No effect of H₂O degassing on the oxidation state of magmatic liquids

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Abstract. The underlying cause for why subduction-zone magmas are systematically more oxidized than those formed at mid-ocean spreading ridges is a topic of vigorous debate. It is either a primary feature inherited from the subduction of oxidized oceanic crust into the mantle or a secondary feature that develops because of H₂O degassing and/or magma differentiation. Low total iron contents and high melt H₂O contents render rhyolites sensitive to any effect of H₂O degassing on ferric-ferrous ratios. Here, pre-eruptive magmatic Fe²⁺ concentrations, measured using Fe-Ti oxides that co-crystallized with silicate phenocrysts under hydrous conditions, are compared with Fe²⁺ post-eruptive concentrations in ten crystal-poor, fully-degassed obsidian samples; five are microlite free. No effect of H₂O degassing on the ferric-ferrous ratio is found. In addition, Fe-Ti oxide data from this study and the literature show that arc magmas are systematically more oxidized than both basalts and hydrous silicic melts from Iceland and Yellowstone prior to extensive degassing. Nor is there any evidence that differentiation (i.e., crystal fractionation, crustal assimilation) is the cause of the higher redox state of arc magmas relative to those of Iceland/Yellowstone rhyolites. Instead, the evidence points to subduction of oxidized crust and the release of an H₂O-rich fluid and/or melt with a

high oxygen fugacity (fO_2), which plays a role during H_2O -flux melting of the mantle in creating basalts that are relatively oxidized.

1. Introduction

A detailed understanding of how degassing of a multicomponent (H-C-S-O-Cl) fluid can change the redox state of a host magma (e.g., Mathez, 1984; Candela, 1986; Burgisser and Scaillet, 2007; Bell and Simon, 2011; Moussallam et al., 2014; Humphreys et al., 2015; Gaillard et al., 2011) is required to address several outstanding questions, including the origin of various ore deposits (e.g., Candela, 1986; Bell and Simon, 2011), the secular evolution of Earth's atmosphere (e.g., Gaillard et al., 2011), and the underlying cause for why subduction-zone magmas are systematically more oxidized than hot-spot magmas (e.g., Iceland/Yellowstone) and mid-ocean spreading ridge basalts (e.g., Carmichael, 1991). The last issue is controversial, with micro-XANES analyses of Fe^{3+}/Fe^T in olivine-hosted melt inclusions indicating that subduction-zone basalts inherit their high oxidation at the time of formation in the mantle (e.g., Kelley and Cottrell, 2009; Brounce et al., 2014; Brounce et al., 2015), most likely from the subduction of oxidized crust (e.g., Carmichael, 1991; Kelley and Cottrell, 2009; Brounce et al., 2015), whereas other studies, based on Zn/Fe and V/Sc ratios, show that the oxygen fugacity (fO_2) of the mantle beneath mid-ocean spreading ridges and subduction zones is uniform (Lee et al., 2010; Mallman and O'Neil, 2009) and that the higher oxidation state of subduction-zone magmas develops later, possibly through volatile degassing, crustal assimilation and/or crystal fractionation (e.g., Lee et al., 2010).

Isolating and understanding the effect of H_2O degassing, independent of other volatile components, on the oxidation state of host melts is critically important because H_2O is the most abundant volatile in subduction-zone magmas and is frequently invoked as the key component

driving melt oxidation during degassing (e.g., Candela, 1986; Burgisser and Scaillet, 2007; Humphreys et al., 2015). Although degassing of other volatile components (i.e., sulfur and/or chlorine) has been demonstrated to change the redox state of melts in some circumstances (e.g., Bell and Simon, 2011; Moussallam et al., 2014), it is necessary to first quantify the magnitude of the effect of H₂O degassing before the relative importance of other volatile degassing on driving a change in melt redox can be fully evaluated.

In this study, we review why degassing of H₂O has been proposed to cause an increase in the oxidation state of magmas. Next, we directly test this hypothesis by comparing the oxidation state of several rhyolitic magmas at depth, which contained high water and low sulfur and chlorine melt concentrations, with analyzed ferric-ferrous ratios in the same samples after degassing and eruption as obsidian. To perform this test, four different types of data were obtained for this study.

First, we document the oxygen fugacities and temperatures recorded by Fe-Ti oxides that co-crystallized with silicate phenocrysts in ten different rhyolitic magmas that erupted as obsidian. The occurrence of titanomagnetite and ilmenite as mineral inclusions in silicate phenocrysts shows that the Fe-Ti oxides are early, near-liquidus phases. Second, we compare the oxidation state recorded by the Fe-Ti oxides with analyzed ferric-ferrous ratios in the obsidian samples. Third, we calculate the maximum sulfur and chlorine contents in the rhyolitic melts prior to degassing, and we use plagioclase-liquid hygrometry to calculate melt water contents during phenocryst growth. Fourth, we test whether the obsidian samples are fully degassed of H₂O, sulfur, and chlorine by direct analysis.

We use the experimental literature to examine the kinetics of whether the ferric-ferrous ratios in rhyolitic melts have sufficient time to re-equilibrate during H₂O degassing upon ascent,

if H₂O degassing drives an increase in oxidation state. In other words, do analyzed ferric-ferrous ratios in erupted obsidian samples accurately record any redox change induced by H₂O degassing during ascent? We additionally examine the kinetics of whether the titanomagnetite and ilmenite mineral phases have slower equilibration times compared to melt ferric-ferrous ratios. In other words, can Fe-Ti oxide minerals preserve the temperature and fO₂ conditions of phenocryst growth at depth during the time interval for magma ascent?

Next, we combine the results from this study with those from the literature to compare the oxidation states recorded by Fe-Ti oxides in erupted magmas from two distinctly different tectonic settings: (1) active subduction zones and (2) Iceland/Yellowstone. We examine whether the Fe-Ti oxides in magmas from these separate tectonic settings record a systematic difference in oxidation state prior to extensive H₂O degassing. We further explore whether there is any difference in the oxidation state recorded by Fe-Ti oxides between effusive and explosive eruptions, which provides an additional test of whether re-equilibration of Fe-Ti oxides occurred during the slower ascent associated with effusive eruptions vs. the extremely rapid ascent of explosive eruptions. Finally, we examine whether the oxidation state recorded by Fe-Ti oxides in rhyolites from these distinctly different tectonic settings is consistent with the occurrence of fayalite vs. orthopyroxene as a co-existing phenocryst, which Carmichael (1967; 1991) showed is dependent on oxidation state. This provides an additional test of whether the Fe-Ti oxides in effusively erupted magmas, like the obsidian samples in this study, preserve the redox conditions at the time of phenocryst growth.

2. Previous Work: Does Degassing of H₂O Drive Melt Oxidation?

There are two proposed reasons for why degassing of the dissolved H₂O component may increase the oxidation state of a melt. The first is that degassing of dissolved H₂O in a melt leads to a fluid phase in which the H₂O component partially dissociates to form both H₂ and O₂:

For this homogeneous reaction, the equilibrium constant is defined as:

$$K = \frac{f_{\text{H}_2} f_{\text{O}_2}^{1/2}}{f_{\text{H}_2\text{O}}} \quad (2)$$

Therefore, at fixed temperature, pressure, and fH₂O, the lower the fO₂ at the time of H₂O degassing, the higher the fH₂, and the more H₂ will form in the fluid phase. This has led to the proposal that degassing of dissolved H₂O (H⁺) to form a fluid phase containing H₂ (H⁰), may increase the melt Fe³⁺/Fe²⁺ ratio (e.g., Candela, 1986; Burgisser and Scaillet, 2007; Humphreys et al., 2015):

An example of this reaction was demonstrated in a series of *disequilibrium* experiments (by design) on hydrous melts held in metal capsules, where a large difference in both fH₂O and fH₂ was introduced across the capsule wall (Humphreys et al., 2015). In these experiments, the fH₂O inside a sealed platinum metal capsule that contained an H₂O fluid-saturated melt was significantly higher than the fH₂O in an atmosphere of pure argon gas on the outside of the capsule. This experimental design creates a strong contrast in fH₂O, and therefore fH₂ (Eq. 2), across the platinum capsule wall. Because platinum metal is permeable only to H₂, selective migration of H₂ out of the melt through the capsule wall leads to melt oxidation (Eq. 3).

However, caution is required before applying the results from this experimental design to natural melts, because imposed gradients in fH₂O and fH₂ across platinum capsule walls, and the

selective migration of H₂ through metal capsules, are not representative of conditions along the bubble-melt interface in natural magmatic melts undergoing equilibrium degassing of H₂O. Whether or not H₂O degassing occurs through equilibrium or disequilibrium processes that impact melt fO₂ is debated in the literature (e.g., Humphreys et al., 2015; Brounce et al., 2014; Crabtree and Lange, 2012).

The second reason why degassing of dissolved H₂O may affect the melt Fe³⁺/Fe²⁺ ratio is through possible effects on the activities of FeO and Fe₂O₃ in the melt:

For this homogeneous reaction, the equilibrium constant is defined as:

$$\ln K = 0.25 \ln f\text{O}_2 + \ln(X_{\text{FeO}_{1.5}}/X_{\text{FeO}}) + \ln(\gamma_{\text{FeO}_{1.5}}/\gamma_{\text{FeO}}) \quad (5)$$

At fixed temperature, pressure, and fO₂, if dissolved H₂O strongly affects the activity coefficient ratio, $\gamma_{\text{FeO}_{1.5}}/\gamma_{\text{FeO}}$, in Eq. (5), then the loss of dissolved H₂O through degassing is expected to change the Fe³⁺/Fe²⁺ ratio in the melt.

There are several published models for iron-bearing silicate melts based on Eq. 5 that relate melt ferric-ferrous ratio to temperature, fO₂, and melt composition; some are calibrated only on natural melts (e.g., Kress and Carmichael, 1991), some only on synthetic four-component melts (e.g., Tangeman et al., 2001), and some on both natural and synthetic melts (Moretti, 2005). Models calibrated on both natural and synthetic melts are necessarily the most complex, owing to the markedly different iron redox behavior between different synthetic melts (e.g., Tangeman et al., 2001), as well as compared to natural melts. In contrast, models calibrated only on natural liquids are the simplest:

$$\ln(X_{\text{Fe}_2\text{O}_3}/X_{\text{FeO}}) = a \ln f\text{O}_2 + b/T + c + \sum X_i d_i \quad (6)$$

where a , b , and d_i are fitted coefficients, T is temperature in K, and X_i is the mole fraction of oxide components in the melt.

A widely used calibration of Eq. 6 (Kress and Carmichael, 1991), which closely recovers the measured wt% FeO of all 47 metaluminous andesite, dacite and rhyolite experimental liquids at 1 bar from six studies (Fudali, 1965; Kilinc et al., 1983; Sack et al., 1980; Thornber et al., 1980; Kress and Carmichael, 1988; Moore et al., 1995) (Fig. 1; Supplementary Table S1), does not include any compositional effect of dissolved H₂O on the melt ferric-ferrous ratio. Relative to this model, at least seven experimental studies have examined the effect of dissolved water on the ferric-ferrous ratio in natural melts. Three studies show no effect of dissolved water (Moore et al., 1995; Botcharnikov et al., 2005; Sisson and Grove, 1993), two other studies show that dissolved water increases the melt Fe³⁺/Fe²⁺ ratio (Gaillard et al., 2002, 2003), and a sixth study shows the opposite effect (Wilke et al., 2002). The seventh study shows no effect of dissolved water on the iron redox ratio at 3-9 wt% H₂O in the melt, but a small decrease in melt Fe³⁺/Fe²⁺ at 1-2 wt% H₂O and a small increase in melt Fe³⁺/Fe²⁺ at 10-11 wt% H₂O (Schuessler et al., 2008).

Although the experimental literature presents a conflicting view of whether degassing of H₂O can drive redox change, and in which direction, there is evidence from analyses of natural basalts, andesites and dacites that no detectable change occurs. For example, a detailed micro-XANES study of Fe³⁺/Fe^T ratios in olivine-hosted melt inclusions from Mariana arc basalts shows no systematic change with extent of H₂O degassing (Kelley and Cottrell, 2009; Kelley and Cottrell, 2012; Brounce et al., 2014). Similarly, a comparison of pre-eruptive (magmatic) Fe²⁺ concentrations in hydrous andesite and dacite magmas during phenocryst growth, on the basis of two Fe-Ti oxide oxygen barometry, with analyses of post-eruptive Fe²⁺ concentrations after

degassing shows no detectable change (Crabtree and Lange, 2012; Grocke et al., 2016). An outstanding question, however, is whether there are compensating effects that may explain these results on basalts through dacites, such as concomitant degassing of dissolved sulfide (Moussallam et al., 2014) and/or the relatively high iron contents of mafic melts rendering them more robust than rhyolitic melts to changes in $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios during H_2O degassing.

The goal of this study, therefore, is to test whether H_2O degassing changes the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in natural rhyolites (erupted as obsidian) by comparing magmatic Fe^{2+} concentrations obtained from Fe-Ti oxide pairs with post-eruptive Fe^{2+} concentrations analyzed directly on the fully degassed obsidian samples. The low total iron contents of rhyolites render them highly sensitive to changes in $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios during H_2O degassing.

3. Strategy

3.1 Choice of samples and consideration of kinetic effects

The ten metaluminous obsidian samples used in this study are fresh (Fig. S1) and phenocryst-poor (<6%), and are from the southern Cascades arc (MLV-36, -37, -44, -45, CAM-49), the western Mexican arc (COMP-3, JAL-10, TEQ-21) and the Long Valley caldera, California (post-caldera Early Rhyolites of Bailey et al., 1976) in the Basin and Range province (PCR-R3, -7). Crystal-poor ($\leq 6\%$; Table 1), jet-black, vesicle-free obsidian samples were specifically chosen for the absence of any post-eruptive alteration and/or hydration. Full petrological descriptions of a subset of these obsidian samples have been previously published in Waters and Lange (2013) and Waters et al. (2015). All samples are multiply saturated with plagioclase + orthopyroxene + titanomagnetite + ilmenite + apatite $\pm$ zircon $\pm$ pyrrhotite and some contain either hornblende or biotite as an accessory hydrous mineral (Table 1). Both titanomagnetite and ilmenite are near-liquidus phases in metaluminous rhyolites (Carmichael,

1967a), which is consistent with their occurrence in these ten samples as mineral inclusions in sparse plagioclase and orthopyroxene phenocrysts (e.g., Waters and Lange, 2013). Reflected light microscopy was used to ensure that only single-phase grains of titanomagnetite and ilmenite occur in each sample. No examples of exsolved Fe-Ti oxide phases were found.

Five of the ten obsidian samples (MLV-36, -44, TEQ-21, PCR-R3, -7) are devoid of plagioclase microlites, which constrains the time interval of their ascent to the surface. A series of decompression experiments (Waters et al., 2015) showed that the suppression of groundmass crystallization of plagioclase, leading to a microlite-free obsidian, requires a relatively rapid ascent, on the order of a few days or less (< 1 week). This is expected to be sufficient time for complete H_2O degassing (e.g., Larsen et al., 2004), which is tested in this study by direct analysis of H_2O contents in the erupted obsidian samples.

If degassing of H_2O during magma ascent results in an increase in the oxygen fugacity of the melt, an outstanding question is whether or not melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios have time to fully re-equilibrate. Kinetic experiments conducted by Gaillard et al. (2002) on a hydrous rhyolite at 800°C show that melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios re-equilibrate within hours (~ 2 hours per 1 log unit change in $f\text{O}_2$). Thus any changes in melt $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, as a consequence of H_2O degassing during an ascent on the order of 1 day or longer, should be detected by direct analysis of the erupted obsidian glasses.

A related question is whether the Fe-Ti oxide mineral phases also have time to re-equilibrate during magma ascent, or if their compositions at the time of phenocryst growth are preserved. This question is addressed by examining the experimental results of Venesky and Rutherford (1999) on the Yn dacite pumice from Mount St. Helens, which contains a narrow compositional range of titanomagnetite and ilmenite, yielding an average temperature of $\sim 800 \pm$

10 °C and a ΔNNO value of +2.0. After holding the Yn dacite at a temperature and redox condition colder and more oxidizing than the natural sample (750 °C and ΔNNO +2.5) for 120 h (~5 days) at $P_{\text{H}_2\text{O}} = 250$ MPa, they report that the titanomagnetites and ilmenites changed little in composition, whereas similar experiments at these conditions held for 220 h (~9 days) resulted in extensive re-equilibration of the Fe-Ti oxide compositions. However, even after 9 days at 750°C, there remained a small subset of Fe-Ti oxides that had compositions that recorded temperatures within 5-10 degrees of the initial starting material as well as nearly identical ΔNNO values.

The experimental results of Venezky and Rutherford (1999) are consistent with those of Lattard et al. (2005), where two-step re-equilibration experiments on coexisting titanomagnetite + ilmenite crystals at two final temperatures (1300 and 1100 °C) were performed at 1 bar. These re-equilibration temperatures are considerably hotter than those of rhyolitic magmas, which commonly record temperatures of 700-1000°C. Lattard et al. (2005) report results for two experiments with final temperatures of 1100 °C where the ΔNNO value of the initial equilibration condition was changed by 0.4 and 2.0 log units, and the samples were then held for 6 and 9 days, respectively, in order to attain equilibrium.

On the basis of the experimental results from Venezky and Rutherford (1999) and Lattard et al. (2005), it is concluded if the obsidian samples from this study ascended and degassed in less than nine days, a small subset of their Fe-Ti oxide crystals should preserve the temperature and $f\text{O}_2$ conditions at the time of their initial growth. Moreover, for the microlite-free obsidian samples in this study, which are constrained to have ascended over a time scale of a few days or less, it is expected that most of their Fe-Ti oxides will preserve their initial compositions at the time of co-crystallization with silicate phenocrysts. The experimental results underscore the

importance of analyzing as many Fe-Ti oxide crystals as possible in each obsidian sample, and using all possible pairs of analyzed ilmenite and titanomagnetite crystals to calculate the full range of temperature and ΔNNO values recorded by the entire population of Fe-Ti oxides. This will enable the full range of wt% FeO values in the melt to be calculated for each sample, derived from all possible Fe-Ti oxide pairs.

3.2 Consideration of pressure effects

Calibration of the Fe-Ti oxide oxybarometer of Ghiorso and Evans (2008) was based on experiments performed at different $f\text{O}_2$, temperature and pressure conditions (e.g., Lattard et al., 2005; Evans et al., 2006). The model of Ghiorso and Evans (2008) reports $f\text{O}_2$ results relative to the Ni-NiO buffer, as ΔNNO values. At one bar, the temperature dependence of how $f\text{O}_2$ varies along the Ni-NiO buffer is nearly identical to the temperature dependence of $f\text{O}_2$ in natural melts at constant ferric-ferrous ratios, rendering ΔNNO values nearly temperature independent (e.g., Kress and Carmichael, 1988). An evaluation of the pressure dependence of magmatic liquid ΔNNO values is made by comparing the volume and compressibility of the FeO and Fe_2O_3 components in a magmatic melt relative to those of crystalline Ni and NiO. On the basis of density and sound speed measurements, Kress and Carmichael (1991) showed that the effect of increasing pressure up to 300 MPa will lead to a change in the magmatic ΔNNO value of ≤ 0.2 log units. For the ten obsidian samples in this study, this magnitude change in ΔNNO will lead to a change in the calculated wt% FeO of 0.01 and 0.03 wt% FeO, respectively, for Fe-Ti oxide crystallization at 100 and 300 MPa, respectively. This effect on the wt% FeO values is smaller than the analytical uncertainty on their measurement (Table 2).

4. Methods and Results

4.1 Magmatic (pre-eruptive) wt% FeO in obsidian melts

Whole-rock compositional analyses for the ten samples were obtained by ICP-MS, using lithium metaborate/tetraborate fusion at Activation Laboratories, Ontario. The obsidians range from 73-75 wt% SiO₂ and 1.2-2.1 wt% FeO^T (Table 1). The uncertainty on the measurement of wt% FeO^T is evaluated through the recovery of standards via ICP-MS analysis. The total concentration of iron (as wt% Fe₂O₃^T) in the standards measured during acquisition of the whole-rock analyses (DNC-1, GBW-07113, W-2a, SY-4, BIR-1a) were all recovered within ≤0.14 wt% (absolute) of the certified values. The analyzed total iron content of the standard with a rhyolitic composition (GBW-07113) deviated from the certified value by 0.04 wt%.

Crystals of titanomagnetite (6-305 μm) and ilmenite (6-250 μm) were analyzed using the CAMECA SX-100 electron microprobe at the University of Michigan, with an accelerating voltage of 15 kV and a beam current of 15 nA. All analyses of titanomagnetite and ilmenite in each sample are presented in Supplementary Tables S2A&B. No exsolution lamellae were observed in any Fe-Ti oxide grains in the obsidian samples. All possible pairings of ilmenite and titanomagnetite were evaluated for equilibrium using the Mg/Mn test (Bacon and Hirschmann, 1988; see Supplementary Material). All possible pairs of ilmenite and titanomagnetite in each sample were used to calculate ΔNNO and temperature, using two Fe-Ti oxides (Ghiorso and Evans, 2008). Average temperatures for the ten samples range from 780-939 °C and average ΔNNO values range from -0.9 to +1.4 (Table 2; Fig. 2).

With temperature and fO₂ known from the Fe-Ti oxides, together with melt composition, the magmatic Fe²⁺ concentration (wt% FeO) in each melt was calculated using Eq. (6), the calibrated model of Kress and Carmichael (1991). An assessment of the accuracy of the Ghiorso and Evans (2008) oxy-barometer is made by evaluating how well it recovers the experimental

data on which it is calibrated (e.g., Lattard et al., 2005; Evans et al., 2006), over the ΔNNO range in Fig. 2, and leads to an uncertainty in ΔNNO of ± 0.25 (see Supplemental Material for a detailed discussion). The uncertainty in ΔNNO propagates through the Kress and Carmichael (1991) model to produce an uncertainty of $\pm \leq 0.04$ wt% FeO for all samples. Analytical uncertainties from microprobe analyses of the Fe-Ti oxides lead to propagated uncertainties of < 0.005 wt% FeO and can be neglected. Analytical uncertainties in the whole rock compositions, for use in the Kress and Carmichael (1991) model equation, lead to an uncertainty of ≤ 0.1 wt% FeO, which is largely derived from the total iron analysis; all other uncertainties in the other oxide component analyses contribute a combined propagated uncertainty of < 0.01 wt% FeO. The total uncertainty in wt% FeO from all sources outlined above is $\leq \pm 0.14$ wt% (Table 2).

The full variation in wt% FeO on the basis all possible pairs of analyzed ilmenite and titanomagnetite in each obsidian sample is plotted as a histogram in Fig. 3. Note that there is little difference in the average and 2-sigma variation in wt% FeO between those obtained from all possible pairs and those that fall within the Bacon and Hirschmann (1988) criteria only. The 2-sigma deviations in wt% FeO shown in Fig. 3, which are derived from the compositional variation among the Fe-Ti oxides in each sample and are not due to analytical errors, are listed in Table 2. These variations (± 0.01 - 0.03 wt% FeO) are always smaller than the propagated analytical uncertainties ($\leq \pm 0.14$ wt% FeO). Also shown in Fig. 3 are the highest values of wt% FeO obtained in each sample.

4.2 Post-eruptive wt% FeO in obsidian samples

The back-titration method of Wilson (1960) was used to measure the Fe^{2+} concentration (wt% FeO) in each obsidian sample. Three to four replications of this measurement were made on each sample, and the average results are presented in Table 2, and the results of individual

titrations are presented in Supplementary Table-S3. This method was tested against four certified standards (USGS standards: BIR-1a, W-2 and QLO-1; Canadian GS standard: SY-4), with three to six replications per standard (Table 2; Supplementary Table-S3). The recovery of wt% FeO on the four certified standards is ≤ 0.10 wt% and the reproducibility is ≤ 0.20 wt%. The Wilson titration method was directly compared to the Wilson colorimetric method in Crabtree and Lange (2012), and both methods give accurate results for four certified standards. The Wilson colorimetric method was used on experimental glasses to calibrate the model of Kress and Carmichael (1991).

4.3 Magmatic (pre-eruptive) wt% H₂O in obsidian melts

Pre-eruptive (magmatic) H₂O contents were determined in each sample with the updated plagioclase-liquid hygrometer model (Waters and Lange, 2015), which is calibrated on a dataset of 214 plagioclase-liquid pairs from water-saturated and anhydrous experiments and can be applied to rhyolites. To apply the plagioclase-liquid hygrometer, temperature must be known and is obtained from the average from all possible pairs of ilmenite and titanomagnetite in each sample (Table 2, Fig. 2). The whole rock composition (Table 1) was used as the liquid composition because of the low overall crystal content (<6%). The most calcic plagioclase phenocryst composition in each sample (Table 1) was used to calculate the melt H₂O concentration at the onset of plagioclase crystallization.

Analyses of plagioclase compositions (for crystals >50 microns) in a subset of the obsidian samples (MLV-36, MLV-37, MLV-45, TEQ-21, JAL-10, COMP-3) are provided in Waters and Lange (2013). For the remaining four samples, plagioclase compositions were measured using the Cameca SX-100 electron microprobe with an accelerating voltage of 15 kV and a beam current of 4 nA. For each sample, the range of plagioclase compositions is shown as

a histogram in Fig. 4, along with the results of the hygrometer. Melt water contents at the onset of plagioclase crystallization range from 1.2 to 6.5 wt% H₂O (Fig. 4, Table 1).

4.4 Post-eruptive wt% H₂O in obsidian samples

Measurements of post-eruptive H₂O contents in the obsidian glasses were made with a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer at the National Museum of Natural History, Washington D.C. Five spectra of groundmass glasses were collected from doubly polished wafers of each of the 10 obsidian samples. In all cases, the only measurable absorption band was 3570 cm⁻¹, due to low water contents. Spectral peak heights (Supplemental Material Table S4) were converted to total water contents using a molar absorptivity of 80 L mol⁻¹ cm⁻¹ (Leschik et al., 2004; Liu et al., 2005). Total water contents obtained for the glasses range from 0.05 to 0.12 wt% (Table 1). The low water contents measured by FTIR analysis illustrate that nearly complete degassing of these obsidian samples occurred over magma ascent time scales on the order of days. This result is consistent with a time scale for H₂O exsolution of ≤ 1 min for melts with viscosities ≤ 10⁸ Pa s (e.g., Larsen et al. 2004) and the efficiency of shear-induced bubble coalescence during magma ascent (e.g., Okumura et al., 2006).

4.5 Magmatic and post-eruptive concentrations of sulfur and chlorine

To evaluate any effect of degassing of sulfur or chlorine on the redox state of the ten obsidian samples, constraints on the magmatic (pre-eruptive) sulfur and chlorine concentrations in each of the ten obsidian samples were evaluated, together with their post-eruptive concentrations. Details of these calculations and analyses are provided in Appendix A, and the results are presented in Table 1. Maximum sulfur contents are ≤ 116 ppm and maximum chlorine

contents are ≤ 0.6 wt % for the ten obsidian samples under magmatic conditions. Post-eruptive sulfur contents are below detection limits (< 20 ppm), and chlorine contents are ≤ 0.09 wt%.

5. Discussion

5.1 No effect of H_2O degassing on the redox state of magmatic liquids

A comparison of magmatic and post-eruptive wt% FeO concentrations for each of the ten obsidian samples is shown in Table 2 and Fig. 5. The difference is $\leq \pm 0.10$ wt% for all ten samples, which is well within analytical uncertainty. If the maximum wt% FeO value is used from the Fe-Ti oxide results, instead of the mean value, the difference between magmatic and post-eruptive FeO is ≤ 0.09 wt% for eight of ten samples and ≤ 0.13 wt% for the remaining two. The data decisively show no evidence that degassing of up to 6.5 wt% H_2O led to any change in the melt ferric-ferrous ratio of the ten obsidian samples from this study, including samples that had magmatic ΔNNO values as low as -0.9 and as high as +1.4. The close correspondence in Fig. 5 cannot be attributed to the compensating effect of degassing of < 116 ppm (< 0.012 wt%) of dissolved sulfide (S^{2-}), which is too low to lead to any detectable change in melt wt% FeO. Degassing of dissolved sulfate and/or chlorine is expected to oxidize the melt and therefore would add to, rather than compensate for, any oxidation caused by H_2O degassing.

Also shown in Fig. 5 are the pre- and post-eruptive Fe^{2+} concentrations from 11 andesite and dacite samples (Crabtree and Lange, 2012), obtained following the same procedures as in this study. Collectively, the data in Fig. 5 strongly support *equilibrium* degassing of H_2O from magmatic liquids, where H_2O in the exsolved fluid phase dissociates to form H_2 and O_2 according to the fH_2O and fO_2 (and therefore, fH_2) of the melt phase, as illustrated in Eq. (2). In the absence of a gradient in fH_2 across the bubble-melt interface, the H_2 component in the fluid

phase cannot escape independently of the other volatile components within the same fluid phase, and the reaction in Eq. (3) cannot take place to increase the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the host melt. The data in Fig. 5 also indicate no resolvable effect of dissolved H_2O on the $\gamma_{\text{FeO}_{1.5}}/\gamma_{\text{FeO}}$ ratio in Eq. (5) for these metaluminous rhyolites, dacites and andesites.

5.2 Magma redox and tectonic setting: differences prior to degassing

In their updated calibration of the Fe-Ti two-oxide thermometer and oxybarometer, Ghiorso and Evans (2008) compiled published analyses of ilmenite and titanomagnetite pairs in silicic magmas erupted both effusively and explosively from several active arcs (e.g., Aleutians, Andes, Cascadia, Indonesia, Japan, Mexico, New Zealand, and Philippines). The resulting ΔNNO values (from Fe-Ti oxide pairs that pass the equilibrium test of Bacon and Hirschmann, 1988; see Supplementary Material) are shown as a histogram in Fig. 6, and mostly range between -0.8 and +1.8, with a peak at +0.9. Also shown in Fig. 6 is the ΔNNO result (+2.0) from Venesky and Rutherford (1999) on the Yn pumice erupted from Mount St. Helens.

In contrast, ΔNNO values for rhyolites erupted along the Yellowstone hotspot track (from Fe-Ti oxide data also compiled by Ghiorso and Evans, 2008, and pass the equilibrium test) are mostly between -0.8 and -2. There is little overlap in the magmatic redox state, *prior to extensive degassing*, between these two datasets from different tectonic settings. Relatively low ΔNNO values (-0.4 to -2; Fig. 5) are also documented from Fe-Ti oxides in rhyolites erupted both effusively and explosively from Iceland (e.g., Carmichael, 1967b; Gunnarsson et al., 1998; Portnyagin et al., 2012). The reduced character of the Icelandic magmas cannot be attributed to lower dissolved H_2O contents compared to arc magmas, because melt inclusion analyses show that melt water concentrations range up to 6.3 wt% (e.g., Portnyagin et al., 2012).

Another important point is that the highest ΔNNO value in Fig. 6 is that obtained from Fe-Ti oxides in the explosively erupted Yn pumice from the 1980 Mount St. Helens eruption, for which there was no time for re-equilibration of the oxides during ascent. Thus, the highest ΔNNO value in Fig. 6 clearly represents the magmatic redox condition and cannot be attributed to degassing of H_2O and subsequent re-equilibration of the Fe-Ti oxides during ascent.

There is one more line of evidence that the ΔNNO values obtained from Fe-Ti oxide pairs provide a record of magmatic conditions and did not undergo significant re-equilibration during ascent. Rhyolites from Yellowstone and Iceland with low ΔNNO values (below the quartz-fayalite-magnetite buffer) typically contain fayalite phenocrysts, whereas rhyolites from subduction zones with ΔNNO values ≥ 0 typically contain orthopyroxene phenocrysts (Fig. 7a). Carmichael (1967a; 1991) noted that the ferromagnesian phenocryst in rhyolite melts strongly reflects the oxidation state during phenocryst growth, with fayalite only occurring in melts with relatively low oxygen fugacities and, therefore, low liquid $\text{Mg\#}$ ($= 100 \cdot X_{\text{MgO}} / [X_{\text{MgO}} + X_{\text{FeO}}]$) (Fig. 7a-b). The $\text{Mg\#}$'s of ferromagnesian phenocrysts and corresponding liquids from $f\text{O}_2$ -buffered phase-equilibrium experiments and natural samples from the literature, for which ΔNNO is known from Fe-Ti oxide pairs, define the relationship between liquid $\text{Mg\#}$ and the stability of fayalite vs. orthopyroxene. In rhyolite melts with low $\text{Mg\#}$'s (≤ 12.5), Fe-rich (>70 mol% ferrosilite) orthopyroxene is unstable (illustrated in Fig. 7a-b), resulting in the crystallization of fayalite as the ferromagnesian phase. For a given liquid, the $\text{Mg\#}$ decreases with decreasing ΔNNO values, due to decreasing $\text{Fe}^{3+}/\text{Fe}^{2+}$, resulting in the stabilization of fayalite instead of orthopyroxene.

Fig. 7b illustrates that TEQ-21, one of the obsidian samples in this study that contains orthopyroxene, has a liquid $\text{Mg\#}$ that is close to the boundary of the fayalite stability field. In

Fig. 7c, it is shown that if H₂O degassing had driven melt oxidation sufficient to convert ≥ 0.06 wt% FeO to ferric iron, and if re-equilibration of the Fe-Ti oxide minerals had adjusted to this small change in redox, this sample should have contained fayalite phenocrysts. The liquid Mg# of this sample, calculated from the ΔNNO value obtained from the Fe-Ti oxides in this sample, predicts the occurrence of orthopyroxene phenocrysts. The consistency between the ferromagnesian phenocryst phase and the ΔNNO values recorded by the Fe-Ti oxides shows that even this small amount of oxidation, converting only ~ 0.06 wt% FeO, did not occur during H₂O degassing (otherwise fayalite phenocrysts would be present), and that the Fe-Ti oxide compositions in this sample accurately reflect those during phenocryst growth.

5.3 Magma redox and tectonic setting: no systematic effect of differentiation

Ilmenite and titanomagnetite pairs, which pass the equilibrium test of Bacon and Hirschmann (1988) (see Supplementary Material), are also found in basalts from both Iceland and the Yellowstone hotspot track (e.g., Stout and Nicholls, 1977; Carmichael, 1967; Gunnarsson et al., 1998). Resulting ΔNNO values (Fig. 8a) are plotted as a function of wt% SiO₂ and reveal no difference in the redox state between basalts and rhyolites in both of these tectonic settings. This result is significant because it shows that whatever differentiation mechanism(s) created the rhyolites— whether crystal fractionation and/or partial melting of pre-existing crust — there is no systematic difference in the redox state between the basalts and the rhyolites, and they are both highly reduced relative to subduction-zone magmas.

In Fig. 8b, ΔNNO values from Fig. 8a are converted to Fe³⁺/Fe^T ratios using the model equation of Kress and Carmichael (1991). This allows a direct comparison of Fe³⁺/Fe^T ratios in basalts from the Yellowstone hotspot track and Iceland (0.09-0.17) to the global average of mid-ocean ridge basalts (0.14 ± 0.04 ; Bézous and Humler, 2005; Cottrell and Kelley, 2011), revealing

a close similarity. Fig. 8b also allows a direct comparison between the 19 arc magmas from Fig. 5 with the analyzed $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios in olivine-hosted melt inclusions in basalts from the Mariana arc (Kelley and Cottrell, 2009; 2012; Brounce et al., 2014), which collectively have distinctly higher $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios (0.17-0.34) relative to those in mid-ocean ridge basalts. Also shown in Fig. 8b are $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios (obtained from Fe-Ti oxides) in andesites and dacites from the Mexican and Cascadia arcs, taken from a representative subset of the literature (Carmichael, 1967a; Wallace and Carmichael, 1994; Luhr, 2000; Grove et al., 2005; Stelten and Cooper, 2012). The results clearly show that magmas from subduction zones show no systematic change in their $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratio as a function of wt% SiO_2 , and that they are all systematically more oxidized than those from Yellowstone and Iceland. The reason why observed differences in ΔNNO values (Fig. 8a) between tectonic settings are also seen in the $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios (Fig. 8b) is because the effect of variable melt composition for metaluminous liquids is relatively minor compared to variable ΔNNO ($f\text{O}_2$ and T), based on calculations with the calibrated model of Kress & Carmichael (1991). The clear conclusion is that differentiation, whether by crystal fractionation, partial melting, and/or crustal assimilation, has no systematic effect on magmatic redox state, irrespective of tectonic setting, and therefore cannot be the explanation for the elevated oxidation states observed in subduction zones (e.g., Lee et al., 2010).

7. Conclusions

There are several key conclusions to be drawn from this study about the role of H_2O degassing in changing the oxidation state of magmatic liquids and the reason why magmas erupted at subduction zones have higher oxidation states relative to those at other tectonic settings. First, a comparison of magmatic Fe^{2+} concentrations obtained from Fe-Ti oxides with post-eruptive Fe^{2+} concentrations in rhyolites erupted as obsidian shows that there is no

resolvable effect of H₂O degassing (up to 6.5 wt%) on melt Fe²⁺/Fe³⁺ ratios. The evidence strongly supports equilibrium degassing of H₂O from magmatic melts, where H₂O in an exsolved fluid phase dissociates to form H₂ and O₂ according to the fH₂O and fO₂ (and therefore, fH₂) of the melt phase, without creating a gradient in either fO₂ or fH₂ across the bubble/melt interface. In the absence of a gradient in fH₂ or fO₂, the H₂ component in the fluid phase cannot segregate independently of the O₂ component in the same fluid phase, which explains no net change in melt redox during H₂O degassing.

Second, a compilation of Fe-Ti oxide data from this study and the literature shows that the distinctly higher oxidation state of arc magmas relative to those erupted from mid-ocean spreading ridges and hotspots (e.g., Iceland and Yellowstone) – noted by Carmichael (1991), Portnyagin et al., (2012) and numerous others – is a magmatic feature, recorded by Fe-Ti oxides during phenocryst growth, and is present prior to extensive H₂O degassing. This same compilation of data also shows that there is no effect of differentiation on the oxidation state of magmatic melts, irrespective of tectonic setting (Iceland, the Yellowstone hotspot track, subduction zones). In other words, basalts and rhyolites from the same tectonic setting share a similar redox state.

Third, because neither H₂O degassing nor differentiation reliably explain the higher oxidation state of subduction-zone magmas relative to those erupted at hot spots or mid-ocean spreading ridges, the evidence points to the subduction of oxidized oceanic crust and the release of an H₂O-rich fluid and/or melt with a high fO₂ (e.g., Carmichael, 1991; Kelley and Cottrell, 2009; Brounce et al., 2014, 2015). The relatively high fO₂ of the slab-derived H₂O-rich fluid and/or melt, which is inherited from the hydrothermally altered, oxidized oceanic crust, is

expected to play a role during H₂O-flux melting of the mantle in creating arc basalts that are relatively oxidized.

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Figure Captions

Figure 1. Comparison of calculated (using Kress and Carmichael, 1991) versus measured wt % FeO for all 47 experimental liquids from six studies (Fudali, 1965; Kilinc et al., 1983; Sack et al., 1980; Thornber et al., 1980; Kress and Carmichael, 1988; Moore et al., 1995) equilibrated at 1 bar over a range of temperatures and fO_2 values, which range from 57-79 wt% SiO_2 and are metaluminous, that were used to calibrate Eq. (6). One of the experimental liquids from the study of Kilinc et al. (1983) is an obsidian sample (CAM-49) that is also used in this study. The average residual is -0.02 wt% FeO, which indicates that application of the widely used calibration of equation of Kress and Carmichael (1991) is accurate when applied to metaluminous melt compositions that range from andesite to rhyolite.

Figure 2. A plot of the average ΔNNO ($\pm$ 2-sigma standard deviation) versus the average temperature ($\pm$ 2-sigma standard deviation) for each obsidian sample calculated from all possible pairs of ilmenite and titanomagnetite using the Fe-Ti two-oxide oxybarometer and thermometer of Ghiorso and Evans (2008). The resulting wt% FeO in the melt and the variance (shown as $\pm$) as recorded by the range of temperatures and ΔNNO values (presented in Table 2 and Fig. 4)

derived from all oxide pairs calculated and Eq. (6) with the calibration of Kress and Carmichael (1991) are shown for each sample.

Figure 3. Histograms of concentrations of wt% FeO calculated with Eq. (6) using temperature and ΔNNO values recorded by all possible pairs of titanomagnetite and ilmenite in each obsidian sample. Values of wt% FeO obtained from Fe-Ti oxide pairs that pass the Bacon and Hirschman (1988) test are grey, whereas all others are black. There is no systematic difference between them. In all cases the 2-sigma variation in wt% FeO derived from all possible pairs is small ($<\pm 0.04$ wt%).

Figure 4. Histograms of analyzed plagioclase phenocrysts+microphenocrysts, shown as a function of mol% An. Also shown in this figure are the results of the plagioclase-liquid hygrometer (Waters and Lange, 2015).

Figure 5. A plot of pre-eruptive (magmatic) wt% FeO ($\pm \leq 0.14$) obtained from Fe-Ti oxides versus post-eruptive wt% FeO ($\pm \leq 0.1$; Table 1) from titrations for all ten obsidian samples (red solid circles), with a 1:1 correspondence line. See text for evaluation of uncertainties. The maximum deviation is ± 0.10 wt% FeO (Table 1). Also shown (blue solid circles) are the results from a similar study on 11 phenocryst-poor andesite and dacite lavas (Crabtree and Lange, 2012). The results show no effect of H_2O degassing on the Fe^{2+} concentration in the melts.

Figure 6. Histogram of ΔNNO values obtained from Fe-Ti two-oxide oxybarometry for silicic magmas (andesite, dacite and rhyolite) from several active arcs (Aleutians, Andes, Cascades,

Indonesia, Japan, Mexico, New Zealand, Philippines; data compiled in Ghirosso and Evans, 2008) and for suites of magmas (i.e., basalts to rhyolites) from Iceland (Carmichael, 1967b; Gunnarsson et al., 1998; Portnyagin et al., 2012) and the Snake River Plain/Yellowstone (SRP/Y) (Stout and Nicholls, 1977). Arc magmas record a systematically higher oxidation state prior to extensive H₂O degassing relative to both rhyolites and basalts from Iceland and the Snake River Plain/Yellowstone. Note that the Icelandic melts contained up to 6.3 wt% dissolved H₂O (Portnyagin et al., 2012) and yet are not as oxidized as arc melts.

Figure 7: (a) Orthopyroxene-liquid (dark grey boxes) and fayalite-liquid (light grey diamonds) pairs from natural samples and H₂O-saturated, fO₂-buffered phase equilibrium experiments on silicic liquids (noted with crosses) are shown as function of the Mg#’s of the crystals and liquids. Natural samples are from Carmichael (1967, 1968), Cathey and Nash (2004), Portnyagin et al. (2012) and Waters and Lange (2013). Experimental crystal liquid pairs are from Scaillet and Scaillet and Evans (1999), Martel et al. (1999), Macdonald (2003), and Tomiya et al. (2010) (see text for discussion). **(b)** The fO₂ values from the experiments and natural samples in (a) are used with the experimental or pre-eruptive temperatures, whole rock compositions, and the model of Kress and Carmichael (1991) to calculate the concentration of ferrous iron, which is then used to calculate liquid Mg# (=100*X_{MgO}/[X_{MgO}+X_{FeO}]). Rhyolites that contain fayalite all have liquid Mg#’s <12.5, and those that contain orthopyroxene all have liquid Mg#’s >12.5. **(c)** Results of the model of Kress and Carmichael (1991) show that oxidation of ≥0.06 wt% FeO is required to shift TEQ-21 from the fayalite to the orthopyroxene stability field (see text for a detailed discussion).

Figure 8. (a) ΔNNO values obtained from Fe-Ti two-oxide oxybarometry plotted as a function of melt wt% SiO_2 . Samples include all those in Figs. 6 and 7, along with representative magmas from the Cascade and Mexican arcs (Stelten and Cooper, 2012; Carmichael, 1967a; Grove et al., 2005; Luhr, 2000; Wallace and Carmichael, 1994). The 2-sigma standard deviations on ΔNNO values derived from all possible pairs of oxides from samples included in this study and that of Crabtree and Lange (2012) are all $\leq \pm 0.3$ ΔNNO (e.g., Table 2). In addition, ΔNNO values are plotted for olivine-hosted basaltic melt inclusions from the Mariana arc (Kelley and Cottrell, 2009; Kelley and Cottrell, 2012; Brounce et al., 2014). These ΔNNO values are calculated from micro-XANES analyses of $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ using the calibration of Kress and Carmichael (1991). There is no trend of increasing ΔNNO with wt% SiO_2 for subduction-zone, Icelandic or SRP/Y magmas. **(b)** Plot $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ versus wt % SiO_2 for all the samples in (a). For reference, the average ($\pm$ 2-sigma standard deviation) $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios for MORB from two studies (Cottrell and Kelley, 2001; Bézoz and Humler, 2005) are shown, and the shaded regions reflect the values of wt% SiO_2 associated with MORB. The magmas erupted from subduction zones all have magmatic $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios, prior to extensive H_2O degassing, that are consistently higher than those from both the Iceland and Yellowstone hotspot and average MORB. There is no trend of increasing $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ with wt% SiO_2 , irrespective of magmatic tectonic setting.

Appendix A

A.1 Maximum magmatic and post-eruptive sulfur contents

Upper limits on pre-eruptive sulfur contents (reported in Table 1) were obtained from sulfur solubility limits at pyrrhotite saturation. These values were calculated by incorporating the temperature and fO_2 values derived from the two Fe-Ti oxides into a series of equations from (Whitney, 1984) to determine the equilibrium composition of pyrrhotite, which in turn was used to calculate the fugacity and solubility of sulfur in the melt (Toulmin and Barton, 1964; Clemente et al., 2004). The temperature and fO_2 derived from the two Fe-Ti oxides were incorporated into a model Eq. (A.1) from Whitney (1984) to obtain the mol fraction of pyrrhotite (X_{po}) in the pyrrhotite solid solution:

$$\log(fO_2) = [-28.77 - 64.37(2 \ln X_{po} - (X_{po} + 1))](1000/T - 1) + 29.42(2 \tanh^{-1} \sqrt{1 - 0.9982X_{po}} - \frac{\sqrt{1 - 0.9981X_{po}}}{0.9981}) - 21.99 \quad (A.1)$$

The value for X_{po} obtained from Eq. (A.1) was then incorporated into Eq. (A.2) from Toulmin and Barton (1964), along with temperatures derived from two Fe-Ti oxides, to obtain the fS_2 at pyrrhotite saturation.

$$\log(fS_2) = (70.03 - 85.83X_{po})(1000/T - 1) + 39.30\sqrt{1 - 0.9981X_{po}} - 11.91 \quad (A.2)$$

The temperature, fO_2 and fS_2 were then incorporated into the sulfur solubility model of Clemente et al. (2004), shown in Eq. (A.3) which allows the S solubility in the melt phase to be determined for a given fS_2 at fixed temperature and fO_2 .

$$\log S(\text{ppm}) = 0.001T - 0.2567(\Delta NNO) - 0.1713(\Delta FFS) + 0.0034(\Delta NNO)(\Delta FFS) \quad (A.3)$$

In Eq. (A.3), the term ΔFFS is defined as the $\log fS_2$ sample - $\log fS_2$ at the Fe-FeS buffer. Using the three equations above, the maximum magmatic sulfur contents for the ten obsidian samples, using the average temperature and ΔNNO value for each sample, range from 74 to 90 ppm S. However, when the 2-sigma variations in temperature and ΔNNO (oxygen fugacity) from the Fe-Ti oxide results (Fig. 2) are propagated through the sulfur solubility calculations, the resulting

maximum sulfur contents range from 78 to 116 ppm (variations range from ± 26 -4 ppm S).

These are the sulfur values reported in Table 1 and in the main text.

To test if any sulfur in the samples could be interfering with the titration results, the groundmass glasses of six of the ten obsidians were analyzed for sulfur using the electron microprobe, with an accelerating voltage of 15 kV and a beam current of 40 nA. For all but one sample, sulfur was found to be below the detection limit (14 ppm; Table 1). In a single sample (MLV-37; Table 1) sulfur content in the groundmass glass was 28 ± 14 ppm, and the effects of 0.0028 wt% sulfur are negligible on the results of the titration.

A.2. Determination of maximum pre- and post-eruptive chlorine contents

Upper limits on magmatic chlorine contents (reported in Table 1) were obtained from solubility limits. The chlorine solubility model of Webster and De'Vivo (2002) was calibrated on a series of experiments conducted at 2000 bars on natural and synthetic liquids that span a range of temperatures (786-1193°C) and a range of water contents (0.5- 3.2 wt%). This model is not calibrated for melt water contents greater than 3.2 wt%. Although only two of the obsidian samples in this study (TEQ-21 and MLV-44), had <3 wt% H₂O during phenocryst growth, this chlorine solubility model was applied to all ten obsidians, with the caveat that an extrapolation was required for the eight samples that contained >3 wt% H₂O (Table 1). The results yield maximum chlorine contents that range from 0.35-0.64 wt% (Table 1), which are strongly correlated ($R^2=0.95$) with wt% CaO in melt (Table 1).

The chlorine contents in groundmass glasses of a subset of six rhyolites were analyzed using the CAMECA SX-100 electron microprobe at the University of Michigan with a defocused 10 μ m beam and accelerating voltage of 15 kV and 10 nA. Measured Cl contents in groundmass glasses (reported in Table 1) range from 0.06-0.09 wt% Cl.

Table 1: Geographic Locations, Whole Rock Geochemistry, Modal Abundances and Volatile Contents

Sample	MLV-36	MLV-37	MLV-44	MLV-45	CAM-49	TEQ-21	JAL-10	COMP-3	PCR-7B	PCR-R3
Lat. (N)	41° 36.97'	41° 34.28'	41° 31.36'	41° 32.20'	41° 35.28'	20° 51.26'	21° 16.68'	21° 09.79'	37° 42.00'	37° 41.74'
Long. (W)	121° 38.48'	121° 41.96'	121° 42.22'	121° 43.51'	121° 30.00'	103° 51.86'	104° 41.86'	104° 42.39'	118° 55.54'	118° 56.88'
Geographic Location	Cascades Arc	Cascades Arc	Cascades Arc	Cascades Arc	Cascades Arc	Mexican Arc	Mexican Arc	Mexican Arc	Basin & Range	Basin & Range
SiO ₂	73.8	74.5	75.5	73.4	72.9	74.1	74.3	75.2	74.3	75.6
TiO ₂	0.27	0.28	0.22	0.23	0.28	0.15	0.26	0.20	0.15	0.15
Al ₂ O ₃	13.2	13.6	13.2	14.5	13.2	13.3	14.2	13.5	13.3	13.5
FeO ^T	2.08	2.12	1.28	1.75	1.81	1.62	1.50	1.31	1.20	1.32
MnO	0.04	0.04	0.04	0.04	0.04	0.06	0.06	0.05	0.04	0.04
MgO	0.27	0.28	0.21	0.38	0.29	0.11	0.38	0.30	0.11	0.13
CaO	1.23	1.25	0.81	1.76	1.29	0.51	1.40	1.30	0.77	0.78
Na ₂ O	3.99	4.01	3.91	3.87	4.02	4.61	4.86	4.55	3.66	3.72
K ₂ O	4.18	4.21	4.73	3.58	4.18	4.83	3.04	3.36	5.05	5.18
P ₂ O ₅	0.06	0.05	0.01	0.03	0.04	0.03	0.07	0.06	0.02	0.02
LOI	0.31	0.40	0.43	0.51	0.30	0.00	0.00	0.70	0.20	0.21
Total	99.4	100.7	100.4	100	98.6	99.4	100.1	99.7	98.9	100.6
Plag	1.9	2.5	<0.1	2.4	2.5	2	1.7	5.4	2.8	2.7
Opx	0.6	0.8	<0.1	0.4	0.8	<0.1	0.3	0.4	0.3	0.4
Cpx	-	-	<0.1	<0.1	0.1	0.1	0	0	-	-
Hbl	-	0.1	-	1.3	-	0	0.2	0.2	-	-
Bte	-	-	-	-	-	-	-	-	0.2	tr
Fe-Ti Ox	0.3	0.3	<0.1	0.5	0.2	0.6	0.5	0.5	<0.1	<0.1
Gdms	97.1*	96.3	99.7*	93.8	96.2	97.1*	97.1	93.6	96.7*	96.8*
¹ Max X _{An}	0.50	0.53	0.27	0.70	0.53	0.17	0.44	0.51	0.31	0.30
² Max H ₂ O (wt%)	4.0	5.0	1.7	5.3	4.1	1.3	6.5	5.7	4.2	3.2
³ H ₂ O _{glass} (wt%)	0.10	0.05	0.10	0.12	0.05	0.10	0.07	0.11	0.10	0.11
±1σ	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.03	0.03
⁴ Max S solubility (ppm)	81	79	83	77	81	90	74	74	116	105
⁵ S _{glass} (ppm)	bdl	28	-	-	bdl	bdl	bdl	bdl	-	-
±1σ	-	14	-	-	-	-	-	-	-	-
⁶ Cl solubility (wt%)	0.52	0.53	0.41	0.60	0.55	0.36	0.55	0.49	0.38	0.38
⁷ Cl _{glass} (wt%)	0.066	0.061	-	-	0.060	0.092	0.058	0.058	-	-
±1σ	0.012	0.009	-	-	0.013	0.016	0.009	0.009	-	-

For the modal abundances abbreviations are defined as: plag, plagioclase; opx, orthopyroxene; cpx, clinopyroxene; hbl, hornblende; bte, biotite; fe-ti ox, iron titanium oxides; gdms, groundmass; groundmasses noted with “*” refer to samples devoid of microlites. ¹The composition of most calcic plagioclase phenocrysts (X_{An}) observed in each sample. ²The wt% H₂O derived from the plagioclase liquid hygrometer (see main text). ³FTIR determinations of (post-eruptive) water contents in obsidian groundmass glasses (see text and supplementary Table S4). ⁴Calculated pre-eruptive, magmatic sulfur concentration (see Appendix A). ⁵Measured sulfur contents in glasses of the natural samples (see Appendix A). ⁶Estimated pre-eruptive, magmatic Cl contents and ⁷Measured Cl contents in groundmass glasses (see Appendix B).

Table 2: Calculations of Pre- and Post-eruptive Concentrations of Ferrous Iron

Sample	Temperature (°C)	Δ NNO	¹ Pre-eruptive FeO (wt%)	² Variance $\pm$ FeO (wt%)	³ Uncertainty $\pm$ FeO (wt%)	⁴ Post-eruptive FeO (wt%)	⁵ n	⁶ Δ wt% FeO (Pre - Post)
MLV-36	852 $\pm$ 25	0.3 $\pm$ 0.2	1.58	0.04	0.14	1.54 $\pm$ 0.02	4	0.04
MLV-37	813 $\pm$ 20	0.4 $\pm$ 0.1	1.60	0.03	0.14	1.57 $\pm$ 0.09	4	0.03
MLV-44	932 $\pm$ 29	0.8 $\pm$ 0.1	0.92	0.01	0.12	0.93 $\pm$ 0.10	4	-0.01
MLV-45	837 $\pm$ 41	0.9 $\pm$ 0.1	1.24	0.03	0.14	1.14 $\pm$ 0.08	4	0.10
CAM-49	849 $\pm$ 51	0.2 $\pm$ 0.2	1.38	0.04	0.14	1.33 $\pm$ 0.07	4	0.05
TEQ-21	939 $\pm$ 39	-0.4 $\pm$ 0.2	1.31	0.02	0.13	1.27 $\pm$ 0.06	4	0.04
JAL-10	780 $\pm$ 50	1.3 $\pm$ 0.1	0.98	0.02	0.12	1.00 $\pm$ 0.08	4	-0.02
COMP-3	801 $\pm$ 16	1.4 $\pm$ 0.1	0.86	0.01	0.10	0.95 $\pm$ 0.15	4	-0.09
PCR-7B	821 $\pm$ 40	-0.9 $\pm$ 0.3	1.01	0.02	0.13	1.02 $\pm$ 0.12	4	0.10
PCR-R3	861 $\pm$ 41	-0.8 $\pm$ 0.3	0.99	0.02	0.13	0.92 $\pm$ 0.05	3	0.07
Standard			Certified wt% FeO			⁴ Measured wt% FeO	⁷ Δ wt% FeO	
QLO-1			2.97 $\pm$ 0.05			2.96 $\pm$ 0.14	6	0.01
SY-4			2.86 $\pm$ 0.09			2.98 $\pm$ 0.20	6	-0.12
BIR-1			8.34 $\pm$ 0.10			8.32 $\pm$ 0.09	3	0.02
W-2			8.34 $\pm$ 0.09			8.25 $\pm$ 0.09	3	0.09

¹Pre-eruptive wt% FeO calculated from Eq. (6) and the calibration of Kress and Carmichael (1991) using temperature and Δ NNO from two Fe-Ti oxides (see text). ²The variance in wt% FeO derived from the range of temperatures and Δ NNO values recorded by all possible pairs of oxides (see text; Fig. 4). ³The analytical uncertainty associated with the various inputs into the model of Kress and Carmichael (1991) (see text). ⁴Average concentration of FeO (wt%) measured by Wilson (1960) titration, along with a 2-sigma standard deviation. ⁵Number of titrations conducted. ⁶The difference between pre-eruptive and post-eruptive wt% FeO. ⁷The difference in wt% FeO between the certified standard and the titrated value in this study.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8