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

Humphreys, M.C.S.1,2, Brooker, R.A.3, Fraser, D.G.2, Burgisser, A.4, Mangan, M.T.5 & McCammon, C.6

1 Department of Earth Sciences, Durham University, Science Labs, Durham, DH1 3LE
Email: madeleine.humphreys@durham.ac.uk; Tel: +44(0)191 334 2300; Fax: +44 (0)191 334 2301
2 Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK
3 School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen’s Road, Bristol, BS8 1RJ, UK
4 Institut des Sciences de la Terre d’Orléans, CNRS, Université d’Orléans, 1A Rue de la Férolerie, 45071 Orléans CEDEX 2, France
5 US Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025-3561, USA
6 Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ABSTRACT

Arc magmas erupted at the earth’s surface are commonly more oxidised than those produced at mid-ocean ridges. Possible explanations for this high oxidation state are that the transfer of fluids during the subduction process results in direct oxidation of the sub-arc mantle wedge; or that oxidation is caused by the effect of later crustal processes, including protracted fractionation and degassing of volatile-rich magmas. This study sets out to investigate the effect of disequilibrium crustal processes that may involve coupled changes in H2O content and Fe oxidation state, by examining the degassing and hydration of sulphur-free rhyolites. We show that experimentally hydrated melts record strong increases in Fe3+/ΣFe with increasing H2O concentration as a result of changes in water activity. This is relevant for the passage of H2O-undersaturated melts from the deep crust towards shallow crustal storage regions, and raises the possibility that vertical variations in fO2 might develop within arc crust.
Conversely, degassing experiments produce an increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ with decreasing H$_2$O concentration. In this case the oxidation is explained by loss of H$_2$ as well as H$_2$O into bubbles during decompression, consistent with thermodynamic modelling, and is relevant for magmas undergoing shallow degassing en route to the surface. We discuss these results in the context of the possible controls on $f\text{O}_2$ during the generation, storage and ascent of magmas in natural arc settings, in particular considering the timescales of equilibration relative to observation as this affects the quality of the petrologic record of magmatic $f\text{O}_2$.

INTRODUCTION

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

It is commonly suggested that increased $f\text{O}_2$ in arc systems compared with other tectonic environments is a primary feature related to mass transfer from the subducting slab to the mantle wedge (e.g. Brandon & Draper 1996; Parkinson & Arculus 1999; Kelley & Cottrell 2009), either directly through addition of volatiles, or indirectly if hydrous fluids carry dissolved $\text{Fe}^{3+}$ or sulphate (Kelley &
However, subduction zone magmatism is also characterised by complex crustal processes that could be expected to exert significant controls on oxidation state. These processes include magma fractionation, decompression, degassing and eruption. Arc magmas tend to be volatile rich and may be more prone to stalling and storage in the crust during ascent; this may increase the importance of fractionation and degassing in particular. Arc magmas also tend to crystallise magnetite early during differentiation, and studies based on the partitioning of redox-sensitive incompatible elements suggest that magmatic differentiation could be one reason for the higher $\frac{Fe^{3+}}{\sum Fe}$ of arc lavas (e.g. Mallman & O'Neill 2009; Lee et al. 2010). Other studies suggest that the influence of volatiles on $fO_2$ could be significant, particularly during crustal processes such as the degassing of C-O-H-S volatile species during shallow magmatic ascent (e.g. Sato 1978; Mathez 1984; Candela 1986; Burgisser & Scaillet 2007; Burgisser et al. 2008; Fiege et al. 2014).

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

In Part I of this study we present a brief review of literature evidence relating to the first problem, that of chemical mechanisms linking volatile dissolution with melt oxidation state, to consider whether volatiles can fundamentally affect oxidation state via melt chemistry. In Part II, we tackle the
second problem, presenting new data to explore the effect of disequilibrium or open system changes in H₂O content on the oxidation state of sulphur-free rhyolite melts and glasses, using a new series of coupled H₂O and Fe³⁺/ΣFe measurements from existing hydration and decompression experiments. We discuss the implications of our results for processes operating in natural magmas, highlighting the need to consider kinetics in these arc systems where there is ample evidence of disequilibrium at a variety of temporal and spatial scales.

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

The effects of variations in anhydrous melt composition on ferric-ferrous ratios at constant fO₂ are well known (e.g. Paul & Douglas 1965; Sack et al. 1980; Kress & Carmichael 1991; Toplis 2005), but there has been considerable debate over the effect of H₂O, as a chemical component of the melt, on Fe³⁺/ΣFe. In particular, it has been suggested that the same process that causes oxidation when alkalis are added into silicate melts at constant fO₂ (e.g. Paul & Douglas 1965) should also operate during dissolution of volatile species (Fraser 2005; Moretti 2005; Toplis 2005), by altering the relative activity coefficients of Fe²⁺ and Fe³⁺ species within the melt.

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

\[
O^0 + O^{2-} = 2O^-
\]

defines the basicity of the solution. Basic oxides such as alkalis (Na₂O or K₂O) dissociate to supply O²⁻ to the system and hence drive depolymerisation (breaking of oxo-bridges; equilibrium [1] moves to the RHS) while acidic oxides
(such as SiO$_2$) react with O$^{2-}$ to form polymer chains. Amphoteric oxides, including Fe$_2$O$_3$, Al$_2$O$_3$, H$_2$O and CO$_2$ (Fraser 1977), can act as an acid or a base depending on the composition of the silicate solution (Kushiro 1975). Fe oxide components in the silicate melt therefore have the following possible reactions (neglecting acidic behaviour of FeO, Fraser 1975; 2005):

$$\text{FeO} = \text{Fe}^{2+} + \text{O}^{2-} \quad \text{[basic, 2a]}$$

$$\text{Fe}_2\text{O}_3 = 2\text{Fe}^{3+} + 3\text{O}^{2-} \quad \text{[basic, 2b]}$$

$$\text{Fe}_2\text{O}_3 + \text{O}^{2-} = 2\text{FeO}^{2-} \quad \text{[acidic, 2c]}$$

where FeO$_2^-$ is part of the structural network, analogous to AlO$_4^-$.

Some evidence suggests that the dissolution of H$_2$O in polymerised silicate melts occurs by a depolymerisation reaction with the tetrahedral network by breaking of T-O-T bridges to form shorter polymer chains terminated by -OH (e.g. Stolper 1982; Xue & Kanzaki 2006; Malfait et al. 2014; though also see Kohn 2000), as well as by incorporation of unreacted molecular H$_2$O (e.g. Burnham 1975; Stolper 1982). This suggests that in these cases, dissolved H$_2$O should also show basic behaviour, similar to K$_2$O or Na$_2$O (in addition to the incorporation of unreacted, molecular water):

$$\text{H}_2\text{O} + \text{O}^0 = 2\text{OH} \quad \text{[basic, 3b]}$$

In strongly basic melts, it was predicted that H$_2$O could also behave as an acidic oxide (Yokokawa 1986; Fraser 1977; Fraser 2005; Moretti 2005):

$$\text{H}_2\text{O} + \text{O}^{2-} = 2\text{OH}^- \quad \text{[acidic, 3a]}$$

where OH$^-$ is “free hydroxyl” that is not bound to the silicate network but complexed with metal cations. This is supported by $^1$H NMR experiments (Xue & Kanzaki 2004) and may contribute to variations in solubility with silicate melt composition (Yokokawa 1986). Similar reactions are suggested for dissolution of CO$_2$, and this is supported by variations in carbon speciation with melt basicity (Brooker et al. 1999) as well as NMR and Raman spectroscopy studies (Mysen et al. 2011).

**Linking H$_2$O solubility, melt basicity and oxidation state**
In silicate melts, the ratios of multi-valent ions such as $\text{Eu}^{3+}/\text{Eu}^{2+}$ increase with increasing melt basicity ($aO_2^-$) at constant $fO_2$ (Morris & Haskin 1974; Tilquin et al. 1997). This is consistent with thermodynamic constraints if amphoteric behaviour of Fe oxide components is considered (reactions 2a-c, Fraser 1975), and explains the observed increase of $\text{Fe}^{3+}/\text{Fe}^{2+}$ with increasing alkali (or basic oxide) content of the melt (e.g. Paul & Douglas 1965; Sack et al. 1980; Kress & Carmichael 1991; Toplis 2005). Increasing the availability of free oxide ($O^2-$) leads to an overall net decrease of $a\text{Fe}_2\text{O}_3$ from reactions 2b and 2c while simultaneously increasing $a\text{FeO}$ from reaction 2a. This produces an overall increase in $\text{Fe}^{3+}/\Sigma\text{Fe}$ at constant $fO_2$, and should also polymerise the melt structure, because of the contribution of $\text{FeO}_2^-$ to the melt framework (Fraser 1977; Ottonello et al. 2001; Fraser 2005; Moretti 2005).

For volatiles, the same approach predicts that (basic) reaction of $\text{H}_2\text{O}$ with the silicate melt to form dissolved -OH [3b] should result in a net increase in $aO^2^-$ (and hence increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$) whereas (acidic) formation of free hydroxyl in very basic melts [3a] results in a net decrease in $aO^2^-$ (and hence decreased $\text{Fe}^{3+}/\Sigma\text{Fe}$). Similarly, dissolution of carbon dioxide in basic melts should result in net decrease in $aO^2^-$, and thus decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$. This provides a testable link between volatile solution mechanisms and melt oxidation state, which we review below.

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

Several previous studies have attempted to discern differences in redox state between equivalent hydrous and anhydrous melt compositions, with somewhat equivocal results. Moore et al. (1995) found no effect of $\text{H}_2\text{O}$ on the Fe oxidation state of hydrous peralkaline rhyolites, supporting an earlier study (Sisson & Grove 1993) that compared $\text{Fe}^{3+}/\Sigma\text{Fe}$ in hydrous basalts with the anhydrous predictions of the Kress & Carmichael (1991) model. Botcharnikov et al. (2005) concluded that $\text{Fe}^{3+}/\Sigma\text{Fe}$ in hydrous ferrobasalt was mainly controlled experimentally by $a\text{H}_2\text{O}$ (and hence $fO_2$) and was within the range predicted by existing anhydrous models.
In contrast, Gaillard et al. (2001) showed that addition of up to 6 wt% H₂O has an oxidising effect on metaluminous rhyolite relative to Kress & Carmichael (1991), but only at lower fO₂ conditions (<NNO+1). Gaillard et al. (2003a) also observed higher Fe³⁺/ΣFe in hydrous vs anhydrous rhyolite and ascribed this to a decrease in the ratio of activity coefficients (γ_{Fe₂O₃}^{L}/γ_{FeO}^{L}) in hydrous melts, or decreasing a_{Fe₂O₃}^{L} for a given XFe₂O₃ and increasing a_{FeO}^{L} for a given XFeO₃. This is essentially the same effect as predicted by acid-base theory (as described above). Schuessler et al. (2008) found that Fe³⁺/ΣFe increased with H₂O content at constant fO₂ in hydrous phonotephrites, which they attributed to the effects of melt basicity as described by Ottonello et al. (2001) and Moretti (2005). These principles are also supported by observations of differences in olivine-melt 20F₄Mg in hydrous and anhydrous melts (Toplis 2005).

Thus, while the results are still unclear, it does seem possible that H₂O has a resolvable effect on melt Fe³⁺/ΣFe through behaviour that is similar to the basic metal oxides (e.g. K₂O). Such an effect is probably minor, but would be most important in relatively polymerised melts and at high pressures where variations in oxidation state could affect the compositions of minerals that could fractionate Fe²⁺ from Fe³⁺. This would appear to justify further work in the context of hydrous subduction zone melts. Finally, the basicity approach highlights that oxidation state should be considered alongside an understanding of melt chemical species and melt structure.

PART II: EFFECT OF VARYING VOLATILE CONTENTS ON OXIDATION STATE

The second part of this paper specifically addresses how variations in melt volatile concentrations during crustal processes may affect melt Fe³⁺/ΣFe. We seek to explore two key processes in particular: (i) dehydration or degassing of volatiles during decompression, and (ii) hydration, due to H₂O-undersaturated magma ascent from high pressures. We present new XANES Fe³⁺/ΣFe analysis for two sets of existing experimental samples to investigate these processes: a set of decompression experiments from the study of Mangan & Sisson (2000),
and a set of partial hydration experiments from Humphreys et al. (2008). A brief description of the experimental procedures is included below.

**Decompression and H$_2$O degassing experiments**

Samples of the experimentally degassed Panum Crater Dome obsidian were taken from the study of Mangan & Sisson (2000; table 1). The starting materials for these experiments were slabs of obsidian, loaded into Pt capsules together with excess H$_2$O. The samples were superheated at 1000 °C for several hours in Hf-Zr-Mo cold-seal pressure vessels at 200 MPa, pressurised using Ar gas, then equilibrated at 900 °C for three days, and finally decompressed isothermally at 0.025 MPa/s to variable final pressure (P$_f$) and immediately quenched. Decompression runs lasted 17 to 117 minutes. There was no attempt to buffer fO$_2$ but rapid H$_2$ diffusion through the Pt capsule would have equilibrated the samples at a high fO$_2$ during the initial 3-day heating. Any observed covariance between H$_2$O loss and Fe$^{3+}$/ΣFe over short lengthscales in the samples must therefore be related to the short decompression phase of the experiment. The resulting glasses are variably vesicular, with bubbles nucleating throughout the capsule in some runs, but only at the margins of the capsule in others (table 1; Mangan & Sisson 2000). Most of the samples analysed by XANES contained primarily marginal bubbles. H$_2$O contents and vesicularity data clearly demonstrate that bubble nucleation was delayed and did not occur at equilibrium (Mangan & Sisson 2000), yielding a suite of glasses with heterogeneous H$_2$O contents over short lengthscales. The anhydrous composition of the glass is constant within analytical uncertainty (table 2), indicating that no other compositional changes to the melt occurred during degassing.

**Partial hydration experiments**

To compare the mechanisms of hydration and H$_2$O degassing, we analysed partially hydrated Lipari obsidian cores as reported in Humphreys et al. (2008). The starting materials for these experiments were cylinders of homogeneous
Lipari obsidian, which were loaded into gold capsules with excess H$_2$O, along with a small amount of finely ground obsidian powder to prevent dissolution of the glass during the experiment. The capsules were then held at super-liquidus conditions, 150-200 MPa and 855-905 °C in cold-seal pressure vessel apparatus pressurised by water. Run times were short (20-80 minutes) and achieved partial hydration of the glass cylinders (table 1; Humphreys et al. 2008). No double capsule oxygen buffer control was used during the experiments but the short run times, low temperatures and use of Au capsules effectively ensure impermeability to H$_2$ during the experiments (Chou 1986). The anhydrous composition of the glass is constant within analytical uncertainty (table 2), indicating that hydration is not associated with any other compositional changes to the melt.

ANALYTICAL METHODS

X-ray Absorption Near Edge Structure (XANES)

Fe$^{3+}$/ΣFe of experimental glasses were measured using Fe K-edge micro X-ray Absorption Near Edge Structure (μXANES) spectroscopy on the I18 (Microfocus Spectroscopy) beamline at the Diamond Light Source, UK. Spectra were recorded in fluorescence mode and the beam size at the sample was approximately 3 x 5 μm. The beamline uses a Si(111) crystal monochromator which gives an energy resolution (ΔE/E) of 1.4×10$^{-4}$ (approximately 1 eV at the Fe K-edge); the energy stability of the beamline is ±0.05 eV per day. Fluorescence X-rays were normalised to the incident beam flux and collected using a 9-element solid state detector. The energy was calibrated by defining the first peak of the first derivative of Fe foil to be at 7112 eV (or 7111.1 eV for comparison with older published literature data, e.g. Wilke et al. 2001). Spectra were recorded from 7028 eV to 7400 eV using a 0.086 eV step over the pre-edge region (7098-7123 eV), 0.259 eV step across the edge (7123-7158 eV) and ~5 eV step to define both the baseline (7028-7098 eV) and the post-edge region. Initial spectra were collected up to 7340 eV but this was extended out to 7400 eV in later runs to aid
the normalisation procedure (see below). Counting times were 2000 msec on all
points. The locations of all points analysed were recorded carefully with
reference to reflected light images of the samples to enable accurate relocation
for later SIMS analyses of the same points.

Fe\(^{3+}/\Sigma\text{Fe}\) measurements were quantified by referencing the centroid
energy of the pre-edge feature to a linear calibration (Figure 1a) constructed
using a suite of anhydrous rhyolite glass standards that were synthesised at 1
atm and a range of \(f_{O_2}\) (FMQ+0.8 to +6) and Fe\(^{3+}/\Sigma\text{Fe}\) from 0.238 to 0.806
(Cottrell et al. 2009; table 3). The raw spectra were normalised by fitting a
straight line to both the low-energy baseline and the post-edge region, using the
Athena software package (Ravel & Newville 2005). The pre-edge feature in Fe
spectra typically shows two overlapping peaks whose centroid energy is
quantitatively proportional to redox state (e.g. Wilke et al. 2001; Berry et al.
2003; Cottrell et al. 2009). The pre-edge regions of the normalised spectra were
fitted between 7106 and \(~7118\) eV, using a cubic baseline plus a Gaussian to
define the rising background towards the main K-edge, and two additional
Gaussian peaks to define the pre-edge region (following Berry et al. 2003;
Cottrell et al. 2009).

**SIMS and EPMA**

Glasses were analysed for \(^1\text{H}^+\), \(^7\text{Li}^+\), \(^{12}\text{C}^+\), \(^{25}\text{Mg}^+/2\), \(^{16}\text{O}^1\text{H}^+\), \(^{19}\text{F}^+\), \(^{23}\text{Na}^+\), \(^{26}\text{Mg}^+\), \(^{30}\text{Si}^+\),
\(^{35}\text{Cl}^+\) and \(^{29}\text{K}^+\) using the CAMECA ims 4f secondary ion mass spectrometer at the
University of Edinburgh. NIST SRM610 was used as the primary calibration
standard; \(^{30}\text{Si}^+\) was the internal standard. Mass 0.7 was used to monitor the
background count rate of the electron multiplier detector. A 10 kV, 2 nA, O-
primary beam was accelerated onto the sample with a net impact energy of 14.5
kV. Secondary ions were extracted at +4.5 eV using a 75 V offset. A pre-sputter
period of approximately 2 minutes, with a nominal 15 µm rastered beam, was
used to clean the sample surface, during which time the mass spectrometer was
 calibrated for the secondary ions. For quantitative analysis, the focused beam
was reduced to \(~10\) µm using a field aperture. H\(_2\)O contents of the glass were
derived using a daily working curve (figure 1b) of measured \(^1\text{H}^+/^{30}\text{Si}^+\) vs. H\(_2\)O in
well-calibrated hydrous glass standards, following the methods of Blundy & Cashman (2005). Typical errors in determining $\text{H}_2\text{O}$ are $\sim$8-12% relative. Where possible, the same points analysed by XANES were targeted for SIMS measurements. Major element glass compositions were analysed using a 5-spectrometer Cameca SX-100 electron microprobe at the University of Cambridge, with a defocused (15 µm), 15 kV, 4 nA electron beam for major elements and a 10 nA beam for minor elements. Other analytical conditions were equivalent to those of Humphreys et al. (2006a).

RESULTS

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

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

$$C = E_1 \frac{A_1}{A_1 + A_2} + E_2 \frac{A_2}{A_1 + A_2}$$

[4]
where $E_i$ is the peak energy of component $i$, and $A_i$ is the total area (or integrated intensity) of component $i$. Average precision on the centroid energy from uncertainties in the fitting parameters is extremely good, ±0.008 eV and far better than the accuracy, which relies on calibration of the centroid energy with $\text{Fe}^{3+}/\Sigma\text{Fe}$. Fully propagated uncertainty for our analyses gave an 80% confidence interval of ~0.067 for $\text{Fe}^{3+}/\Sigma\text{Fe}$, but with very high precision. This translates to $\Delta f_{O_2}$ of approximately ±0.6 log units. This method assumes similar Fe coordination in the calibration standards and the unknowns because the intensities of the pre-edge components can vary with both $\text{Fe}^{3+}/\Sigma\text{Fe}$ and iron coordination (Wilke et al. 2001). All our samples have similar total pre-edge intensity (figure 3), which suggests no significant change in Fe environment and indicates an average Fe-coordination number of approximately [5], consistent with a stable mixture of [4] and [6] environments (Wilke et al. 2001) for both Fe$^{2+}$ and Fe$^{3+}$. The most oxidised reference glasses plot at slightly higher total intensity than the unknowns, which may be a result of slight self-absorption effects (which has negligible effect on the centroid position, Bajt et al. 1994).

**H$_2$O degassing**

The experimentally degassed samples show a range of H$_2$O contents as measured by ion probe and inferred from greyscale variations (figure 4). Water contents range from 2.3 to 6.4 wt% H$_2$O, with one measurement at 7.2 wt% H$_2$O (figure 4c; table 4). These values are higher than the volatile contents as measured by FTIR (1.8 – 5.4 wt% H$_2$O, Mangan & Sisson 2000) but span a similar range. The cause of the discrepancy between the SIMS and FTIR data is unclear; however the key point for this study is that the glasses show clear relative variations of H$_2$O with $\text{Fe}^{3+}/\Sigma\text{Fe}$. Back-scattered SEM images of individual samples typically show clear increases in greyscale intensity that correlate well with decreasing H$_2$O concentration (figure 4b) from the core to the rim of samples with only marginal bubbles. This indicates progressive diffusive loss of H$_2$O to the margins of the sample to feed the growing marginal bubbles. Those samples with more vesicular interiors did not show any clear variations of BSE intensity and typically showed more limited H$_2$O variation.
XANES spectra for these samples have a relatively small range in pre-edge centroid energy from 7114.05 to 7114.15 eV (table 4). Total pre-edge intensity increases with increasing centroid energy (figure 3), consistent with previous observations for silicate glasses (Wilke et al. 2005). The pre-edge centroid energies for these samples correspond to an overall iron oxidation state, Fe$^{3+}$/$\Sigma$Fe of 0.52 to 0.64. Although this variation is small compared to the fully propagated measurement uncertainty, there are clear relative variations both between and within samples. There is a correlation between H$_2$O concentration and oxidation state, consistent with an increase in Fe$^{3+}$/$\Sigma$Fe due to degassing of H$_2$O from the melt.

Hydration

The margins of the Lipari obsidian samples are strongly hydrated, with water contents approaching the equilibrium values calculated for the experimental run conditions (4.8-5.6 wt%, Humphreys et al. 2008), while the interiors remain unhydrated and record the initial volatile content of the Lipari obsidian starting material (~0.2 wt% H$_2$O; table 5). The variation in H$_2$O contents is clearly visible as a strong outward decreases in back-scattered SEM intensity (e.g. figure 5a; Humphreys et al. 2008). The influx of water into the samples was previously modelled successfully based on established concentration-dependent H$_2$O diffusivity data (Nowak & Behrens 1997; Zhang & Behrens 2000) and is consistent with H$_2$O diffusion into the samples over the timescale of the experiments (Humphreys et al 2008).

XANES spectra for the high-temperature hydrated samples show strong changes in pre-edge centroid energy from 7113.65 to 7114.1 eV, with one outlier at 7113.60 eV (table 5), corresponding to Fe$^{3+}$/$\Sigma$Fe values from 0.04 to 0.60 (figure 5b). In marked contrast to the degassed samples, H$_2$O concentration correlates positively with oxidation state, indicating increasing Fe$^{3+}$/$\Sigma$Fe linked to diffusion of H$_2$O into the sample. This is further demonstrated by the close correspondence in the shapes of the compositional profiles with distance from the margin of each chip (Figure 6). These spatial profiles also highlight a small
but apparently significant (in that it is present in each sample) negative deviation of Fe$^{3+}$/ΣFe at low H$_2$O contents (~0.5-1.5 wt% H$_2$O).

**INTERPRETATION**

**Oxidation due to melt hydration**

The hydrated samples show clearly that increasing H$_2$O content causes an increase in the Fe oxidation state (figures 5 and 6). This observation is very similar to the results of an earlier equilibrium study (Botcharnikov et al. 2005), which used long run times and an AuPd capsule that is permeable to H$_2$ to control fO$_2$ in the experiments, according to the equilibrium constant for the dissociation reaction:

$$
H_2O (g) = H_2 (g) + \frac{1}{2} O_2 (g) \quad [5]
$$

$$
K_{eq}^{fl} = (fH_2 \cdot fO_2^{1/2}) / fH_2O^{fl} \quad [6]
$$

Although fH$_2$ of the fluid was fixed (via a Shaw membrane), variations of XH$_2$O$^0$ between capsules introduced differences in equilibrium fO$_2$ in different experimental runs (Botcharnikov et al. 2005), because fH$_2$O = aH$_2$O * f$^0$H$_2$O (and assuming ideal behaviour, aH$_2$O ~ XH$_2$O). The actual fO$_2$ experienced was calculated from the imposed fO$_2$ and XH$_2$O (Botcharnikov et al. 2005):

$$
log fO_2 (actual) = log fO_2 (imposed) + 2 \log XH_2O \quad [7]
$$

In our experiments, we assume that the use of an Au capsule (minimally permeable to H$_2$ at our experimental temperatures, Chou 1986) and very short run times (20-80 minutes) resulted in approximately constant fH$_2$ fluid inside the experiments (see later). Our experiments were not equilibrated, and diffusion of H$_2$O from the fluid into the melt resulted in wide variations of XH$_2$O within each quenched glass chip, from water-saturated at the hydrated margin (~5.5 to 6 wt% H$_2$O) to highly undersaturated in the unhydrated core (~0.2 wt% H$_2$O). We can write equivalent reactions to [5-6] that apply for the melt phase, even though equilibration was incomplete. We therefore calculated the apparent change in log fO$_2$ (melt) following the approach of Botcharnikov et al. (2005).
assumed constant $fH_2$, and used either $H_2O_i$ (the total amount of $H_2O$ dissolved in
the melt) or the molecular $H_2O_m$ (estimated from Silver et al. 1990) to calculate
log $XH_2O_i$ or log $XH_2O_m$, i.e., $XH_2O_i = H_2O_i/H_2O_{sat}$ and $XH_2O_m = H_2O_m/H_2O_{sat}$. We
also assumed that the marginal glass is $H_2O$-saturated, i.e. that $XH_2O_i = 1$ at the
rim, as the rim $H_2O_i$ concentrations agree with solubility models (Humphreys et
al. 2008). Calculated $fO_2$ was converted to $Fe^{3+}/ΣFe$ using the anhydrous
algorithm of Kress & Carmichael (1991) for the major element composition of
the sample and known experimental conditions. Using this approach, the overall
change in $Fe^{3+}/ΣFe$ from core to rim in the glass samples is matched by the
predictions based on observed changes in $XH_2O$ (figure 7). The lengthscale of the
changes in $Fe^{3+}/ΣFe$ is also equivalent to the lengthscale of $H_2O$ diffusion
gradients, modelled using existing $H_2O_m$ diffusivity data (Humphreys et al. 2008),
demonstrating that $Fe^{3+}/ΣFe$ varies at a rate controlled largely by the diffusivity
of $H_2O_m$. (figure 6). This implies that $Fe$ oxidation state is dominated by
variations in $XH_2O$ during hydration.

However, the shapes of the $H_2O$-$Fe^{3+}/ΣFe$ profiles do not fit well to the
modelled trend (figure 7), which suggests that $Fe$ oxidation state was only partly
controlled by the disequilibrium changes in $XH_2O$. In particular, there is a
significant deviation from the modelled curve to lower $Fe^{3+}$ at low to
intermediate water contents (figure 7). This is in contrast to equilibrium data
(Botcharnikov et al. 2005), which fit the model well (figure 7). The discrepancy
with the equilibrium data cannot be explained by significant changes in average
melt $Fe$ coordination, because the overall intensity of the pre-edge region does
not vary significantly with oxidation state (see figure 3; although this does not
preclude that coordination changes might occur).

Another possibility is that some ‘significant’ diffusion of $H_2$ did occur
across the Au capsule during the course of even these short experiments. As the
experiments were unbuffered it is difficult to quantify these effects but we note
that any $H_2$ loss from the capsule fluid would result in anomalously oxidised
sample margins, while $H_2$ gain would result in anomalously reduced sample
margins, relative to predicted values. Instead, $Fe^{3+}/ΣFe$ at the sample margins is
well matched by the predictions – instead the unhydrated cores of the chips are
anomalously reduced relative to the predicted curves (Figure 7). Furthermore, there is no difference in profile shape between the shortest (20 minutes) and longest experiment (117 minutes), which supports our interpretation that the experiments approximately represent a closed system. There is also no difference in the width of the low-Fe\textsuperscript{3+} region between the shortest and longest experimental runs (figure 6). This suggests that rapid migration of H\textsubscript{2} preceding the H\textsubscript{2}O diffusion front at high temperature cannot explain the discrepancy between model and observations (cf. Gaillard et al. 2002; 2003b).

Our best explanation is therefore that, although the interconversion reaction between H\textsubscript{2}O and OH in the silicate melt is rapid at experimental temperatures (Zhang et al. 1991), reactions involving the Fe species are slower, or may involve intermediate reactions, at low H\textsubscript{2}O contents where the melt viscosity is higher. The effect of this would be that any change in Fe\textsuperscript{3+}/ΣFe is offset to higher XH\textsubscript{2}O in these disequilibrium experiments. This could also explain why the longer duration, equilibrium experiments of Botcharnikov et al. (2005) are more consistent with the shape of the modelled curves (see figure 7). This interpretation is consistent with the observations that relatively slow redox equilibration in metaluminous rhyolites may be linked to intermediate changes in complexing of network-modifying cations (Gaillard et al. 2003c), such as:

\[ \text{NaFe}^{3+}\text{O}_2 + 2 \text{Si-OH} = 2\text{OH} + 2\text{Fe}^{2+\text{0.5}}\text{-O-Si} \] \[8\]

or

\[ \text{H}_2 + 2\text{NaFe}^{3+}\text{O}_2 + 2 \text{Si-O-Si} = 2\text{NaOH} + 4\text{Fe}^{2+\text{0.5}}\text{OSi} \] \[9\]

This emphasises that changes in melt oxidation state are closely linked to variations in melt chemistry and structure. Melt basicity theory may be a useful additional tool for investigation of these sorts of coupled changes than simply f\textsubscript{O\textsubscript{2}} measured relative to traditional oxygen buffers.

**Oxidation due to H\textsubscript{2}O degassing**

The data from the experimentally degassed rhyolites are scattered but show a general trend of oxidation by ~0.5 to 1 log unit f\textsubscript{O\textsubscript{2}} (Fe\textsuperscript{3+}/ΣFe varies from 0.53 to 0.65) as H\textsubscript{2}O contents decrease from ~7 to ~2 wt\% (figure 4c; table 4). During decompression, the melt became H\textsubscript{2}O-saturated and nucleated bubbles of a free
H₂O vapour phase. We infer that subsequent re-equilibration of fH₂ and fH₂O in the vapour bubble occurred through sequestration of H₂ from the melt, resulting in increased Fe³⁺/ΣFe through the reaction:

\[ H_2 (g) + Fe_2O_3 (m) = H_2O (m) + 2FeO (m) \]  \[10\]

Although the initial fO₂ of the melt in these experiments was quite high, as a result of prolonged equilibration at high pressure in the cold seal apparatus (Mangan & Sisson 2000), this oxidation pattern is consistent with theoretical calculations of increasing oxidation state with degassing for sulphur-free melts (e.g. Mueller 1971; Candela 1986; Burgisser & Scaillet 2007). We used the approach of Burgisser et al. (2008) to simulate the change in OH partitioning between gas and melt during pressurisation in a closed system. Each pressure step results in incremental changes to the species fugacities and their concentrations in the melt, which are calculated using species solubilities, mass balance, and reaction [5]. The scale of the observed fO₂ increase is somewhat less than that predicted by the model when starting with negligible initial fluid (figure 4d). This discrepancy is unlikely to be related to significant changes in fH₂ during the course of the experiments, because the decompression run times are very short (17 to 117 minutes). Moreover, the experimental apparatus was pressurised by Ar gas, so H₂ would tend to migrate out through the capsule, decreasing fH₂ and leading to more oxidised conditions. Instead, it is more likely that:

(i) The modelling does not take into account the buffering capacity of FeO in the melt, which could reduce the absolute increase in oxidation state, particularly at higher initial fO₂ (Candela 1986). However, for a melt with only 1 wt% FeO (as in the case of the Panum Dome rhyolite) this should account for <0.2 log units change in fO₂ (Burgisser & Scaillet 2007).

(ii) The high proportion of fluid in the experimental capsules is buffering the changes in fO₂. The experimental starting materials include ~20 wt% fluid so there is likely to be substantial excess fluid at the beginning of each decompression run. When the modelling is repeated with 10 wt% and 20 wt% initial fluid the scale of the fO₂ increase is substantially reduced.
relative to the run with 0.1 wt% initial fluid (figure 4d), consistent with the observations.

The other important difference between the experiments and the modelling is that the experiments were run without equilibration at each pressure step (Mangan & Sisson 2000); i.e., they represent disequilibrium degassing. The disequilibrium arises from delayed bubble nucleation, which is offset to lower pressure than the equilibrium case, but because they were run with a pure H$_2$O fluid there is no effect on the relationship between Fe$^{3+}$/ΣFe and H$_2$O. However, more significant kinetic factors could arise in multi-component fluids with significant differences in volatile species diffusivities. This is highlighted in experiments by Fiege et al. (2014) that showed enhanced transfer of sulphur into the fluid relative to the melt at high decompression rates, decreasing to equilibrium values with annealing and producing lower melt Fe$^{3+}$/ΣFe than predicted by equilibrium (closed-system) models.

DISCUSSION

Our data demonstrate that magma degassing and hydration can both result in significant melt oxidation coupled to changes in volatile content. On H$_2$O saturation, the formation of a free H$_2$O vapour phase partitions H$_2$ from the melt into the vapour and results in melt oxidation. During hydration, oxidation is caused by changes in water activity. These mechanisms should therefore be considered as one possible way to explain the high oxidation state observed in arc magmas (e.g. Carmichael 1991). Both processes have direct relevance for crustal processes and may be important in different regions of the arc crust (figure 8). Magma ascent from shallow storage regions is dominated by degassing of H$_2$O vapour from the melt, while rise of H$_2$O-undersaturated magma from the deep crust would be associated with increasing water activity. However, arc magmas are complicated by a general lack of equilibrium conditions, instead representing different components or sub-systems that may be in equilibrium at different points in the volcanic system. We therefore need to
consider what controls \( fO_2 \) and what phases would record it accurately over varying timescales.

**Degassing in natural systems**

Arc magma ascent through a conduit and eruption at the surface is associated with significant volatile degassing (figure 8). Our new data and modelling demonstrate that degassing of a pure or dominantly \( \text{H}_2\text{O} \)-bearing fluid results in significant melt oxidation. Under closed-system degassing conditions, this can be moderated by the presence of large volumes of gas. Furthermore, the melt can be expected to oxidise even if degassing occurs during disequilibrium degassing (delayed bubble nucleation), provided that the volatile budget is dominated by \( \text{H}_2\text{O} \). In natural systems, we would therefore expect to observe a systematic deviation between the oxidation state of the melt relative to that of the pre-eruptive magma (as measured, for example, by 2-oxide equilibria).

Crabtree & Lange (2012) showed that bulk rock \( \text{Fe}^{3+}/\Sigma \text{Fe} \) in degassed, crystal-poor andesites from the Mexican volcanic arc was within error of the pre-eruptive \( \text{Fe}^{3+}/\Sigma \text{Fe} \) of the hydrous melt, as determined by 2-oxide thermobarometry. This was interpreted to mean that extensive degassing (of up to 8 wt% \( \text{H}_2\text{O} \)) during ascent had no measurable effect on magma oxidation state. Our data indicate that such strong \( \text{H}_2\text{O} \) degassing *should* leave a clear signature of oxidation in the melt phase. We therefore suggest that the magma may also have degassed additional multi-valent gas species (e.g. sulphur) that would counteract the melt oxidation driven by loss of \( \text{H}_2\text{O} \) (Burgisser et al. 2008). Alternatively, the bulk rock measurements of oxidation state in the degassed magmas may have been insufficiently sensitive to resolve any degassing effects. Direct, *in situ* measurements of melt oxidation state (e.g. by XANES) are more likely to resolve these late-stage changes.

Surface volcanic gas emissions represent the counterpart to the continuously degassing melt that is erupted (figure 8), but gas \( fO_2 \) measurements are commonly different from those of their host lavas. This has been interpreted as the result of oxidation state changes to the melt during degassing (e.g. loss of
SO$_2$ from basalt, Anderson & Wright 1972; Helz 2009) or mixing and integration of multi-component gases released over a range of pressures (Edmonds et al. 2010). In some cases, disequilibrium in the gas phase is evident from lack of correspondence of $f_{O_2}$ estimates using different gas ratios (e.g. H$_2$/H$_2$O cf. CO/CO$_2$, Hammouya et al. 1998) and probably results from mixing of gas components with different origins, decoupled from magma ascent (Edmonds et al. 2010). In other cases the gases appear to be in equilibrium with the lavas (e.g. Gerlach 1993; Roeder et al. 2003; Gerlach 2004; Roeder et al. 2004) and the discrepancy may relate to kinetic differences in the response rate of different redox pairs (H$_2$-H$_2$O > SO$_2$-H$_2$S > CO-CO$_2$-CH$_4$, Giggenbach 1987).

These problems indicate that where multiple volatile species are present, the effects of degassing of natural arc magmas on oxidation state are complex, and strongly influenced by temperature, pressure, degassing kinetics and the initial $f_{O_2}$ (Fiege et al. 2014; Burgisser & Scaillet 2007) as well as the mode of degassing (open system or closed system). This means that analysis of oxidation state during degassing of natural melts is unlikely to yield unique interpretations, although it is clear that arc magma degassing could significantly affect the oxidation state of the melt. Attaining a real understanding of the effects of magmatic degassing on oxidation state will probably require direct measurements of the concentrations and speciation of all major volatiles in the melt, as well as melt Fe$^{3+}$/ΣFe and the corresponding gas compositions.

**Magma ascent from the deep crust**

Recent models of arc magma genesis involve prolonged periods of deep (mafic) magma intrusion, differentiation and partial melting (e.g. Annen et al. 2006), followed by magma ascent towards upper crustal magma reservoirs where storage, degassing and mingling may also occur (Humphreys et al. 2008; Edmonds et al. 2010; Johnson et al. 2010). Our partial hydration experiments have relevance for the passage of hydrous melts or magmas between the lower crust and shallow magma storage reservoirs (figure 8). Although magmas originating from the deep storage are thought to be hydrous, they are highly unlikely to be H$_2$O-saturated. This means that melt aH$_2$O will increase during
ascent, as the magma gets closer to volatile saturation. By analogy with our experimental results, such ascent could result in significant oxidation of the melt under conditions of incomplete diffusive equilibration. Although H₂O diffusion is rapid, we calculate that even in 10,000 years significant diffusion would only be observed over a distance of only ~20 m at 900 °C (using the diffusivity model from Nowak & Behrens 1997). This means that incomplete equilibration in ascending magmas must be carefully considered as a possible source of Fe³⁺/ΣFe heterogeneity. Moreover, this reasoning also suggests that, depending on timescales, magmas in the middle to lower crust could be substantially more reducing than those in the upper levels of magma storage, and hence that crustal-scale variations in fO₂ may be possible at subduction zones.

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

What controls fO₂ in magmatic systems?
Although estimates of \( f_O^2 \) for many magmas plot close to solid oxygen buffers (e.g. nickel - nickel oxide, NNO; or quartz-fayalite-magnetite, QFM), these phases typically do not (co)exist and it is highly unlikely that those solid buffers are controlling magma \( f_O^2 \); instead they are useful reference lines in \( T-f_O^2 \) space. However, it has been suggested that gas-melt redox equilibria could actually control magma \( f_O^2 \), if there is abundant free vapour present in the magma. For example, Matthews et al. (1994) suggest that the sulphide-sulphate gas-phase reaction

\[
\text{SO}_2 (g) + \text{H}_2\text{O} (g) = \text{H}_2\text{S} (g) + \frac{3}{2} \text{O}_2 (g)
\]  

buffered magma \( f_O^2 \) at Lascar Volcano, Chile, leading to more oxidised magmas (relative to the NNO-buffer) as temperature decreases. This mechanism would require relatively sulphur-rich gases to be present, although the gas-driven buffer could be very effective because of its rapid response and large valence change (Matthews et al. 1994). The pattern of increasing divergence from oxide buffers (e.g. \( \Delta \text{NNO} \)) with decreasing temperature, in a trend more parallel to the sulphide-sulphate buffer, is seen at several other volcanoes (figure 9a), including Augustine, USA (Roman et al. 2006), Shiveluch, Kamchatka (Humphreys et al. 2006), Quizapu, Chile (Ruprecht et al. 2012) and Pinatubo (Pallister et al. 1996). Data for Mount St Helens, USA as a whole lie parallel to NNO, but individual samples do not (Blundy et al. 2008), instead plotting parallel to the sulphide-sulphate buffer (figure 9a).

This suggests that sulphide-sulphate oxygen exchange between the gas and melt might be a common and effective oxygen buffering mechanism for shallowly stored magmas. However, the arrays of \( T-f_O^2 \) points from coexisting oxide compositions are also parallel to isopleths of constant \( \text{hm/ilm} \) (taken from Buddington & Lindsley 1964; figure 9b). Isopleths of constant \( \text{mt/üsp} \) in titanomagnetite are at a slightly steeper angle (figure 9b). Therefore, the oxide data could also be explained by increased temperature causing increasing \( \text{üp} \) content while \( \text{hm/ilm} \) remains constant. This is consistent with the slower diffusion rates in ilm-hm solid solution than in mt-üsp (Hammond & Taylor 1982). A simpler interpretation for these \( T-f_O^2 \) trends is therefore that late-stage heating has resulted in a diffusive increase in \( \text{üp} \)-content of titanomagnetites,
while adjustment of ilmenite compositions is kinetically inhibited. The increased
temperature could be due to release of latent heat of crystallisation (Blundy et al.
2006) or to mingling with hotter magmas (e.g. Devine et al. 2003; Ruprecht et al.
2012). This is consistent with compositional variations in oxides from Soufrière
Hills Volcano, Montserrat (figure 9b; data from Devine et al. 2003). Ilmenites are
uniform, while titanomagnetites have zoned rims with high TiO$_2$ due to magma
mixing (Devine et al. 2003). The apparent T-fO$_2$ data plot along hm-ilm isopleths
and lie parallel to the sulphide-sulphate buffer (figure 9b). Demonstrating fO$_2$
control by gas-melt equilibria such as [11] would require evidence of constant
melt redox ratios for the redox couple of interest, probably through analysis of
suites of melt inclusions.

Disequilibrium between crystals and melt is a ubiquitous feature of
shallow crustal arc magma storage: arc magmas typically comprise components
or sub-systems that may be only in equilibrium at certain points in the volcanic
system (e.g. Pichavant et al. 2007). For minerals, equilibration timescales are
poorly known but probably slow, except for Fe-Ti oxides, which may equilibrate
relatively quickly (i.e., < 5 years at 900 °C for complete equilibration of a 250 µm
oxide phenocryst, Freer & Hauptman 1978). This means that fO$_2$ calculated from
solid-melt equilibria involving homogeneous Fe-Ti oxide phenocrysts (± H$_2$O)
should be an accurate record (sensor) of stable magma storage conditions in the
shallow system. However, oxides will probably not provide a good record of
erlier or longer-term changes in fO$_2$ during fractionation, nor of late-stage
changes during magma ascent. Instead, more slowly equilibrating phenocrysts
such as pyroxene or hornblende, or oxides brought rapidly to the surface in
cumulate nodules, may be more useful as a record of longer term changes;
whereas melt redox couples will be needed to investigate variations immediately
prior to eruption.

SUMMARY
Direct measurement of coupled changes in melt Fe\textsuperscript{3+}/ΣFe and H\textsubscript{2}O content in partially hydrated and degassed experimental rhyolites confirms that significant changes in oxidation state can occur in response to changes in volatile content. During hydration, increases in aH\textsubscript{2}O produced strong melt oxidation. This suggests that ascent of H\textsubscript{2}O-undersaturated arc magmas from the deep crust could cause significant oxidation, depending on the timescales required for equilibration relative to magma storage times. During degassing, oxidation arises due to loss of H\textsubscript{2} together with H\textsubscript{2}O, consistent with theoretical modelling for H\textsubscript{2}O fluids. It is therefore possible that significant vertical variations in magma oxidation state may develop within the arc crust. During the fractionation, storage and ascent of natural arc magmas, the controls on fO\textsubscript{2} may be expected to vary depending on the nature and duration of magma storage, as well as kinetic factors and the timescales of observation and equilibration. The differing response times of possible oxygen buffers and/or fO\textsubscript{2} sensors (such as oxide pairs) need to be considered alongside the degree of attainment of equilibrium in the magma. It is clear that attaining a real understanding of the effects of magmatic degassing on oxidation state will probably require direct measurements of the concentrations and speciation of all major volatiles in the melt, as well as melt Fe\textsuperscript{3+}/ΣFe and the corresponding gas compositions. In this respect, melt structure and chemistry should be considered alongside variations of fO\textsubscript{2} relative to traditional buffers.

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**FIGURES**

Calibration lines for determining Fe$^{3+}$/ΣFe from XANES centroid energy (a) and $\text{H}_2\text{O}$ from $^1$H$^+$/$^{30}$Si$^+$ ion probe measurements (b). In (a) errors in Fe$^{3+}$/ΣFe are derived from Mossbauer spectroscopy (Cottrell et al. 2009) while uncertainties in centroid energy are equivalent to the fitting uncertainty. Data are presented as linear deviation of centroid energy from 7113.6 eV, to facilitate regression. Solid line: best fit linear regression. Dashed lines: fully propagated uncertainties at 80% confidence limits based on the linear regression. (b) Typical daily ion microprobe calibration curve for $^1$H$^+$/$^{30}$Si$^+$ vs $\text{H}_2\text{O}$ showing best fit linear regression (solid line) and upper and lower 95% confidence limits (dashed lines).
Uncertainties in H$_2$O are the errors on independently measured H$_2$O contents of the standard glasses.

Figure 2

a) Typical normalised, background-corrected XANES spectrum for rhyolite standard glass. Boxes show parts of the spectrum that show variations with oxidation state. b) The pre-edge region shows two peaks; the relative importance of the higher-energy peak increases with increasing Fe$^{3+}$/ΣFe. Each spectrum is offset by 0.02 on the y-axis. c) The energy of the main edge increases systematically with increasing Fe$^{3+}$/ΣFe (spectra are not offset). d) The energy of the peak and post-edge trough increases with Fe$^{3+}$/ΣFe, though higher energy resolution in this region is needed to use this feature quantitatively. Each spectrum is offset by 0.02 on the y-axis. NB. Where additional symbol markers are used, these represent every fifth data point.

Figure 3


Figure 4

a) Backscattered electron SEM images of representative glass chips from Mangan & Sisson (2000), in which heterogeneous bubble nucleation at the margins of the chips was dominant. Scale bar is 1mm. Lower greyscale intensity in the core indicates higher water contents, as demonstrated by the negative linear correlation between greyscale and H$_2$O (b). Degassing of H$_2$O is associated with
increasing Fe$^{3+}/\Sigma$Fe (c) and $fO_2$ relative to the Nickel-Nickel oxide buffer (d).

Errors in (c) relate to ~10% uncertainty in H$_2$O and 80% confidence limits for Fe$^{3+}/\Sigma$Fe. Note that the analytical precision is smaller than the size of the individual points. Modelled trends in (d) are theoretical predictions for degassing of S-free rhyolite following Burgisser et al. (2008), starting at different initial $fO_2$ and with no free fluid (0.1 wt% initial gas, red line) or with 10 wt% (green) or 20 wt% (black) initial fluid.

Figure 5

Backscattered electron SEM image showing variation of greyscale intensity related to inward diffusion of H$_2$O into the Lipari glass chips at high temperature (a), reproduced from Humphreys et al. (2008). (b) Co-variation of Fe$^{3+}/\Sigma$Fe with H$_2$O content and equivalent $fO_2$ variation relative to the NNO buffer. Representative error bars shown for sample LIPRF5.

Figure 6

Spatial variability of Fe$^{3+}/\Sigma$Fe (grey squares) and H$_2$O (black triangles) with distance from the margin of each chip hydrated at high temperature. Fe$^{3+}/\Sigma$Fe in the un-hydrated starting material is marked by a grey band in each figure. Horizontal error bars in (a) are the estimated maximum uncertainty on spatial location of each point. Errors in Fe$^{3+}/\Sigma$Fe and H$_2$O are reported in previous figures.

Figure 7

Variation of Fe$^{3+}/\Sigma$Fe and H$_2$O within experimentally hydrated glass chips (squares). Modelled variation of Fe$^{3+}/\Sigma$Fe based on changing water activity is shown by the bold lines (calculated from $XH_2O_m$) and dashed lines (calculated from $XH_2Ot$). Calculated variations for two different illustrative initial $fO_2$ conditions are shown (black and grey lines and labels).
Figure 8

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

Figure 9

Temperature-$fO_2$ variations in intermediate arc magmas (a). Different oxygen buffers are shown in bold black lines (constant sulphide-sulphate ratios) and grey dashed lines (NNO, NNO+1). Data points are from two-oxide equilibria. Data sources are Blundy et al (2008) for Mount St Helens, USA; Humphreys et al. (2006) for Shiveluch Volcano, Kamchatka; Roman et al. (2006) for Augustine, Aleutians; Crabtree & Lange (2012) for the Mexican arc; Murphy et al. (2000) for Soufriere Hills, Montserrat; Sparks et al. (2008) for Uturuncu Volcano, Bolivia; Pallister et al. (1996) for Mount Pinatubo, Philippines; and Matthews et al. (1994) for Lascar Volcano, Chile. The pale grey arrow shows the data trend from part (b), which also shows isopleths (thin grey lines) of constant hm-ilm and Usp-mt composition from Buddington & Lindsley (1969). Black circles in (b) are data on zoned magnetite grains from Soufrière Hills Volcano, Montserrat (from Devine et al. 2003) which plot along lines of constant hm-ilm and also lie parallel to the sulphide-sulphate buffer.
(a) Graph showing the relationship between $\Delta$ centroid energy (eV) and $\text{Fe}^{3+}/\Sigma\text{Fe}$. The data points are scattered around a line with the equation $y = 3.934x - 0.0357$, and $R^2 = 0.985$.

(b) Graph showing the relationship between $\text{wt}\%\text{H}_2\text{O}$ and $^{1}\text{H}^+/^{30}\text{Si}^+$. The data points follow the linear equation $y = 3.934x - 0.0357$, and $R^2 = 0.985$.
Figure 2

Fe$^{3+}$/$\Sigma$Fe = 0.806
Fe$^{3+}$/$\Sigma$Fe = 0.66
Fe$^{3+}$/$\Sigma$Fe = 0.63
Fe$^{3+}$/$\Sigma$Fe = 0.60
Fe$^{3+}$/$\Sigma$Fe = 0.32
Fe$^{3+}$/$\Sigma$Fe = 0.238
\[
\text{wt}\% \text{ H}_2\text{O} (\text{SIMS})
\]

\[
y = -0.40043x + 52.23817 \\
R^2 = 0.97115
\]

\[
y = -0.3735x + 49.366 \\
R^2 = 0.99997
\]

\[
\Delta \text{NNO}
\]

\[
\text{wt}\% \text{ H}_2\text{O}
\]

\[
\text{(SIMS)}
\]

\[
0.1\% - 10\% - 20\% - 0.1\%
\]

\[
\text{10\% - 20\% - 0.1\%}
\]
Figure 7

Fe$^{3+}/\Sigma$Fe vs. wt% H$_2$O

Botcharnikov et al. (2005)

Sample codes:
- LIPRF3
- LIPRF7
- LIPRF2
- LIPRF5

---

Fe$^{3+}/\Sigma$Fe vs. wt% H$_2$O
Magma ascent and degassing.
Fe$^{3+}$/ΣFe (m) controlled by gas-melt equilibria
\[ \text{e.g. } H_2O(m) + FeO(m) = Fe_2O_3(m) + H_2(g) \]
\pm closed-system groundmass xlln

Magma chamber storage.
fO$_2$ controlled by solid-melt and/or melt-gas buffers over variable timescales

Fe-Ti oxides equilibrate fast - a good record of stable magma storage conditions

Other mafic phases may record longer-term changes in fO$_2$?

H$_2$O-undersaturated magma ascent.
fO$_2$ increases with increasing XH$_2$O(m)

Closed-system fractionation.
fO$_2$ controlled by exchange of H$_2$ with country rocks?

Gas emissions.
fO$_2$ controlled by disequilibrium degassing; decoupling of magma/gas; mixing of gases from range of P

Figure 8
Figure 9
Table 1 - XANES fit components, calculated centroid and total intensity for rhyolite standards. Fe$^{3+}$/ΣFe values are from Mossbauer spectroscopy (Cottrell et al. 2009).

<table>
<thead>
<tr>
<th>Analysis number</th>
<th>Sample</th>
<th>Fe$^{2+}$ component</th>
<th>Fe$^{3+}$ component</th>
<th>Centroid, eV</th>
<th>Total intensity</th>
<th>Fe$^{3+}$/ΣFe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample</td>
<td>Fe$^{2+}$ peak location</td>
<td>Width</td>
<td>Intensity</td>
<td>Fe$^{3+}$ peak location</td>
<td>Width</td>
</tr>
<tr>
<td>8446</td>
<td>DT31</td>
<td>7113.03 ± 0.058</td>
<td>2.098 ± 0.081</td>
<td>0.059 ± 0.004</td>
<td>7114.51 ± 0.012</td>
<td>1.654 ± 0.015</td>
</tr>
<tr>
<td>8447</td>
<td>DT18</td>
<td>7113.90 ± 0.038</td>
<td>2.940 ± 0.044</td>
<td>0.141 ± 0.007</td>
<td>7114.52 ± 0.004</td>
<td>1.429 ± 0.013</td>
</tr>
<tr>
<td>8448</td>
<td>568_2</td>
<td>7112.81 ± 0.019</td>
<td>1.852 ± 0.033</td>
<td>0.060 ± 0.002</td>
<td>7114.47 ± 0.011</td>
<td>1.622 ± 0.020</td>
</tr>
<tr>
<td>8450</td>
<td>DT29</td>
<td>7113.97 ± 0.028</td>
<td>2.741 ± 0.034</td>
<td>0.131 ± 0.004</td>
<td>7114.53 ± 0.005</td>
<td>1.448 ± 0.016</td>
</tr>
<tr>
<td>8492</td>
<td>DT39</td>
<td>7112.91 ± 0.024</td>
<td>1.953 ± 0.039</td>
<td>0.073 ± 0.002</td>
<td>7114.50 ± 0.009</td>
<td>1.571 ± 0.016</td>
</tr>
<tr>
<td>8494</td>
<td>DT46</td>
<td>7113.03 ± 0.039</td>
<td>2.049 ± 0.059</td>
<td>0.069 ± 0.004</td>
<td>7114.50 ± 0.009</td>
<td>1.554 ± 0.012</td>
</tr>
</tbody>
</table>
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)

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>P, MPa</th>
<th>T °C</th>
<th>Run time (min)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIPRF2</td>
<td>200</td>
<td>857</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>LIPRF3</td>
<td>200</td>
<td>859</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>LIPRF5</td>
<td>150</td>
<td>899</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>LIPRF7</td>
<td>150</td>
<td>901</td>
<td>20</td>
<td></td>
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</tbody>
</table>
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

<table>
<thead>
<tr>
<th></th>
<th>Panum dome (Mangan &amp; Sisson 2000)</th>
<th>Lipari obsidian (Humphreys et al. 2008)</th>
<th>Napa Valley Glass Mountain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starting material</td>
<td>Avg run products (anhydrous)</td>
<td>1 sigma</td>
</tr>
<tr>
<td>SiO₂</td>
<td>75.64</td>
<td>76.94</td>
<td>0.52</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.38</td>
<td>12.56</td>
<td>1.05</td>
</tr>
<tr>
<td>FeO</td>
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<td>0.13</td>
</tr>
<tr>
<td>Na₂O</td>
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<td>3.79</td>
<td>0.53</td>
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<tr>
<td>K₂O</td>
<td>4.72</td>
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<td>0.59</td>
</tr>
<tr>
<td>Cl</td>
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<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>F</td>
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<td>0.18</td>
<td>0.23</td>
</tr>
<tr>
<td>H₂O</td>
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</tr>
<tr>
<td>Total</td>
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<td>99.99</td>
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</tr>
<tr>
<td>n</td>
<td>33</td>
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<td></td>
</tr>
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</table>
Table 4 - XANES fit components, calculated centroid and total intensity, and calculated Fe$^{3+}$/ΣFe for the high-T decompression samples. H$_2$O contents are measured from SIMS. Δ NNO is calculated for 900 °C.
<table>
<thead>
<tr>
<th>Analysis number</th>
<th>Sample</th>
<th>Fe(^{2+}) component</th>
<th>Fe(^{3+}) component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe(^{2+}) peak location</td>
<td>± Width ± Intensity ±</td>
</tr>
<tr>
<td>7272</td>
<td>LIRPF5-1</td>
<td>7112.83 0.0285 1.7839 0.0494 0.0416 0.0020</td>
<td>7144.55 0.0078 1.722 0.013 0.139 0.002</td>
</tr>
<tr>
<td>7273</td>
<td>LIRPF5-2</td>
<td>7112.87 0.0303 1.8349 0.0521 0.0479 0.0023</td>
<td>7144.57 0.0099 1.687 0.017 0.120 0.002</td>
</tr>
<tr>
<td>7274</td>
<td>LIRPF5-3</td>
<td>7112.85 0.0259 1.8216 0.0454 0.0498 0.0021</td>
<td>7144.57 0.0094 1.696 0.017 0.113 0.002</td>
</tr>
<tr>
<td>7275</td>
<td>LIRPF5-4</td>
<td>7112.8 0.0207 1.7912 0.0363 0.0510 0.0018</td>
<td>7144.53 0.0083 1.714 0.016 0.111 0.002</td>
</tr>
<tr>
<td>7276</td>
<td>LIRPF5-5</td>
<td>7112.81 0.0209 1.8227 0.0372 0.0515 0.0019</td>
<td>7144.54 0.0091 1.694 0.018 0.104 0.002</td>
</tr>
<tr>
<td>7277</td>
<td>LIRPF5-6</td>
<td>7112.82 0.0187 1.7890 0.0329 0.0572 0.0018</td>
<td>7144.55 0.0093 1.698 0.020 0.096 0.002</td>
</tr>
<tr>
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<td>LIRPF5-7</td>
<td>7112.85 0.0170 1.8093 0.0308 0.0673 0.0019</td>
<td>7144.56 0.0119 1.632 0.025 0.073 0.002</td>
</tr>
<tr>
<td>7279</td>
<td>LIRPF5-8</td>
<td>7112.8 0.0144 1.7891 0.0255 0.0701 0.0016</td>
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</tr>
<tr>
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<td>LIRPF5-9</td>
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<tr>
<td>7281</td>
<td>LIRPF7-1</td>
<td>7112.82 0.0365 1.8057 0.0625 0.0437 0.0026</td>
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<tr>
<td>7282</td>
<td>LIRPF7-2</td>
<td>7112.81 0.0277 1.8060 0.0480 0.0480 0.0022</td>
<td>7144.54 0.0099 1.724 0.018 0.118 0.002</td>
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<tr>
<td>7283</td>
<td>LIRPF7-3</td>
<td>7112.8 0.0230 1.8522 0.0404 0.0519 0.0019</td>
<td>7144.54 0.0086 1.716 0.015 0.115 0.002</td>
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<tr>
<td>7284</td>
<td>LIRPF7-4</td>
<td>7112.84 0.0211 1.8496 0.0371 0.0572 0.0019</td>
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</tr>
<tr>
<td>7285</td>
<td>LIRPF7-5</td>
<td>7112.87 0.0150 1.8345 0.0271 0.0686 0.0017</td>
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</tr>
<tr>
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<td>LIRPF7-6</td>
<td>7112.84 0.0171 1.8011 0.0301 0.0649 0.0018</td>
<td>7144.56 0.0108 1.664 0.024 0.080 0.002</td>
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<tr>
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<td>LIRPF2-1</td>
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<td>7144.51 0.0087 1.787 0.018 0.111 0.002</td>
</tr>
<tr>
<td>4662</td>
<td>LIRPF2-2</td>
<td>7112.84 0.0327 1.8514 0.0556 0.0472 0.0025</td>
<td>7144.57 0.0120 1.737 0.021 0.108 0.002</td>
</tr>
<tr>
<td>4663</td>
<td>LIRPF2-3</td>
<td>7112.83 0.0240 1.8290 0.0419 0.0502 0.0020</td>
<td>7144.57 0.0094 1.723 0.018 0.107 0.002</td>
</tr>
<tr>
<td>4664</td>
<td>LIRPF2-4</td>
<td>7112.78 0.0213 1.8283 0.0369 0.0537 0.0018</td>
<td>7144.52 0.0093 1.728 0.019 0.102 0.002</td>
</tr>
<tr>
<td>4670</td>
<td>LIRPF2-5</td>
<td>7112.84 0.0248 1.8271 0.0434 0.0582 0.0023</td>
<td>7144.57 0.0126 1.690 0.026 0.091 0.003</td>
</tr>
<tr>
<td>4665</td>
<td>LIRPF2-6</td>
<td>7112.76 0.0176 1.7885 0.0314 0.0628 0.0018</td>
<td>7144.49 0.0117 1.668 0.026 0.076 0.002</td>
</tr>
<tr>
<td></td>
<td>LIPRF2-7</td>
<td>LIPRF2-8</td>
<td>LIPRF2-9</td>
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<td>------</td>
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<td>1.7353</td>
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<tr>
<td>7287</td>
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<td>0.0155</td>
<td>1.7998</td>
</tr>
</tbody>
</table>

Table 5 - XANES fit components, calculated centroid and total intensity, and calculated Fe$^{3+}$/ΣFe for the high-T hydration samples. H$_2$O contents are measured from SIMS.
| Analysis number | XANES analysis | SIMS analysis | Distance (microns) | \( \text{Fe}^{2+} \) component | | \( \text{Fe}^{3+} \) component | | | | \( \text{Fe}^{2+} \) peak location | Width | Intensity | \( \text{Fe}^{3+} \) peak location | Width | Intensity | Centroid, eV | Total intensity | \( \text{H}_2\text{O} \) wt% (SIMS) | \( \text{H}_2\text{O} \) wt% (greyscale) |
|-----------------|----------------|---------------|-------------------|------------------|---|------------------|---|------------------|---|------------------|-----------------|------------------|-------------------|-------------------|
| 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, NVGM_3 | -279, -64     | 50, 10            | 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              |
| 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              |
| 8483            | NVGM_4, NVGM_5 | -35, 55       | 10, 10            | 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              |
| 8484            | NVGM_6         | -80           | 25                | 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         | 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_8, 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            | NVGM_9         | -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            | NVGM_10        | -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_11        | 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_12        | 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 \( \text{Fe}^{3+}/\Sigma\text{Fe} \) for the low-T hydration samples. H\( \text{2O} \) 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).