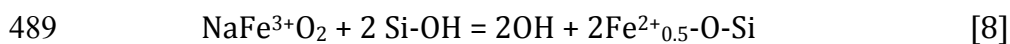
438 assumed constant f_{H_2} , and used either H_2O_t (the total amount of H_2O dissolved in
439 the melt) or the molecular H_2O_m (estimated from Silver et al. 1990) to calculate
440 $\log X_{\text{H}_2\text{O}_t}$ or $\log X_{\text{H}_2\text{O}_m}$, i.e., $X_{\text{H}_2\text{O}_t} = \text{H}_2\text{O}_t/\text{H}_2\text{O}_{\text{sat}}$ and $X_{\text{H}_2\text{O}_m} = \text{H}_2\text{O}_m/\text{H}_2\text{O}_{\text{sat}}$. We
441 also assumed that the marginal glass is H_2O -saturated, i.e. that $X_{\text{H}_2\text{O}_t} = 1$ at the
442 rim, as the rim H_2O_t concentrations agree with solubility models (Humphreys et
443 al. 2008). Calculated f_{O_2} was converted to $\text{Fe}^{3+}/\Sigma\text{Fe}$ using the anhydrous
444 algorithm of Kress & Carmichael (1991) for the major element composition of
445 the sample and known experimental conditions. Using this approach, the overall
446 change in $\text{Fe}^{3+}/\Sigma\text{Fe}$ from core to rim in the glass samples is matched by the
447 predictions based on observed changes in $X_{\text{H}_2\text{O}}$ (figure 7). The lengthscale of the
448 changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ is also equivalent to the lengthscale of H_2O diffusion
449 gradients, modelled using existing H_2O_m diffusivity data (Humphreys et al. 2008),
450 demonstrating that $\text{Fe}^{3+}/\Sigma\text{Fe}$ varies at a rate controlled largely by the diffusivity
451 of H_2O_m . (figure 6). This implies that Fe oxidation state is dominated by
452 variations in $X_{\text{H}_2\text{O}}$ during hydration.

453 However, the shapes of the H_2O - $\text{Fe}^{3+}/\Sigma\text{Fe}$ profiles do not fit well to the
454 modelled trend (figure 7), which suggests that Fe oxidation state was only partly
455 controlled by the disequilibrium changes in $X_{\text{H}_2\text{O}}$. In particular, there is a
456 significant deviation from the modelled curve to lower Fe^{3+} at low to
457 intermediate water contents (figure 7). This is in contrast to equilibrium data
458 (Botcharnikov et al. 2005), which fit the model well (figure 7). The discrepancy
459 with the equilibrium data cannot be explained by significant changes in average
460 melt Fe coordination, because the overall intensity of the pre-edge region does
461 not vary significantly with oxidation state (see figure 3; although this does not
462 preclude that coordination changes might occur).

463 Another possibility is that some ‘significant’ diffusion of H_2 did occur
464 across the Au capsule during the course of even these short experiments. As the
465 experiments were unbuffered it is difficult to quantify these effects but we note
466 that any H_2 loss from the capsule fluid would result in anomalously oxidised
467 sample margins, while H_2 gain would result in anomalously reduced sample
468 margins, relative to predicted values. Instead, $\text{Fe}^{3+}/\Sigma\text{Fe}$ at the sample margins is
469 well matched by the predictions – instead the unhydrated cores of the chips are

470 anomalously reduced relative to the predicted curves (Figure 7). Furthermore,
471 there is no difference in profile shape between the shortest (20 minutes) and
472 longest experiment (117 minutes), which supports our interpretation that the
473 experiments approximately represent a closed system. There is also no
474 difference in the width of the low-Fe³⁺ region between the shortest and longest
475 experimental runs (figure 6). This suggests that rapid migration of H₂ preceding
476 the H₂O diffusion front at high temperature cannot explain the discrepancy
477 between model and observations (cf. Gaillard et al. 2002; 2003b).

478 Our best explanation is therefore that, although the interconversion
479 reaction between H₂O and OH in the silicate melt is rapid at experimental
480 temperatures (Zhang et al. 1991), reactions involving the Fe species are slower,
481 or may involve intermediate reactions, at low H₂O contents where the melt
482 viscosity is higher. The effect of this would be that any change in Fe³⁺/ΣFe is
483 offset to higher XH₂O in these disequilibrium experiments. This could also
484 explain why the longer duration, equilibrium experiments of Botcharnikov et al.
485 (2005) are more consistent with the shape of the modelled curves (see figure 7).
486 This interpretation is consistent with the observations that relatively slow redox
487 equilibration in metaluminous rhyolites may be linked to intermediate changes
488 in complexing of network-modifying cations (Gaillard et al. 2003c), such as:



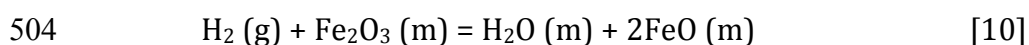
491 This emphasises that changes in melt oxidation state are closely linked to
492 variations in melt chemistry and structure. Melt basicity theory may be a useful
493 additional tool for investigation of these sorts of coupled changes than simply *f*O₂
494 measured relative to traditional oxygen buffers.

495

496 **Oxidation due to H₂O degassing**

497 The data from the experimentally degassed rhyolites are scattered but show a
498 general trend of oxidation by ~0.5 to 1 log unit *f*O₂ (Fe³⁺/ΣFe varies from 0.53 to
499 0.65) as H₂O contents decrease from ~7 to ~2 wt% (figure 4c; table 4). During
500 decompression, the melt became H₂O-saturated and nucleated bubbles of a free

501 H₂O vapour phase. We infer that subsequent re-equilibration of f_{H_2} and $f_{\text{H}_2\text{O}}$ in
502 the vapour bubble occurred through sequestration of H₂ from the melt, resulting
503 in increased $\text{Fe}^{3+}/\Sigma\text{Fe}$ through the reaction:



505 Although the initial f_{O_2} of the melt in these experiments was quite high, as a
506 result of prolonged equilibration at high pressure in the cold seal apparatus
507 (Mangan & Sisson 2000), this oxidation pattern is consistent with theoretical
508 calculations of increasing oxidation state with degassing for sulphur-free melts
509 (e.g. Mueller 1971; Candela 1986; Burgisser & Scaillet 2007). We used the
510 approach of Burgisser et al. (2008) to simulate the change in OH partitioning
511 between gas and melt during pressurisation in a closed system. Each pressure
512 step results in incremental changes to the species fugacities and their
513 concentrations in the melt, which are calculated using species solubilities, mass
514 balance, and reaction [5]. The scale of the observed f_{O_2} increase is somewhat less
515 than that predicted by the model when starting with negligible initial fluid
516 (figure 4d). This discrepancy is unlikely to be related to significant changes in f_{H_2}
517 during the course of the experiments, because the decompression run times are
518 very short (17 to 117 minutes). Moreover, the experimental apparatus was
519 pressurised by Ar gas, so H₂ would tend to migrate out through the capsule,
520 decreasing f_{H_2} and leading to *more* oxidised conditions. Instead, it is more likely
521 that:

- 522 (i) The modelling does not take into account the buffering capacity of FeO in
523 the melt, which could reduce the absolute increase in oxidation state,
524 particularly at higher initial f_{O_2} (Candela 1986). However, for a melt with
525 only 1 wt% FeO (as in the case of the Panum Dome rhyolite) this should
526 account for <0.2 log units change in f_{O_2} (Burgisser & Scaillet 2007).
- 527 (ii) The high proportion of fluid in the experimental capsules is buffering the
528 changes in f_{O_2} . The experimental starting materials include ~20 wt% fluid
529 so there is likely to be substantial excess fluid at the beginning of each
530 decompression run. When the modelling is repeated with 10 wt% and 20
531 wt% initial fluid the scale of the f_{O_2} increase is substantially reduced

532 relative to the run with 0.1 wt% initial fluid (figure 4d), consistent with the
533 observations.

534 The other important difference between the experiments and the modelling is
535 that the experiments were run without equilibration at each pressure step
536 (Mangan & Sisson 2000); i.e., they represent disequilibrium degassing. The
537 disequilibrium arises from delayed bubble nucleation, which is offset to lower
538 pressure than the equilibrium case, but because they were run with a pure H₂O
539 fluid there is no effect on the relationship between Fe³⁺/ΣFe and H₂O. However,
540 more significant kinetic factors could arise in multi-component fluids with
541 significant differences in volatile species diffusivities. This is highlighted in
542 experiments by Fiege et al. (2014) that showed enhanced transfer of sulphur into
543 the fluid relative to the melt at high decompression rates, decreasing to
544 equilibrium values with annealing and producing lower melt Fe³⁺/ΣFe than
545 predicted by equilibrium (closed-system) models.

546

547

548 **DISCUSSION**

549 Our data demonstrate that magma degassing and hydration can both result in
550 significant melt oxidation coupled to changes in volatile content. On H₂O
551 saturation, the formation of a free H₂O vapour phase partitions H₂ from the melt
552 into the vapour and results in melt oxidation. During hydration, oxidation is
553 caused by changes in water activity. These mechanisms should therefore be
554 considered as one possible way to explain the high oxidation state observed in
555 arc magmas (e.g. Carmichael 1991). Both processes have direct relevance for
556 crustal processes and may be important in different regions of the arc crust
557 (figure 8). Magma ascent from shallow storage regions is dominated by
558 degassing of H₂O vapour from the melt, while rise of H₂O-undersaturated magma
559 from the deep crust would be associated with increasing water activity.
560 However, arc magmas are complicated by a general lack of equilibrium
561 conditions, instead representing different components or sub-systems that may
562 be in equilibrium at different points in the volcanic system. We therefore need to

563 consider what controls fO_2 and what phases would record it accurately over
564 varying timescales.

565

566 **Degassing in natural systems**

567 Arc magma ascent through a conduit and eruption at the surface is associated
568 with significant volatile degassing (figure 8). Our new data and modelling
569 demonstrate that degassing of a pure or dominantly H₂O-bearing fluid results in
570 significant melt oxidation. Under closed-system degassing conditions, this can be
571 moderated by the presence of large volumes of gas. Furthermore, the melt can be
572 expected to oxidise even if degassing occurs during disequilibrium degassing
573 (delayed bubble nucleation), provided that the volatile budget is dominated by
574 H₂O. In natural systems, we would therefore expect to observe a systematic
575 deviation between the oxidation state of the melt relative to that of the pre-
576 eruptive magma (as measured, for example, by 2-oxide equilibria).

577 Crabtree & Lange (2012) showed that bulk rock $Fe^{3+}/\Sigma Fe$ in degassed,
578 crystal-poor andesites from the Mexican volcanic arc was within error of the pre-
579 eruptive $Fe^{3+}/\Sigma Fe$ of the hydrous melt, as determined by 2-oxide
580 thermobarometry. This was interpreted to mean that extensive degassing (of up
581 to 8 wt% H₂O) during ascent had no measurable effect on magma oxidation state.
582 Our data indicate that such strong H₂O degassing *should* leave a clear signature of
583 oxidation in the melt phase. We therefore suggest that the magma may also have
584 degassed additional multi-valent gas species (e.g. sulphur) that would counteract
585 the melt oxidation driven by loss of H₂O (Burgisser et al. 2008). Alternatively, the
586 bulk rock measurements of oxidation state in the degassed magmas may have
587 been insufficiently sensitive to resolve any degassing effects. Direct, *in situ*
588 measurements of melt oxidation state (e.g. by XANES) are more likely to resolve
589 these late-stage changes.

590 Surface volcanic gas emissions represent the counterpart to the
591 continuously degassing melt that is erupted (figure 8), but gas fO_2 measurements
592 are commonly different from those of their host lavas. This has been interpreted
593 as the result of oxidation state changes to the melt during degassing (e.g. loss of

594 SO₂ from basalt, Anderson & Wright 1972; Helz 2009) or mixing and integration
595 of multi-component gases released over a range of pressures (Edmonds et al.
596 2010). In some cases, disequilibrium in the gas phase is evident from lack of
597 correspondence of fO_2 estimates using different gas ratios (e.g. H₂/H₂O *cf.*
598 CO/CO₂, Hammouya et al. 1998) and probably results from mixing of gas
599 components with different origins, decoupled from magma ascent (Edmonds et
600 al. 2010). In other cases the gases appear to be in equilibrium with the lavas (e.g.
601 Gerlach 1993; Roeder et al. 2003; Gerlach 2004; Roeder et al. 2004) and the
602 discrepancy may relate to kinetic differences in the response rate of different
603 redox pairs (H₂-H₂O > SO₂-H₂S > CO-CO₂-CH₄, Giggenbach 1987).

604 These problems indicate that where multiple volatile species are present,
605 the effects of degassing of natural arc magmas on oxidation state are complex,
606 and strongly influenced by temperature, pressure, degassing kinetics and the
607 initial fO_2 (Fiege et al. 2014; Burgisser & Scaillet 2007) as well as the mode of
608 degassing (open system or closed system). This means that analysis of oxidation
609 state during degassing of natural melts is unlikely to yield unique
610 interpretations, although it is clear that arc magma degassing could significantly
611 affect the oxidation state of the melt. Attaining a real understanding of the effects
612 of magmatic degassing on oxidation state will probably require direct
613 measurements of the concentrations and speciation of all major volatiles in the
614 melt, as well as melt Fe³⁺/ΣFe and the corresponding gas compositions.

615

616 **Magma ascent from the deep crust**

617 Recent models of arc magma genesis involve prolonged periods of deep (mafic)
618 magma intrusion, differentiation and partial melting (e.g. Annen et al. 2006),
619 followed by magma ascent towards upper crustal magma reservoirs where
620 storage, degassing and mingling may also occur (Humphreys et al. 2008;
621 Edmonds et al. 2010; Johnson et al. 2010). Our partial hydration experiments
622 have relevance for the passage of hydrous melts or magmas between the lower
623 crust and shallow magma storage reservoirs (figure 8). Although magmas
624 originating from the deep crust are thought to be hydrous, they are highly
625 unlikely to be H₂O-saturated. This means that melt aH₂O will increase during

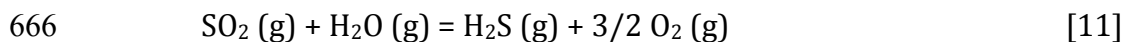
626 ascent, as the magma gets closer to volatile saturation. By analogy with our
627 experimental results, such ascent could result in significant oxidation of the melt
628 under conditions of incomplete diffusive equilibration. Although H₂O diffusion is
629 rapid, we calculate that even in 10,000 years significant diffusion would only be
630 observed over a distance of only ~20 m at 900 °C (using the diffusivity model
631 from Nowak & Behrens 1997). This means that incomplete equilibration in
632 ascending magmas must be carefully considered as a possible source of Fe³⁺/ΣFe
633 heterogeneity. Moreover, this reasoning also suggests that, depending on
634 timescales, magmas in the middle to lower crust could be substantially more
635 reducing than those in the upper levels of magma storage, and hence that
636 crustal-scale variations in *f*O₂ may be possible at subduction zones.

637 There are already some hints of strong changes in oxidation state during
638 formation of arc magmas. For example, the cores of a population of plagioclase
639 phenocrysts in intermediate arc magmas are highly anorthitic and corroded,
640 consistent with resorption during H₂O-undersaturated magma ascent
641 (Humphreys et al. 2006). These cores may contain sulphide inclusions, indicating
642 that these plagioclase phenocrysts formed in a more reducing environment than
643 the host magmas, which are typically too oxidising to have stable sulphides. The
644 presence of Cu-Fe-sulphide inclusions in phenocrysts appears to be a relatively
645 common feature in intermediate arc magmas (e.g. Shiveluch Volcano, Kamchatka,
646 Humphreys et al. 2006; Santiaguito, Guatemala, Scott et al. 2013; Satsuma-
647 Iwojima, Japan, Ueda & Itaya 1981; Mount Pinatubo, Philippines, Pallister et al.
648 1996; and Popocatepetl, Mexico, Schaaf et al. 2005), and in their cumulates (Lee
649 et al. 2012). Sulphide crystallisation could reflect a stage of fractionation under
650 deep, more reducing, low aH₂O conditions; or alternatively may be coupled to
651 melt redox changes resulting from magnetite crystallisation (Carmichael &
652 Ghiorso 1986; Sun et al. 2004; Jenner et al. 2010), resulting in constant or
653 reducing melt Fe³⁺/ΣFe but changing SO₄²⁻/S²⁻ (Sun et al. 2004; Moretti & Papale
654 2004). In any case, these variations in oxidation state could have important
655 implications for the distribution and transport of metals within the arc crust.

656

657 **What controls *f*O₂ in magmatic systems?**

658 Although estimates of fO_2 for many magmas plot close to solid oxygen buffers
659 (e.g. nickel - nickel oxide, NNO; or quartz-fayalite-magnetite, QFM), these phases
660 typically do not (co)exist and it is highly unlikely that those solid buffers are
661 controlling magma fO_2 ; instead they are useful reference lines in T- fO_2 space.
662 However, it has been suggested that gas-melt redox equilibria could actually
663 control magma fO_2 , if there is abundant free vapour present in the magma. For
664 example, Matthews et al. (1994) suggest that the sulphide-sulphate gas-phase
665 reaction



667 buffered magma fO_2 at Lascar Volcano, Chile, leading to more oxidised magmas
668 (relative to the NNO-buffer) as temperature decreases. This mechanism would
669 require relatively sulphur-rich gases to be present, although the gas-driven
670 buffer could be very effective because of its rapid response and large valence
671 change (Matthews et al. 1994). The pattern of increasing divergence from oxide
672 buffers (e.g. ΔNNO) with decreasing temperature, in a trend more parallel to the
673 sulphide-sulphate buffer, is seen at several other volcanoes (figure 9a), including
674 Augustine, USA (Roman et al. 2006), Shiveluch, Kamchatka (Humphreys et al.
675 2006), Quizapu, Chile (Ruprecht et al. 2012) and Pinatubo (Pallister et al. 1996).
676 Data for Mount St Helens, USA as a whole lie parallel to NNO, but individual
677 samples do not (Blundy et al. 2008), instead plotting parallel to the sulphide-
678 sulphate buffer (figure 9a).

679 This suggests that sulphide-sulphate oxygen exchange between the gas
680 and melt might be a common and effective oxygen buffering mechanism for
681 shallowly stored magmas. However, the arrays of T- fO_2 points from coexisting
682 oxide compositions are also parallel to isopleths of constant hm/ilm (taken from
683 Buddington & Lindsley 1964; figure 9b). Isopleths of constant mt/üsp in
684 titanomagnetite are at a slightly steeper angle (figure 9b). Therefore, the oxide
685 data could also be explained by increased temperature causing increasing üsp
686 content while hm/ilm remains constant. This is consistent with the slower
687 diffusion rates in ilm-hm solid solution than in mt-üsp (Hammond & Taylor
688 1982). A simpler interpretation for these T- fO_2 trends is therefore that late-stage
689 heating has resulted in a diffusive increase in üsp-content of titanomagnetites,

690 while adjustment of ilmenite compositions is kinetically inhibited. The increased
691 temperature could be due to release of latent heat of crystallisation (Blundy et al.
692 2006) or to mingling with hotter magmas (e.g. Devine et al. 2003; Ruprecht et al.
693 2012). This is consistent with compositional variations in oxides from Soufrière
694 Hills Volcano, Montserrat (figure 9b; data from Devine et al. 2003). Ilmenites are
695 uniform, while titanomagnetites have zoned rims with high TiO₂ due to magma
696 mixing (Devine et al. 2003). The apparent T-*f*O₂ data plot along hm-ilmenite isopleths
697 and lie parallel to the sulphide-sulphate buffer (figure 9b). Demonstrating *f*O₂
698 control by gas-melt equilibria such as [11] would require evidence of constant
699 melt redox ratios for the redox couple of interest, probably through analysis of
700 suites of melt inclusions.

701 Disequilibrium between crystals and melt is a ubiquitous feature of
702 shallow crustal arc magma storage: arc magmas typically comprise components
703 or sub-systems that may be only in equilibrium at certain points in the volcanic
704 system (e.g. Pichavant et al. 2007). For minerals, equilibration timescales are
705 poorly known but probably slow, except for Fe-Ti oxides, which may equilibrate
706 relatively quickly (i.e., < 5 years at 900 °C for complete equilibration of a 250 µm
707 oxide phenocryst, Freer & Hauptman 1978). This means that *f*O₂ calculated from
708 solid-melt equilibria involving homogeneous Fe-Ti oxide phenocrysts (± H₂O)
709 should be an accurate record (sensor) of stable magma storage conditions in the
710 shallow system. However, oxides will probably not provide a good record of
711 earlier or longer-term changes in *f*O₂ during fractionation, nor of late-stage
712 changes during magma ascent. Instead, more slowly equilibrating phenocrysts
713 such as pyroxene or hornblende, or oxides brought rapidly to the surface in
714 cumulate nodules, may be more useful as a record of longer term changes;
715 whereas melt redox couples will be needed to investigate variations immediately
716 prior to eruption.

717

718

719 **SUMMARY**

720 Direct measurement of coupled changes in melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ and H_2O content in
721 partially hydrated and degassed experimental rhyolites confirms that significant
722 changes in oxidation state can occur in response to changes in volatile content.
723 During hydration, increases in aH_2O produced strong melt oxidation. This
724 suggests that ascent of H_2O -undersaturated arc magmas from the deep crust
725 could cause significant oxidation, depending on the timescales required for
726 equilibration relative to magma storage times. During degassing, oxidation arises
727 due to loss of H_2 together with H_2O , consistent with theoretical modelling for H_2O
728 fluids. It is therefore possible that significant vertical variations in magma
729 oxidation state may develop within the arc crust. During the fractionation,
730 storage and ascent of natural arc magmas, the controls on $f\text{O}_2$ may be expected to
731 vary depending on the nature and duration of magma storage, as well as kinetic
732 factors and the timescales of observation and equilibration. The differing
733 response times of possible oxygen buffers and/or $f\text{O}_2$ sensors (such as oxide
734 pairs) need to be considered alongside the degree of attainment of equilibrium in
735 the magma. It is clear that attaining a real understanding of the effects of
736 magmatic degassing on oxidation state will probably require direct
737 measurements of the concentrations and speciation of all major volatiles in the
738 melt, as well as melt $\text{Fe}^{3+}/\Sigma\text{Fe}$ and the corresponding gas compositions. In this
739 respect, melt structure and chemistry should be considered alongside variations
740 of $f\text{O}_2$ relative to traditional buffers.

741

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757

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1004

1005 **FIGURES**

1006 Figure1

1007 Calibration lines for determining $\text{Fe}^{3+}/\Sigma\text{Fe}$ from XANES centroid energy (a) and
1008 H_2O from $^1\text{H}/^{30}\text{Si}^+$ ion probe measurements (b). In (a) errors in $\text{Fe}^{3+}/\Sigma\text{Fe}$ are
1009 derived from Mossbauer spectroscopy (Cottrell et al. 2009) while uncertainties
1010 in centroid energy are equivalent to the fitting uncertainty. Data are presented as
1011 linear deviation of centroid energy from 7113.6 eV, to facilitate regression. Solid
1012 line: best fit linear regression. Dashed lines: fully propagated uncertainties at
1013 80% confidence limits based on the linear regression. (b) Typical daily ion
1014 microprobe calibration curve for $^1\text{H}/^{30}\text{Si}^+$ vs H_2O showing best fit linear
1015 regression (solid line) and upper and lower 95% confidence limits (dashed

1016 lines). Uncertainties in H₂O are the errors on independently measured H₂O
1017 contents of the standard glasses.

1018

1019 Figure 2

1020 a) Typical normalised, background-corrected XANES spectrum for rhyolite
1021 standard glass. Boxes show parts of the spectrum that show variations with
1022 oxidation state. b) The pre-edge region shows two peaks; the relative importance
1023 of the higher-energy peak increases with increasing Fe³⁺/ΣFe. Each spectrum is
1024 offset by 0.02 on the y-axis. c) The energy of the main edge increases
1025 systematically with increasing Fe³⁺/ΣFe (spectra are not offset). d) The energy of
1026 the peak and post-edge trough increases with Fe³⁺/ΣFe, though higher energy
1027 resolution in this region is needed to use this feature quantitatively. Each
1028 spectrum is offset by 0.02 on the y-axis. NB. Where additional symbol markers
1029 are used, these represent every fifth data point.

1030

1031 Figure 3

1032 Total pre-edge intensity plotted against pre-edge centroid energy, after Wilke et
1033 al. (2005). Light grey dots and dashed curves represent Fe coordination end-
1034 member positions and mixing lines derived from Wilke et al. (2005). Triangles –
1035 rhyolite glass standards, Cottrell et al. (2009). Squares: partially hydrated Lipari
1036 rhyolite. Circles: high-temperature degassed rhyolites from Mangan & Sisson
1037 (2000). Solid grey curve represents the range of standard glasses presented by
1038 Wilke et al. (2005).

1039

1040 Figure 4

1041 a) Backscattered electron SEM images of representative glass chips from Mangan
1042 & Sisson (2000), in which heterogeneous bubble nucleation at the margins of the
1043 chips was dominant. Scale bar is 1mm. Lower greyscale intensity in the core
1044 indicates higher water contents, as demonstrated by the negative linear
1045 correlation between greyscale and H₂O (b). Degassing of H₂O is associated with

1046 increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (c) and $f\text{O}_2$ relative to the Nickel-Nickel oxide buffer (d).
1047 Errors in (c) relate to $\sim 10\%$ uncertainty in H_2O and 80% confidence limits for
1048 $\text{Fe}^{3+}/\Sigma\text{Fe}$. Note that the analytical *precision* is smaller than the size of the
1049 individual points. Modelled trends in (d) are theoretical predictions for
1050 degassing of S-free rhyolite following Burgisser et al. (2008), starting at different
1051 initial $f\text{O}_2$ and with no free fluid (0.1 wt% initial gas, red line) or with 10 wt%
1052 (green) or 20 wt% (black) initial fluid.

1053

1054 Figure 5

1055 Backscattered electron SEM image showing variation of greyscale intensity
1056 related to inward diffusion of H_2O into the Lipari glass chips at high temperature
1057 (a), reproduced from Humphreys et al. (2008). (b) Co-variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ with
1058 H_2O content and equivalent $f\text{O}_2$ variation relative to the NNO buffer.
1059 Representative error bars shown for sample LIPRF5.

1060

1061 Figure 6

1062 Spatial variability of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (grey squares) and H_2O (black triangles) with
1063 distance from the margin of each chip hydrated at high temperature. $\text{Fe}^{3+}/\Sigma\text{Fe}$ in
1064 the un-hydrated starting material is marked by a grey band in each figure.
1065 Horizontal error bars in (a) are the estimated maximum uncertainty on spatial
1066 location of each point. Errors in $\text{Fe}^{3+}/\Sigma\text{Fe}$ and H_2O are reported in previous
1067 figures.

1068

1069 Figure 7

1070 Variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and H_2O within experimentally hydrated glass chips
1071 (squares). Modelled variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ based on changing water activity is
1072 shown by the bold lines (calculated from XH_2O_m) and dashed lines (calculated
1073 from XH_2O_t). Calculated variations for two different illustrative initial $f\text{O}_2$
1074 conditions are shown (black and grey lines and labels).

1075

1076 Figure 8

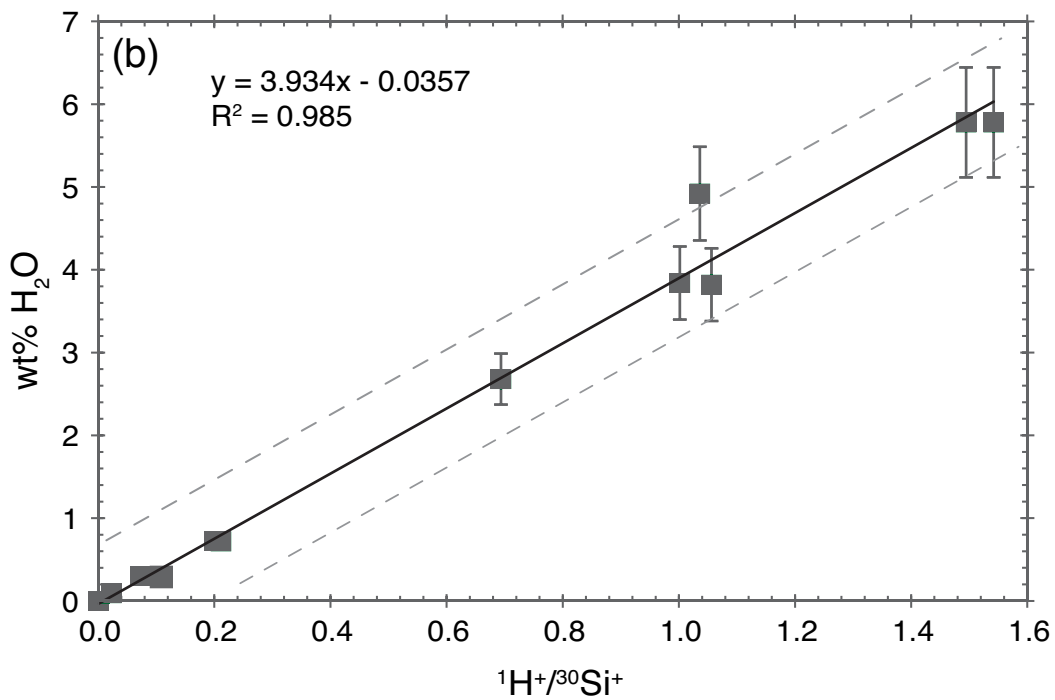
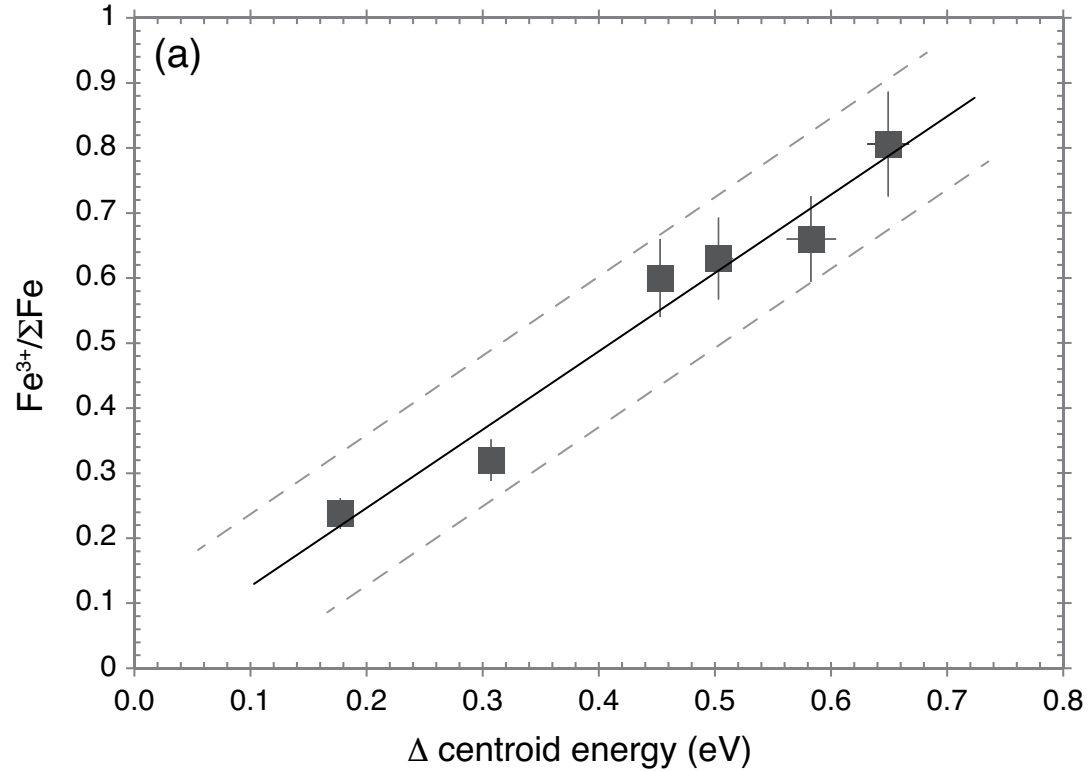
1077 Schematic figure showing the possible variations in importance of possible
1078 different fO_2 control mechanisms in different parts of the volcanic system and
1079 crust, depending on kinetics and degree of equilibration. See text for discussion.

1080

1081 Figure 9

1082 Temperature- fO_2 variations in intermediate arc magmas (a). Different oxygen
1083 buffers are shown in bold black lines (constant sulphide-sulphate ratios) and
1084 grey dashed lines (NNO, NNO+1). Data points are from two-oxide equilibria. Data
1085 sources are Blundy et al (2008) for Mount St Helens, USA; Humphreys et al.
1086 (2006) for Shiveluch Volcano, Kamchatka; Roman et al. (2006) for Augustine,
1087 Aleutians; Crabtree & Lange (2012) for the Mexican arc; Murphy et al. (2000) for
1088 Soufriere Hills, Montserrat; Sparks et al. (2008) for Uturuncu Volcano, Bolivia;
1089 Pallister et al. (1996) for Mount Pinatubo, Philippines; and Matthews et al.
1090 (1994) for Lascar Volcano, Chile. The pale grey arrow shows the data trend from
1091 part (b), which also shows isopleths (thin grey lines) of constant hm-ilm and
1092 Usp-mt composition from Buddington & Lindsley (1969). Black circles in (b) are
1093 data on zoned magnetite grains from Soufrière Hills Volcano, Montserrat (from
1094 Devine et al. 2003) which plot along lines of constant hm-ilm and also lie parallel
1095 to the sulphide-sulphate buffer.

1096



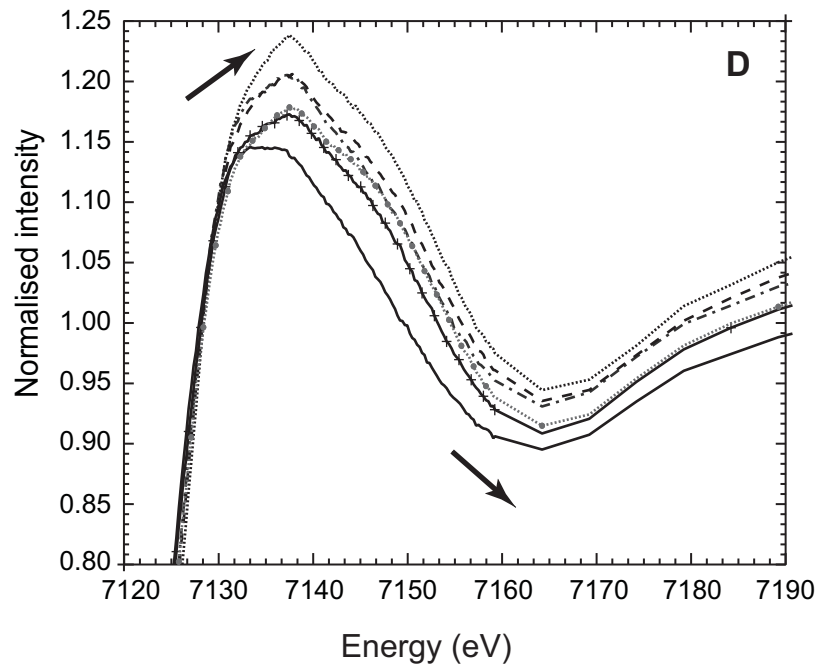
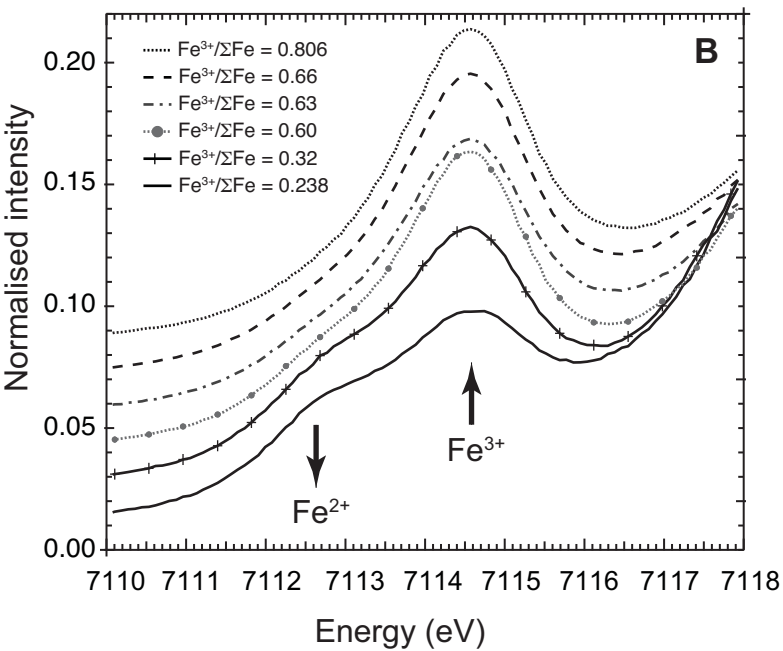
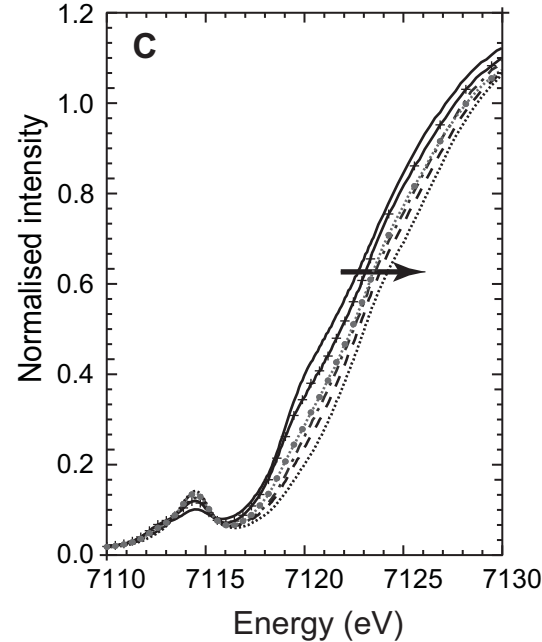
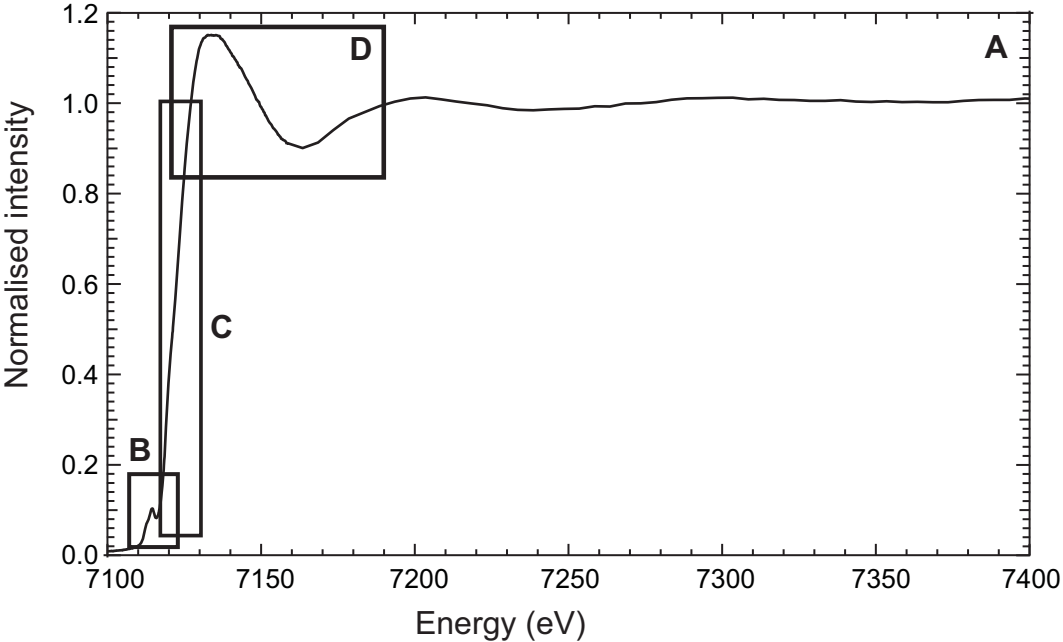


Figure 2

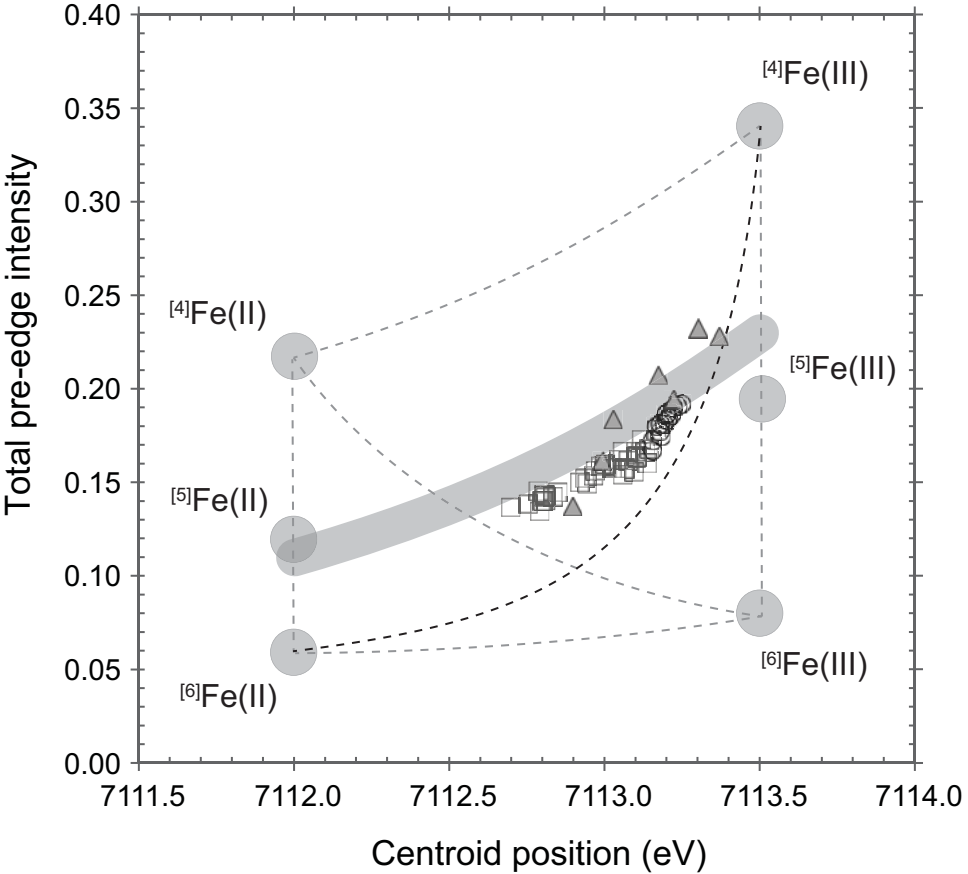
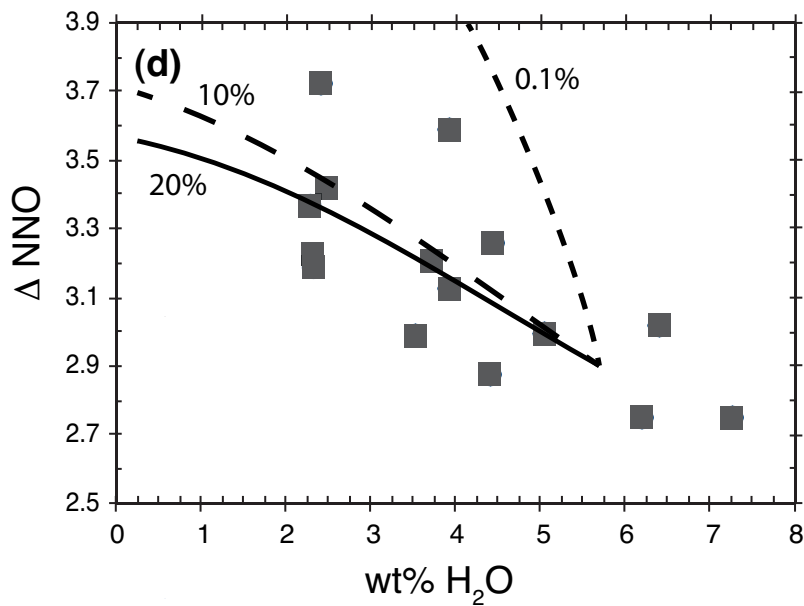
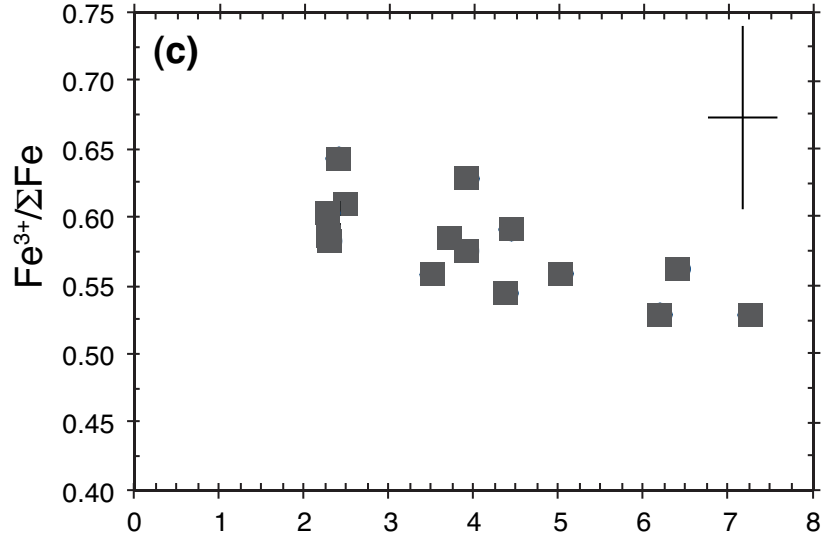
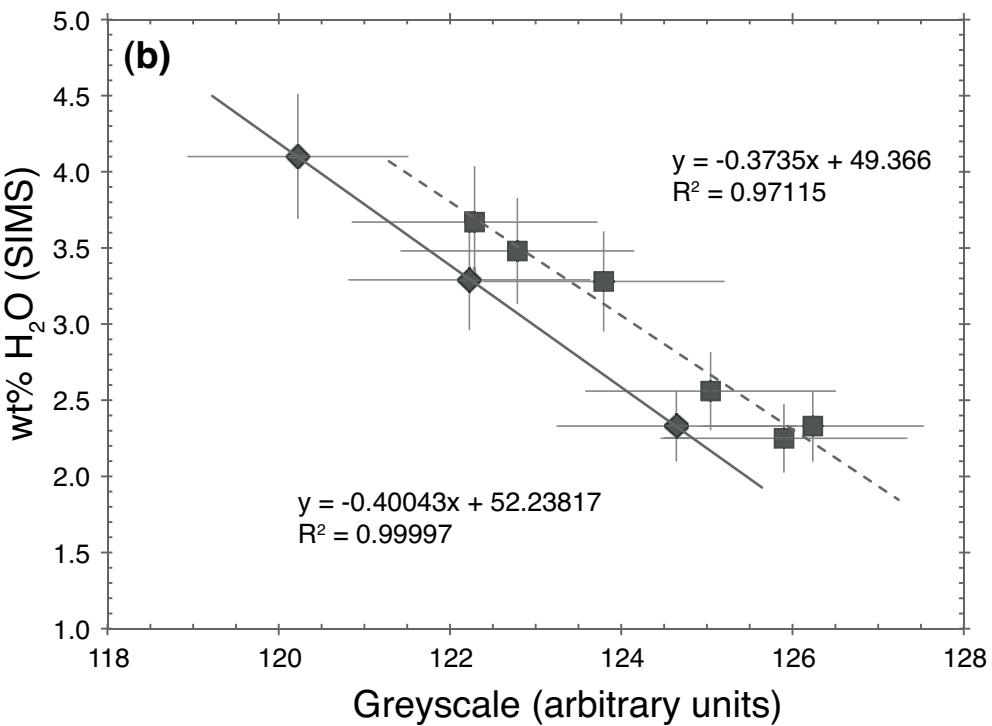
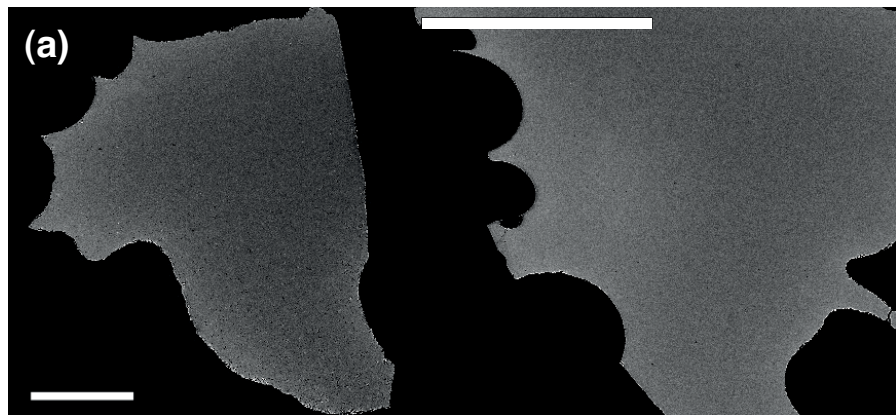
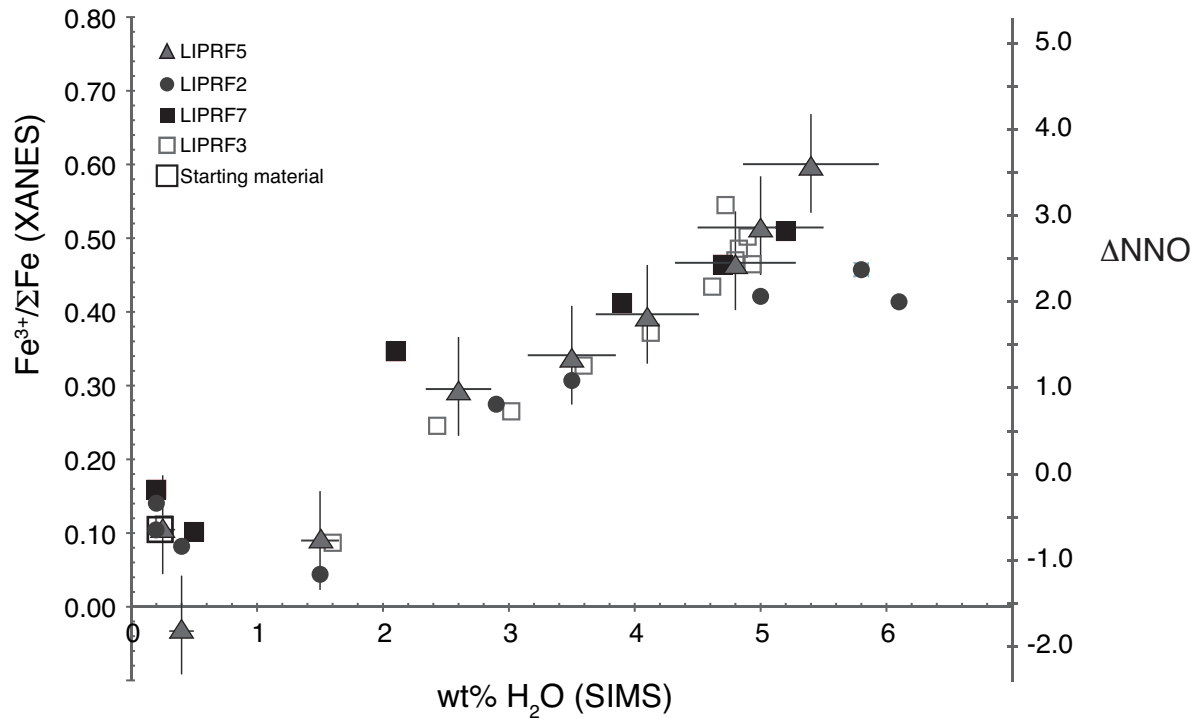
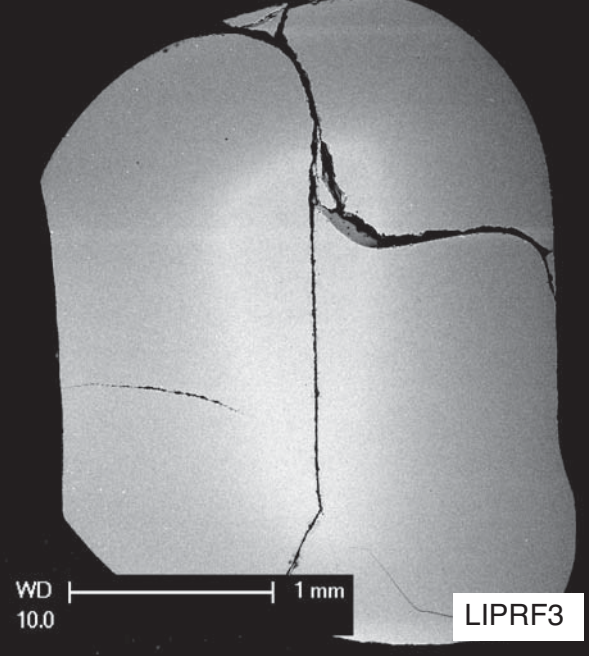
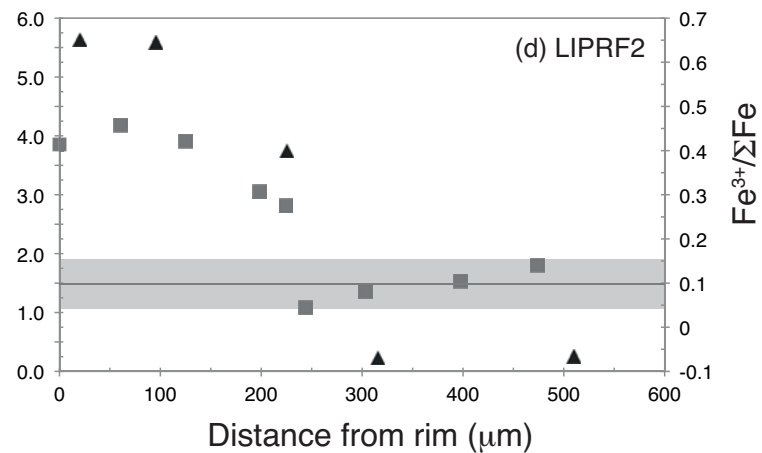
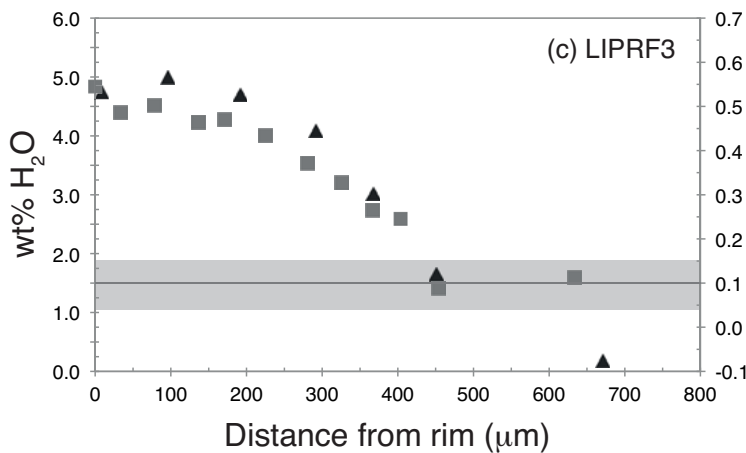
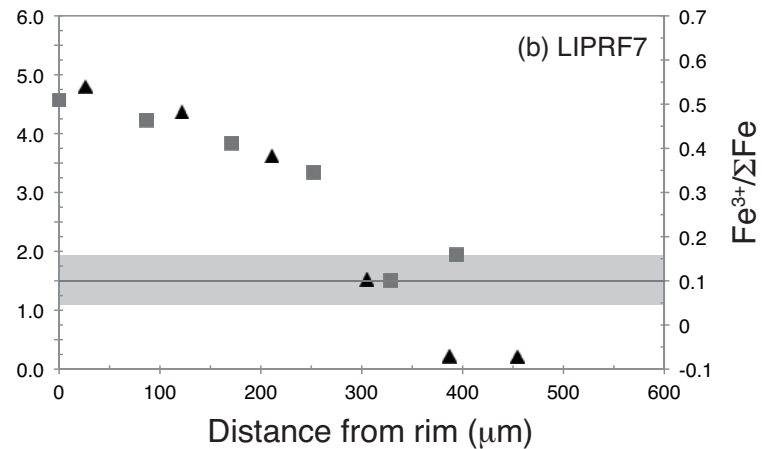
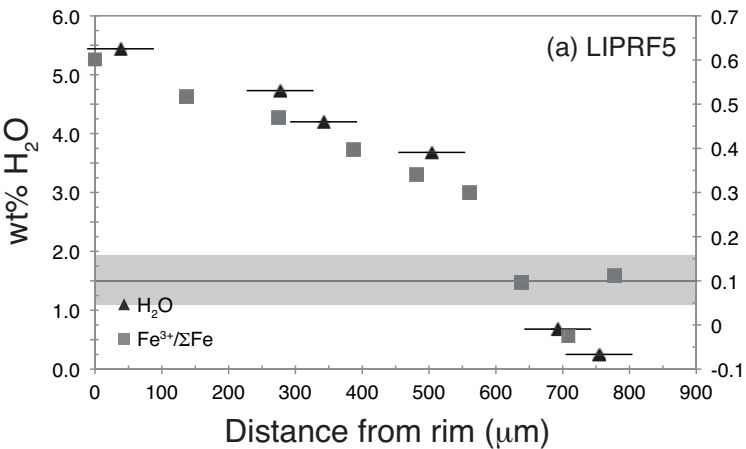


Figure 3







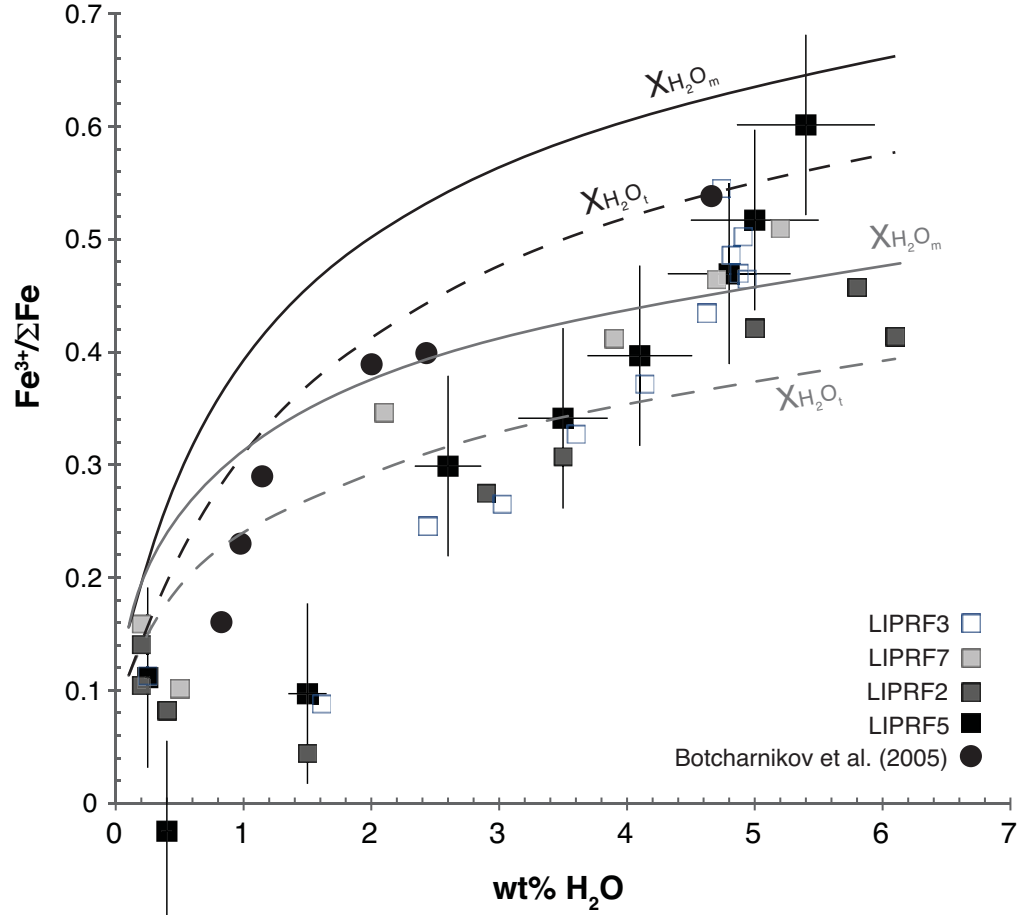


Figure 7

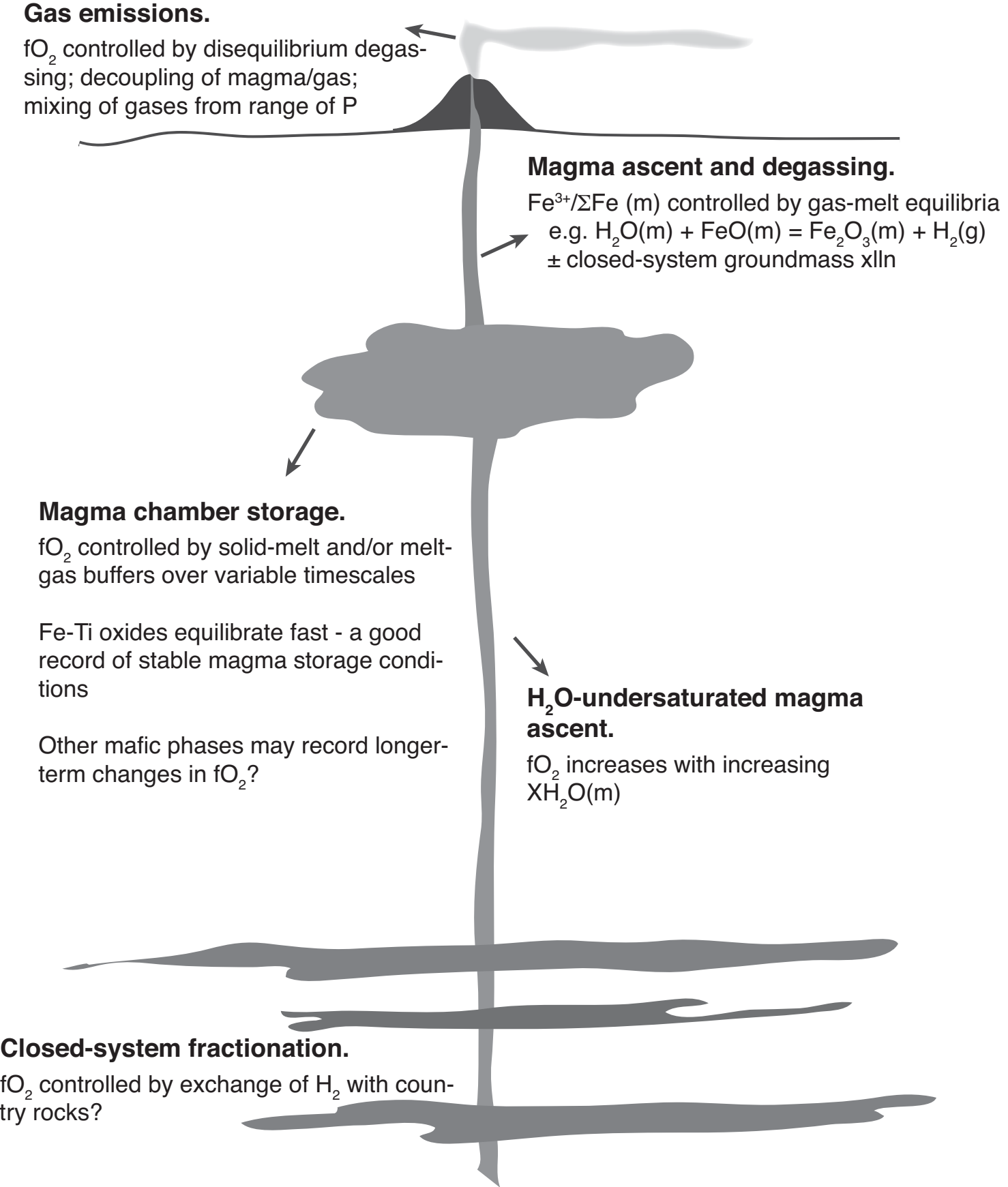


Figure 8

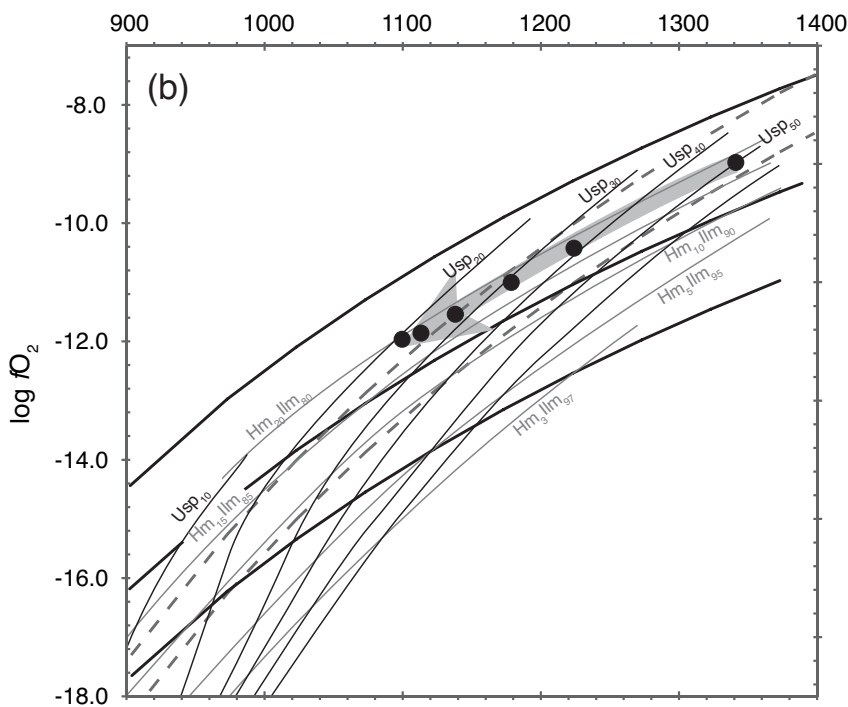
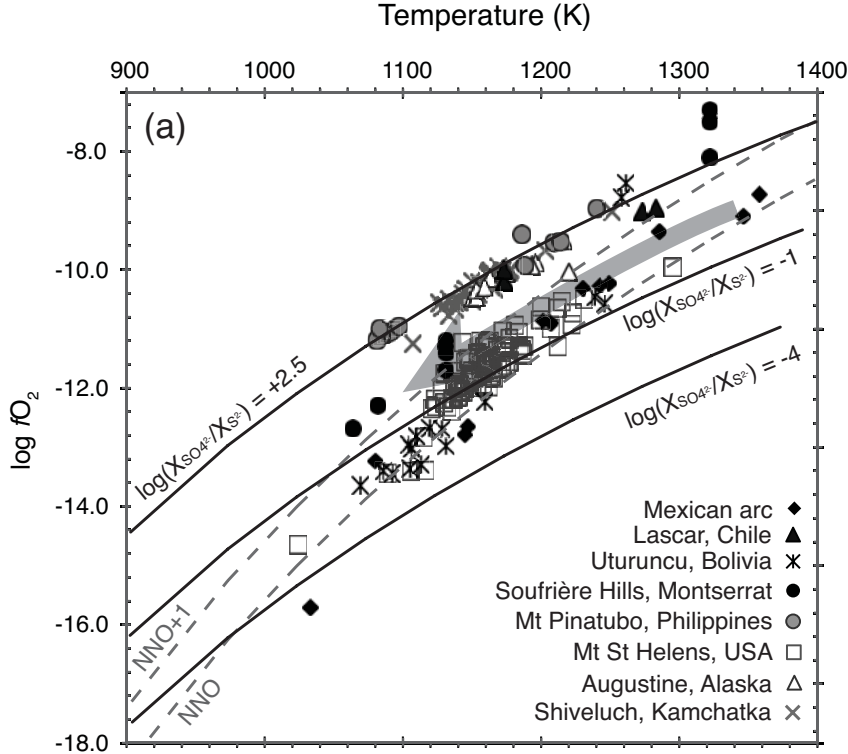


Figure 9

Table 1 - XANES fit components, calculated centroid and total intensity for rhyolite standards. $\text{Fe}^{3+}/\Sigma\text{Fe}$ values are from Mossbauer spectroscopy (Cottrell et al. 2009).

Analysis number	Sample	Fe ²⁺ component						Fe ³⁺ component						Centroid, eV	Total intensity	Fe ³⁺ /Σfe
		Fe ²⁺ peak location	±	Width	±	Intensity	±	Fe ³⁺ peak location	±	Width	±	Intensity	±			
8446	DT31	7113.03	0.058	2.098	0.081	0.059	0.004	7114.51	0.012	1.654	0.015	0.136	0.004	7114.12	0.194	0.63
8447	DT18	7113.90	0.038	2.940	0.044	0.141	0.007	7114.52	0.004	1.429	0.013	0.091	0.003	7114.20	0.232	0.66
8448	568_2	7112.81	0.019	1.852	0.033	0.060	0.002	7114.47	0.011	1.622	0.020	0.077	0.002	7113.80	0.137	0.238
8450	DT29	7113.97	0.028	2.741	0.034	0.131	0.004	7114.53	0.005	1.448	0.016	0.097	0.003	7114.27	0.228	0.806
8492	DT39	7112.91	0.024	1.953	0.039	0.073	0.002	7114.50	0.009	1.571	0.016	0.110	0.002	7113.93	0.184	0.315
8494	DT46	7113.03	0.039	2.049	0.059	0.069	0.004	7114.50	0.009	1.554	0.012	0.139	0.003	7114.07	0.207	0.569

Table 2 - (a) Experimental details for Panum dome rhyolite samples from Mangan & Sisson (2000). Pf - final pressure. (b) Experimental details for Lipari obsidian from Humphreys et al. (2008)

Sample	dP/dt, MPa/s	Pf, MPa	Run time (min)	Comments
58	0.025	25	117	Pervasive bubble cloud
63	0.025	100	67	Fringe bubbles only
65	0.025	31	113	Pervasive bubble cloud
68	0.025	175	17	Fringe bubbles only

Sample	P, MPa	T °C	Run time (min)	Comments
LIPRF2	200	857	20	
LIPRF3	200	859	80	
LIPRF5	150	899	67	
LIPRF7	150	901	20	

Table 3 - Electron microprobe compositions of starting glass and experimental run products, reported on anhydrous basis. 1σ uncertainties are derived from electron microprobe analysis. 'n', number of analyses

	Panum dome (Mangan & Sisson 2000)			Lipari obsidian (Humphreys et al. 2008)			Napa Valley Glass Mountain	
	Starting material	Avg run products (anhydrous)	1 sigma	Starting material	Avg run products (anhydrous)	1 sigma	Avg (anhydrous)	1 sigma
SiO ₂	75.64	76.94	0.52	74.17	74.39	1.6	76.59	0.51
TiO ₂	0.08	0.06	0.02	0.08	0.08	0.03	0.08	0.02
Al ₂ O ₃	12.38	12.56	1.05	12.76	12.95	1.08	12.3	1.03
FeO	0.94	1.01	0.26	1.57	1.59	0.45	1.16	0.27
MnO	0.07	0.05	0.11	0.05	0.07	0.11	0.04	0.1
MgO	0.03	0.03	0.05	0.04	0.04	0.01	0.01	0.05
CaO	0.54	0.54	0.13	0.74	0.75	0.12	0.37	0.11
Na ₂ O	4.17	3.79	0.53	4.24	4.16	0.73	4.4	0.56
K ₂ O	4.72	4.94	0.59	5.39	5.49	0.65	4.61	0.56
Cl	0.06	0.07	0.03	0.32	0.31	0.04	0.08	0.03
F				0.16	0.18	0.23		
H ₂ O	0.17			0.23			0.25	
Total	98.8	99.99		99.75	100.01		99.89	
n		33			110		12	

Analysis number	Fe ²⁺ component					Fe ³⁺ component					Centroid, Total								
	Sample	Fe ²⁺ peak location ±	Width ±	Intensity ±		Fe ³⁺ peak location ±	Width ±	Intensity ±		eV	intensity	Fe ³⁺ /ΣFe	wt% H ₂ O	Δ NNO	±				
8452	68-3	7112.78	0.044	1.886	0.066	0.043	0.003	7114.42	0.013	1.74	0.018	0.124	0.002	7114.05	0.167	0.529	7.27	2.7	0.55
8453	68-1	7112.74	0.035	1.840	0.055	0.043	0.002	7114.41	0.010	1.77	0.016	0.129	0.002	7114.05	0.172	0.529	6.20	2.8	0.55
8454	68-2	7112.75	0.040	1.808	0.063	0.041	0.003	7114.41	0.011	1.75	0.017	0.134	0.002	7114.08	0.175	0.562	6.42	3.0	0.57
8455	65-1	7112.93	0.067	1.983	0.093	0.047	0.004	7114.46	0.014	1.70	0.017	0.145	0.004	7114.15	0.192	0.643	2.41	3.7	0.69
8456	65-3	7112.85	0.051	1.915	0.076	0.046	0.003	7114.44	0.012	1.68	0.016	0.137	0.003	7114.10	0.183	0.585	3.72	3.2	0.60
8457	65-3A	7112.80	0.050	1.861	0.077	0.043	0.003	7114.42	0.013	1.70	0.018	0.138	0.003	7114.09	0.181	0.575	3.92	3.1	0.59
8458	65-5A	7113.00	0.076	2.089	0.103	0.053	0.005	7114.47	0.015	1.67	0.017	0.137	0.004	7114.12	0.190	0.610	2.49	3.4	0.63
8459	65-7	7112.81	0.050	1.907	0.075	0.046	0.003	7114.42	0.013	1.70	0.018	0.134	0.003	7114.07	0.180	0.545	4.38	2.9	0.56
8460	65-9	7112.92	0.085	1.976	0.119	0.047	0.005	7114.45	0.018	1.69	0.021	0.144	0.005	7114.14	0.191	0.629	3.92	3.6	0.66
8461	65-8	7112.87	0.052	1.982	0.077	0.049	0.004	7114.44	0.012	1.68	0.016	0.133	0.003	7114.08	0.181	0.558	3.52	3.0	0.57
8462	58-3	7112.96	0.054	2.059	0.076	0.053	0.004	7114.47	0.012	1.67	0.014	0.134	0.003	7114.10	0.187	0.586	2.30	3.2	0.60
8463	58-2	7112.94	0.053	2.025	0.074	0.052	0.004	7114.46	0.012	1.68	0.014	0.135	0.003	7114.10	0.186	0.583	2.31	3.2	0.60
8464	58-1	7112.93	0.053	1.971	0.076	0.049	0.004	7114.46	0.012	1.68	0.015	0.137	0.003	7114.12	0.186	0.603	2.29	3.4	0.62
8465	63-1	7112.83	0.047	1.913	0.070	0.044	0.003	7114.43	0.011	1.71	0.015	0.140	0.003	7114.11	0.185	0.591	4.45	3.3	0.61
8466	63-3	7112.74	0.038	1.806	0.060	0.041	0.003	7114.40	0.010	1.74	0.016	0.136	0.002	7114.08	0.177	0.559	5.04	3.0	0.57

Table 4 - XANES fit components, calculated centroid and total intensity, and calculated Fe³⁺/ΣFe for the high-T decompression samples. H₂O contents are measured from SIMS. Δ NNO is calculated for 900 °C.

Analysis number	Sample	Fe ²⁺ component						Fe ³⁺ component						Centroid, eV	Total intensity	Distance from rim (μm)	Fe ³⁺ /ΣFe	wt% H ₂ O (SIMS)
		Fe ²⁺ peak location	±	Width	±	Intensity	±	Fe ³⁺ peak location	±	Width	±	Intensity	±					
7272	LIRPF5-1	7112.83	0.0285	1.7839	0.0494	0.0416	0.0020	7114.55	0.0078	1.722	0.013	0.139	0.002	7114.11	0.181	0	0.60	5.44
7273	LIPRF5-2	7112.87	0.0303	1.8349	0.0521	0.0479	0.0023	7114.57	0.0099	1.687	0.017	0.120	0.002	7114.04	0.168	136	0.52	5.00
7274	LIRPF5-3	7112.85	0.0259	1.8216	0.0454	0.0498	0.0021	7114.57	0.0094	1.696	0.017	0.113	0.002	7114.01	0.163	274	0.47	4.80
7275	LIPRF5-4	7112.8	0.0207	1.7912	0.0363	0.0510	0.0018	7114.53	0.0083	1.714	0.016	0.111	0.002	7113.95	0.162	387	0.40	4.10
7276	LIPRF5-5	7112.81	0.0209	1.8227	0.0371	0.0551	0.0019	7114.54	0.0091	1.694	0.018	0.104	0.002	7113.90	0.159	482	0.34	3.50
7277	LIRPF5-6	7112.82	0.0187	1.7890	0.0329	0.0572	0.0018	7114.55	0.0093	1.698	0.020	0.096	0.002	7113.86	0.153	561	0.30	2.60
7278	LIPRF5-7	7112.85	0.0170	1.8093	0.0308	0.0673	0.0019	7114.56	0.0119	1.632	0.025	0.073	0.002	7113.70	0.140	638	0.10	1.50
7279	LIPRF5-8	7112.8	0.0144	1.7891	0.0255	0.0701	0.0016	7114.52	0.0115	1.650	0.028	0.067	0.002	7113.60	0.137	708	-0.02	0.40
7280	LIRPF5-9	7112.82	0.0175	1.7884	0.0308	0.0658	0.0019	7114.54	0.0117	1.667	0.027	0.077	0.002	7113.71	0.143	778	0.11	0.25
7281	LIPRF7-1	7112.82	0.0365	1.8057	0.0625	0.0437	0.0026	7114.55	0.0125	1.752	0.022	0.117	0.002	7114.04	0.160	0	0.51	5.20
7282	LIPRF7-2	7112.81	0.0277	1.8060	0.0480	0.0480	0.0022	7114.54	0.0099	1.724	0.018	0.118	0.002	7114.00	0.167	86	0.46	4.70
7283	LIPRF7-3	7112.8	0.0230	1.8522	0.0404	0.0519	0.0019	7114.54	0.0086	1.716	0.015	0.115	0.002	7113.96	0.167	171	0.41	3.90
7284	LIPRF7-4	7112.84	0.0211	1.8498	0.0371	0.0572	0.0019	7114.56	0.0092	1.684	0.017	0.102	0.002	7113.90	0.160	252	0.35	2.10
7285	LIPRF7-5	7112.87	0.0150	1.8345	0.0271	0.0686	0.0017	7114.58	0.0103	1.621	0.022	0.071	0.002	7113.70	0.140	329	0.10	0.50
7286	LIPRF7-6	7112.84	0.0171	1.8011	0.0301	0.0649	0.0018	7114.56	0.0108	1.664	0.024	0.080	0.002	7113.75	0.145	394	0.16	0.20
4660	LIPRF2-1	7112.72	0.0231	1.7718	0.0412	0.0431	0.0017	7114.51	0.0087	1.787	0.018	0.111	0.002	7113.96	0.154	0	0.41	6.10
4662	LIPRF2-2	7112.84	0.0327	1.8514	0.0556	0.0472	0.0025	7114.57	0.0120	1.737	0.021	0.108	0.002	7114.00	0.156	61	0.46	5.80
4663	LIPRF2-3	7112.83	0.0240	1.8290	0.0419	0.0502	0.0020	7114.57	0.0094	1.723	0.018	0.107	0.002	7113.97	0.157	125	0.42	5.00
4664	LIPRF2-4	7112.78	0.0213	1.8283	0.0369	0.0537	0.0018	7114.52	0.0093	1.728	0.019	0.102	0.002	7113.87	0.156	199	0.31	3.50
4670	LIPRF2-5	7112.84	0.0248	1.8271	0.0434	0.0582	0.0023	7114.57	0.0126	1.690	0.026	0.091	0.003	7113.84	0.149	225	0.27	2.90
4665	LIPRF2-6	7112.76	0.0176	1.7885	0.0314	0.0628	0.0018	7114.49	0.0117	1.668	0.026	0.076	0.002	7113.65	0.138	244	0.04	1.50

4666	LIPRF2-7	7112.8	0.0167	1.8094	0.0299	0.0667	0.0018	7114.53	0.0108	1.663	0.025	0.079	0.002	7113.69	0.145	303	0.08	0.40
4667	LIPRF2-8	7112.82	0.0199	1.7933	0.0354	0.0649	0.0021	7114.54	0.0132	1.665	0.029	0.077	0.002	7113.70	0.142	398	0.10	0.20
4668	LIPRF2-9	7112.88	0.0161	1.8471	0.0288	0.0671	0.0017	7114.59	0.0103	1.642	0.022	0.075	0.002	7113.73	0.142	474	0.14	0.20
4671	LIPRF3-1	7112.86	0.0410	1.8802	0.0669	0.0447	0.0028	7114.54	0.0111	1.714	0.017	0.133	0.002	7114.07	0.178	0	0.54	5.40
4672	LIPRF3-2	7112.83	0.0361	1.8774	0.0600	0.0469	0.0026	7114.53	0.0108	1.722	0.018	0.126	0.002	7114.02	0.173	34	0.49	5.40
4673	LIPRF3-3	7112.81	0.0289	1.7642	0.0493	0.0433	0.0021	7114.53	0.0096	1.744	0.018	0.123	0.002	7114.03	0.166	78	0.50	5.30
4674	LIPRF3-4	7112.85	0.0299	1.8570	0.0514	0.0492	0.0023	7114.57	0.0104	1.706	0.018	0.114	0.002	7114.00	0.163	136	0.46	5.00
4675	LIPRF3-5	7112.85	0.0280	1.8431	0.0486	0.0497	0.0023	7114.58	0.0102	1.720	0.018	0.114	0.002	7114.01	0.164	171	0.47	4.80
4676	LIPRF3-6	7112.83	0.0277	1.8342	0.0491	0.0505	0.0023	7114.57	0.0105	1.711	0.019	0.111	0.002	7113.98	0.162	225	0.43	4.70
4677	LIPRF3-7	7112.83	0.0288	1.8502	0.0504	0.0521	0.0024	7114.54	0.0112	1.685	0.020	0.105	0.002	7113.92	0.158	281	0.37	4.70
4678	LIPRF3-8	7112.74	0.0263	1.7600	0.0472	0.0507	0.0023	7114.5	0.0112	1.729	0.024	0.108	0.002	7113.89	0.159	326	0.33	4.40
4679	LIPRF3-9	7112.78	0.0196	1.7886	0.0349	0.0548	0.0018	7114.51	0.0094	1.700	0.019	0.097	0.002	7113.84	0.152	367	0.27	4.40
4680	LIPRF3-10	7112.81	0.0239	1.8159	0.0407	0.0575	0.0022	7114.53	0.0123	1.709	0.025	0.092	0.002	7113.82	0.150	404	0.25	4.00
4681	LIPRF3-11	7112.81	0.0156	1.7353	0.0271	0.0617	0.0016	7114.53	0.0114	1.698	0.027	0.073	0.002	7113.69	0.135	454	0.09	3.60
4682	LIPRF3-12	7112.83	0.0161	1.7828	0.0293	0.0647	0.0017	7114.56	0.0108	1.647	0.024	0.075	0.002	7113.71	0.140	633	0.11	0.90
7287	Starting material	7112.81	0.0155	1.7998	0.0274	0.0657	0.0017	7114.54	0.0103	1.669	0.023	0.077	0.002	7113.70	0.143		0.10	0.23

Table 5 - XANES fit components, calculated centroid and total intensity, and calculated $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the high-T hydration samples. H_2O contents are measured from SIMS.

Analysis number	XANES analysis	SIMS analysis	Distance (microns)	±	Fe ²⁺ component					Fe ³⁺ component					Centroid, eV	Total intensity	H ₂ O wt% Fe ³⁺ /ΣFe (SIMS)	H ₂ O wt% (greyscale)		
					Fe ²⁺ peak location ±	Width ±	Intensity ±	Fe ³⁺ peak location ±	Width ±	Intensity ±										
4650		NVGM_1	-515	50	7112.87	0.022	1.853	0.038	0.061	0.002	7114.59	0.010	1.683	0.021	0.100	0.002	7113.89	0.160	0.33	0.27
8486		NVGM_2	-279	50	7112.85	0.027	1.945	0.044	0.062	0.002	7114.48	0.010	1.631	0.019	0.099	0.002	7113.91	0.161	0.36	0.28
		NVGM_3	-64	10	7112.79	0.027	1.850	0.043	0.053	0.002	7114.45	0.010	1.694	0.019	0.110	0.002	7113.97	0.163		0.29
8482	NVGM_3		-112	25	7112.79	0.027	1.850	0.043	0.053	0.002	7114.45	0.010	1.694	0.019	0.110	0.002	7113.97	0.163	0.43	0.68
		NVGM_4	-35	10															0.96	
8483	NVGM_4		-80	25	7112.83	0.026	1.927	0.042	0.055	0.002	7114.47	0.009	1.665	0.014	0.109	0.002	7113.98	0.164	0.44	0.48
		NVGM_5	55	10																2.79
		NVGM_6	22	10																3.05
8484	NVGM_6		10	10	7112.8	0.032	1.873	0.052	0.050	0.002	7114.46	0.010	1.673	0.017	0.116	0.002	7114.02	0.165	0.49	1.9
8485	NVGM_7	NVGM_7	148	25	7112.83	0.029	1.939	0.044	0.048	0.002	7114.46	0.009	1.697	0.013	0.111	0.002	7114.03	0.160	0.50	3.33
8487	NVGM_4A		-58	10	7112.8	0.035	1.887	0.053	0.049	0.003	7114.45	0.012	1.722	0.020	0.113	0.003	7114.01	0.163	0.47	0.64
4651			-300	50	7112.87	0.017	1.880	0.030	0.060	0.002	7114.54	0.008	1.633	0.013	0.095	0.001	7113.84	0.155	0.27	0.27
4686			-300	50	7112.88	0.025	1.899	0.044	0.061	0.002	7114.56	0.010	1.643	0.018	0.104	0.002	7113.89	0.164	0.33	0.27
4687	NVGM_9		30	50	7112.8	0.034	1.823	0.056	0.041	0.002	7114.52	0.011	1.784	0.019	0.117	0.002	7114.03	0.158	0.49	2.25
4688	NVGM_8		30	50	7112.87	0.045	1.895	0.073	0.044	0.003	7114.57	0.014	1.748	0.021	0.120	0.003	7114.06	0.164	0.54	2.53

Table 6 - XANES fit components, calculated centroid and total intensity, and calculated Fe³⁺/ΣFe for the low-T hydration samples. H₂O contents are measured from SIMS or estimated from greyscale calibrations. Distance is measured relative to a prominent crack in the sample rim (see figure 7).