Dissolved Cl, Oxygen Fugacity, and Their Effects on Fe Behavior in a Hydrous Rhyodacitic Melt  

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Abstract

We have conducted a series of experiments to evaluate the intrinsic effects of dissolved chlorine on Fe³⁺/ΣFe and magnetite solubility in hydrous chloride-rich rhyodacitic liquids. The addition of Cl to the melt appears to have two prominent effects on iron in the melt: 1) Dissolved Cl appears to perturb the magnetite-melt equilibrium, such that greater FeOtotal contents are required to support magnetite saturation in Cl-bearing melts than in Cl-free melts of equivalent bulk compositions; and 2) a systematic and progressive decrease of the measured Fe³⁺/ΣFe as fO₂ is increased. These two intimately related effects each have important implications for redox processes occurring in Cl-enriched arc magmas.

Introduction

Iron is by far the most abundant multivalent element present in terrestrial magmas (Wilke 2005) and therefore exerts a proportionally large influence on the overall redox behavior of natural silicate melts. Much analytical and experimental effort has been exerted in order to illuminate the relationships between the molar ratio of FeO₁.₅/FeO and intensive parameters such as bulk melt composition, pressure, and temperature (Sack et al. 1980; Kilinc et al. 1983; Kress and Carmichael 1991; Tangeman et al., 2001; Ottonello et al. 2001; Jaysauria et al. 2004; Moretti 2005; Borisov and McCammon 2010). Previous efforts have also been extended to account for the effects of dissolved volatile constituents on Fe redox behavior. Specifically, the intrinsic effects of dissolved water on the equilibrium ratio of ferric and ferrous iron have been the subject of several studies as well as the source of much debate and controversy (Moore et al. 1995; Baker and Rutherford 1996; Gaillard et al. 2001; Wilke et al. 2002).
Though a considerable quantity of work has been directed toward understanding dissolved water’s
effects on the redox systematics of Fe, the potential effects of other volatile elements that fill anionic
structural roles have only been investigated to a limited extent. After dissolved hydroxyl, chlorine is the
second-most abundant anionic volatile component in evolved, subduction-related silicate magmas
(Wallace 2005). Given the propensity for Cl to form ionic bonds with divalent cations in silicate melts
(Carroll and Webster 1994; Webster and DeVivo 2002; Zimova and Webb 2006; Filliberto and Trieman
2009; Filliberto et al. 2014; Webb et al. 2014; Webster et al. 2015), it is reasonable to hypothesize that
dissolved chlorine may exert a significant influence on redox behavior of iron. Such an effect would have
important implications for the stability fields of Fe-bearing minerals in equilibrium with chlorinated
melts, as well as understanding the relationship between the measured, formal valence of iron and
magmatic $f_{O2}$. The latter point is of considerable importance, as the formation of Fe-Cl species in the
melt (i.e. the formation of a FeCl$_2$ melt component analogous to the oxide component FeO) requires
that the relative concentration of Fe$^{2+}$ in the melt is not exclusively determined by magmatic $f_{O2}$, but is
rather a function of both $f_{O2}$ and the Cl content (i.e. $f_{Cl_2}$) of the melt.

This initial hypothesis is supported by the data and conclusions drawn from a number of previous
studies on Cl solubility. The pioneering work of Webster and DeVivo (2002) established a quantitative
link between the concentration of divalent cations such as Mg, Fe, and Ca and melt Cl-dissolution
capacity. Several studies on the effects of Cl on the viscosity of silicate melts observed that the addition
of Cl to some Fe-bearing melts results in an increase in the viscosity of these liquids, suggesting that
dissolved Cl bonds with Fe$^{2+}$ in the melt and disrupts its network-modifying structural role (Dingwell and
Hess 1998; Zimova and Webb 2006; Webb et al. 2014). Additionally, a recent XANES (X-ray Absorption
Near Edge Structure) study conducted by Evans et al. (2008) identified dissolved Cl bonded to divalent
ations in the form of Mg-Cl and Ca-Cl species in haplobasaltic glasses. Although the melts of this study
did not contain Fe, the authors concluded that divalent Ca and Mg form Cl complexes with a short-range
structure similar to that of crystalline MgCl$_2$ and CaCl$_2$. Given the strong similarities between the ionic
radius and field strength of Fe$^{2+}$ and Mg$^{2+}$, it seems probable that Fe-Cl complexes also exist as species in
silicate melts. In this work we present a series of experiments designed to investigate the potential
relationship between Fe and Cl in a hydrous rhyodacitic liquid. While this work in no way represents a
comprehensive study of the effects of Cl on Fe in melts, the experiments presented do provide some
new and unique insight into potential Fe-Cl interactions in felsic melts.

**Experimental Design and Rationale**

Two sets of experiments were conducted, each with a different purpose.

The first set of experiments was designed to investigate the effect of dissolved Cl on magnetite
solubility in hydrous chlorinated rhyodacitic melts at controlled $f_{O_2}$. Iron was added to the starting
charges as a single chip of magnetite or a mixture of glass and magnetite powder that was located at
one end of the capsule. These experiments were purposefully configured in this manner, so that the
melt from only one end of the experimental charge would be in direct contact with magnetite. This set
of experiments will be referred to as the MagLiq series.

A second set of melt-only experiments was designed to examine the potential effects of
dissolved Cl on the Fe$^{3+}/\Sigma$Fe of the quenched rhyodacitic melts over a range of $f_{O_2}$ values. These
experiments have been designated the SRD series. In addition to the Cl-bearing experiments, a few
redox-controlled experiments were performed in order to develop additional dacitic-glass XANES
standards. Experimental conditions, Fe and Cl concentrations, and the XANES measured Fe$^{3+}/\Sigma$Fe values
for the quenched melts are presented in Table 1.

All of the SRD and MagLiq experiments were performed in 3 mm (OD) × 2.7 mm (ID) × 20 mm
(length) Au capsules. At the temperatures of the experiments in this study, Au capsules are sufficiently
H$_2$ permeable to attain redox equilibrium within the first several hours of the experiment (Gaillard et al.
2001). Water and Cl were added to the charges in the form of a Na-K-H chloride solution. Appropriate
quantities (10-15 mg) of a prepared NaCl-KCl-HCl solution (ΣCl = 7.5 wt. %) were added to each SRD2 capsule with a micro-pipette to ensure that each charge remained fluid-saturated throughout the duration of the experiment (each experiment contained from 30-45 mg SRD2 starting glass). The fluid-melt ratios for these experiments are somewhat variable, therefore the extent of Fe scavenging and alkali exchange have differently affected the melt composition of each experiment, albeit to a relatively limited extent. For the MagLiq runs, special care was taken to minimize the fluid-melt ratio present at run conditions in order to mitigate Fe loss and alkali exchange due to fluid scavenging (Bell and Simon 2011).

Experiments were conducted in a Shaw membrane-equipped internally-heated pressure vessel apparatus at the American Museum of Natural History (AMNH). All experimental runs were conducted at 950°C and pressures of either 130 MPa or 150 MPa. Run durations for the equilibrium MagLiq and SRD experiments ranged from 132 to 212 hours. Temperature and thermal gradients were measured with two factory-calibrated, Inconel-sheathed type-K thermocouples. The maximum measured thermal gradient (ΔT) over the length of an experimental capsule was ±7°C. Pressure was measured with a bourdon tube-type strain gauge with a precision of ±10 bar. Experiments were isobarically quenched at approximately 10 °C sec⁻¹.

The oxidation state of the experimental charges was controlled with a platinum-sheathed Shaw membrane that was positioned immediately adjacent to the experimental capsules. The partial pressure of H₂ transmitted from the membrane to the Ar pressure medium in the vessel was monitored with a high-precision bourdon tube gauge. Oxygen fugacities imposed by the membrane were verified with a solid-state Co-Pd-CoO redox sensor identical to those described by Taylor et al. (1991). Oxygen fugacity calculated from the redox sensor alloy composition (Co₃₉.₅Pd₄₀.₅) was \( \log_{10} f_{O_2} = -11.75 \pm 0.10 \), in excellent agreement with the anticipated \( f_{O_2} \) of the sensor runs, and therefore all reported \( pH_2 \) and \( f_{O_2} \) values are believed to be comparably accurate. The oxygen fugacity of each experimental charge was
calculated using the $f_{\text{H}_2}$ imposed by the Shaw membrane, the $f_{\text{H}_2\text{O}}$ of the experimental charge, and $\text{H}_2\text{O}$ formation constant from Robie and Hemmingway (1995).

**EPMA and XANES Analytical Details**

The EPMA-determined compositions of the equilibrium MagLiq glasses and the glasses from the magnetite-free SRD2 runs are given in Electronic Appendix I. This appendix also contains detailed discussion of the EPMA and XANES analytical procedures, standards, and new XANES standard development.

**Results and Discussion**

**Using Magnetite-Dissolution Experiments to Examine Potential Fe-Cl Interactions in the Melt**

Perhaps the most direct way to observe potential Fe-Cl interactions in the melt is by examining the total Fe content (where total Fe content is equal to the sum of all Fe species present in the melt, i.e. Fe-O species and Fe-Cl species) of melts with various Cl contents in equilibrium with magnetite. Many of the MagLiq series experiments did not attain a homogenous Fe distribution in the melt; therefore these experiments were considered to be failed and will not be discussed in this section.

The melts in four of the MagLiq series experiments appear to have achieved a uniform Fe distribution, and thus are believed to have attained a steady state. The results from only these experiments will be discussed in this section. The run conditions and the EMP determined Fe and Cl concentrations of the equilibrium MagLiq melts are presented in Table 1.

With these MagLiq series experiments we have attempted to isolate the effects of dissolved chlorine on the Fe\textsuperscript{total} content of the liquid required to support magnetite saturation. The equilibria governing magnetite dissolution illustrate how Cl may affect the EPMA measured iron content (which is reported with the EPMA data as “FeO”) of the magnetite saturated melt. The magnetite dissolution reaction may be written as:

\[
\text{Fe}_3\text{O}_4^{\text{mag}} = \text{FeO}^{\text{melt}} + 2\text{FeO}_{1.5}^{\text{melt}}
\]
or alternatively expressed as a simple solubility product:

\[ K_1 = (a\text{FeO}^{\text{melt}}) \cdot (a\text{FeO}_{1.5}^{\text{melt}})^2 \]

Additionally, fixing the \( f\text{O}_2 \) fixes the ratio of \( a\text{FeO} \) to \( a\text{FeO}_{1.5} \) in melt via the homogenous redox reaction

\[ \text{FeO} + 0.25\text{O}_2 = \text{FeO}_{1.5} \]

\[ K_2^* (f\text{O}_2)^{-0.25} = \frac{a\text{FeO}}{a\text{FeO}_{1.5}} \]

From these reactions it is clear that perturbation of either \( a\text{FeO} \) or \( a\text{FeO}_{1.5} \) due to changing \( f\text{O}_2 \) in the melt must be accompanied by either the dissolution or precipitation of magnetite to maintain equilibrium. However at fixed \( P \), \( T \), and \( f\text{O}_2 \), the only way to perturb the total iron concentration in the melt is by altering the activity coefficients for either \( \text{FeO} \) or \( \text{FeO}_{1.5} \) in the melt. The addition of \( \text{Cl} \) to the melt appears to produce this result. The results of the MagLiq experiments unequivocally show that the addition of \( \text{Cl} \) to the melt is accompanied by a significant increase in the EPMA-determined total iron content of the quenched melt (see Table 1). For example, experiments MagLiq5 (Cl-bearing) and MagLiq6 (Cl-free) have EPMA-determined total Fe contents of 4.9 ± 0.16 wt % and 4.2 ± 0.21 wt %, respectively (these values are reported as FeO in Table 1). The magnitude of the increase in Fe is not large, yet it is shown to be highly statistically significant when evaluated with a Student’s T-test (the calculated two-tailed P-value for MagLiq 5 and 6 is <0.0001).

The observed increase in the iron concentration of the Cl-bearing experiments requires the presence of dissolved Cl to depress \( a\text{FeO} \) or \( a\text{FeO}_{1.5} \) in the melt. Given what is known about potential Cl speciation in melts, there are two possible explanations for this behavior. The simplest explanation is that anionic Cl bonds with Fe in the melt to form stable Fe-Cl complexes, therefore lowering the activities of the Fe-O species in the melt. The second explanation requires the formation of \( \text{Mg}^{2+} \)-Cl, \( \text{Ca}^{2+} \)-Cl, or \( \text{Na}^{+} \)-Cl in the melt; the presence of these complexes in some way fundamentally and indirectly changes \( a\text{FeO} \) and \( a\text{FeO}_{1.5} \). It is important to note that the mechanisms presented above are not mutually exclusive, and that dissolved Cl is likely distributed among many competing divalent and
monovalent cations. Unfortunately the magnetite dissolution experiments cannot be used to rigorously
test the “direct Fe-Cl speciation” hypothesis versus the “indirect complexing effect” hypothesis. The
experiments described in the next two sections supplement the observations from the MagLiq
experiments, further clarifying the chemical links between Fe and Cl in the melt.

Evidence for Fe-Cl Interaction from a Failed, Disequilibrium Magnetite Dissolution Experiment

As discussed in the previous section, many of the magnetite-dissolution experiments failed to attain a
uniform iron distribution in the melt. Although the failed experiments do not accurately depict the
equilibrium iron content of the melt, they do capture a unique kinetic aspect of the magnetite-
dissolution process that illuminates the chemical link between Fe and Cl in the melt. This section
presents EPMA data from an analytical transect taken from the run products of one of the “failed”
experiments. Figure 1a is a composite BSE (backscattered electron) image of the condensed products of
one of the “disequilibrium” magnetite-dissolution experiments. Superimposed on this BSE image is the
location of an EMP analytical transect across the quenched liquid. The compositional data plotted in
Figure 1b show a thought-provoking relationship between the concentration profiles for FeO$_{\text{total}}$ and Cl.
As expected, the FeO$_{\text{total}}$ content of the liquid monotonically decreases with distance from the interface
of the magnetite-bearing and magnetite-free portions of the melt. The FeO$_{\text{total}}$ content of the liquid
nearest to the magnetite bearing melt appears to be a uniform ~5.5 wt% before decreasing to
approximately 3.5 wt % in the distal portion of the glass.

We have interpreted this FeO$_{\text{total}}$ distribution as a diffusion profile. In contrast to Fe, Cl appears to
increase as the magnetite-melt interface is approached. The apparent redistribution of what was in the
initial hours of the experiment a homogenous Cl concentration suggests that a Cl speciation reaction co-
occurring with magnetite dissolution is causing this behavior. An example of such a speciation reaction
involving Fe-Cl species is:

\[
\text{CaCl}_2^{\text{melt}} + \text{FeO}^{\text{melt}} = \text{FeCl}_2^{\text{melt}} + \text{CaO}^{\text{melt}}
\]
The addition of Fe to the melt from the magnetite dissolution results in the formation of Fe-Cl species. The Fe-enrichment of the melt causes in the stabilization of Fe-Cl species results in a melt with higher Cl solubility. It is the enhanced Cl solubility that is responsible for inducing a temporary Cl chemical potential in the melt. The existence of this gradient causes the observed “uphill” diffusive flux of Cl. If no interactions between melt components were occurring, the Cl content of the melt would simply decrease by dilution in the region adjacent to the magnetite-melt interface. Similar dissolution-diffusion arguments for melt speciation reactions have been invoked to describe homogenous alkali-Al speciation reactions in hydrous, haplogranitic melts (Acosta-Vigil et al. 2002, 2006). Using reasoning analogous to that presented in those studies, we conclude that the observed correlation between Fe and Cl concentrations suggests the occurrence of a Fe-Cl speciation reaction in the melt. The speciation reaction presented above should not be interpreted to mean that no other Cl species exist in the melt, but rather that Cl is distributed among the available cations in the melt in a manner that reflects the hierarchy of their relative stabilities. It is important to note that the results of the dis-equilibrium dissolution experiments cannot indicate which form of iron oxidation state -ferric or ferrous- is primarily involved in the proposed Cl-complexing reactions.

A Causal Link between Fe-Cl Speciation and the Relationship between Fe\(^{3+}/\Sigma Fe\) and \(fO_2\)?

In this section we focus primarily on the relationship between \(fO_2\) and the response of the measured Fe valence in the melt. It is important to point out that XANES measurements themselves can only yield information about the formal valence state of iron in the melt; therefore, the XANES-measured Fe\(^{3+}/\Sigma Fe\) values of the glasses for the SRD experiments are given in Table 1 and have been plotted in Figure 2. The measured Fe\(^{3+}/\Sigma Fe\) ranges from a low of 0.28 a high of 0.42. This relatively restricted range of values is remarkable, considering that the \(fO_2\) varied in excess of three orders of magnitude in these experiments. The Fe\(^{3+}/\Sigma Fe\) only increases by approximately 13%, as the experimentally imposed \(fO_2\) increases from FMQ to FMQ + 3.2. To place this observation in context, the Kress and Carmichael (1991) model
indicates that $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the SRD melt should increase at nearly twice this rate in response to a 3.2 log unit increase in $fO_2$. The relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $fO_2$ that we have observed for the chlorinated SRD melts is unique. No previous studies have yielded similar results with respect to the slope of the ferric-ferrous ratio as a function of $fO_2$. In all previous studies of hydrous melts, none of which contained Cl, the observed relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $fO_2$ has been consistent with the apparent reaction stoichiometry as either defined by the Kress and Carmichael (1991) equation, or the theoretical reaction stoichiometry (Jayasauria et al. 2004). The Fe valence data from the SRD experiments suggest that the addition of Cl to the melt fundamentally changes the relationship between Fe valence and $fO_2$, as the rate at which the measured $\text{Fe}^{3+}$ abundance increases in the melt appears to be damped.

The relationship between $\text{Fe}^{3+}/\Sigma\text{Fe}$ and $fO_2$ observed in the SRD experiments may be interpreted in a number of different ways. Here we present two possible interpretations of the $\text{Fe}^{3+}/\text{Fe}$ data: (1) the formation of $\text{Fe}^{2+}$-Cl species partially decouples the measured formal valence ratio from the imposed experimental $fO_2$, and (2) the changes in Cl-speciation in the melt co-occurring with Fe oxidation alter the activity ratio of FeO and FeO$_{1.5}$ in the melt. It is important to note that these interpretations are not mutually exclusive, and that the mechanisms proposed may both significantly affect the equilibrium $\text{Fe}^{3+}/\Sigma\text{Fe}$.

In the first interpretation, the addition of Cl to the melt results in the formation of $\text{Fe}^{2+}$-Cl species. If such a species exists in the melt, then the denominator of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio is partially controlled by the abundance of the $\text{Fe}^{2+}$-Cl species in the melt. As $fO_2$ in the melt is increased, the FeO$_{1.5}$/FeO ratio may indeed still increase following the expected stoichiometry, however, the persistent presence of $\text{Fe}^{2+}$-Cl species in the higher $fO_2$ experiments acts to suppress the expected increase in the measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ with $fO_2$. Realistically, this simplified explanation may be complicated by homogenous Cl speciation.
reactions, as the abundance of FeCl species may be, in part, linked to the activity of FeO in a complex way.

It is also possible to rationalize the observed Fe$^{3+}$/Fe$^{2+}$ versus $f_{O_2}$ trend by considering how the distribution of Cl species in the melt changes as a function of $f_{O_2}$. The preponderance of the available Cl solubility and phase equilibrium studies suggest that many different cations are ultimately involved in forming Cl species within the melt. Therefore it follows that the Cl content of the melt is not simply determined by a single canonical Cl species, but rather it is a reflection of a hierarchical distribution, where Cl is appropriated among the various competing cations according to the relative stabilities of their Cl complexes. The results of Webster and DeVivo (2002) indicate that the relative stability of Cl species follows a general pattern where Ca$^{2+}$-Cl = Mg$^{2+}$-Cl > Fe$^{2+}$-Cl >> Na$^{+}$-Cl > K$^{+}$-Cl. As such the distribution of Cl species in the melt can be described as a series of homogenous speciation reactions:

\[
\begin{align*}
\text{FeCl}_2 + \text{Na}_2\text{O} &= \text{FeO} + 2\text{NaCl} \\
\text{FeCl}_2 + \text{CaO} &= \text{FeO} + \text{CaCl}_2 \\
\text{FeCl}_2 + \text{K}_2\text{O} &= \text{FeO} + 2\text{KCl}
\end{align*}
\]

At fixed melt composition, temperature, pressure, and $f_{O_2}$, the distribution of Cl species is fully defined by a combination of the appropriate homogenous speciation equilibria. It therefore follows that under more oxidized conditions the apparent speciation behavior of Cl should change substantially. In the case of our experiments, it appears that increasing $f_{O_2}$ disturbs the equilibrium distribution of Cl in the melt by decreasing the availability of Fe$^{2+}$ to form FeCl$_2$ species. If the Cl concentration of the melt remains nearly constant, as it does in our experiments, then the decreased FeO content of the melt must be accompanied by a concomitant shift in the Cl species distribution. Increasing $f_{O_2}$ effectively redistributes some Cl that was formerly bonded to Fe$^{2+}$ to form Cl complexes with the alkalis and alkaline earth cations. In other words, at higher $f_{O_2}$, the Cl speciation shifts to favor the formation of Na-Cl or Ca-Cl...
species over Fe\textsuperscript{2+}-Cl species. The result of this process is an effective depression of the Na\textsubscript{2}O/NaCl, K\textsubscript{2}O/KCl and CaO/CaCl\textsubscript{2} ratios in the melt.

Redox-induced changes in Cl speciation may also be responsible for suppressing the formation of Fe\textsubscript{O1.5} with increasing experimental f\textsubscript{O2}. Increased abundances of CaCl\textsubscript{2}, NaCl, and KCl in the melt appear to decrease the “effective” alkalinity of the melt, thus depressing the equilibrium \( \text{Fe}^{3+}/\Sigma\text{Fe} \). The relationship between melt alkalinity and \( \text{Fe}^{3+}/\Sigma\text{Fe} \) has been well documented by numerous studies (Mysen et al. 1980; Sack et al. 1980; Kress and Carmichael 1991). These studies have unanimously shown that increasing concentrations of K\textsubscript{2}O, Na\textsubscript{2}O, and CaO cause an increase in the equilibrium \( \text{Fe}^{3+}/\Sigma\text{Fe} \) at constant f\textsubscript{O2}. This effect has been attributed to the structural role of these cations as possible charge compensators for \( ^{IV}\text{Fe}^{3+} \) in the melt by forming species such as NaFe\textsuperscript{3+}O\textsubscript{2} (Mysen et al. 1980). Our data suggest chlorinated alkalis may not effectively act as charge compensators for \( ^{IV}\text{Fe}^{3+} \) in bonding configurations such as Fe\textsuperscript{3+}-Cl-Na\textsuperscript{+}. Alternatively, the effects of changing Cl-speciation on the melt alkalinity may be understood in terms of the link between polymerization state and optical basicity of a melt and its equilibrium \( \text{Fe}^{3+}/\Sigma\text{Fe} \) (Ottonello et al. 2001). In the case of our experiments, formation of alkali- and alkaline earth-Cl complexes may decrease the NBO/T (non-bridging oxygen per tetrahedral cation) and basicity of the melt, thereby enhancing the stability of Fe\textsuperscript{2+}O species in the melt. The effects of Cl on the NBO/T of natural aluminosilicate melts may in fact be significantly more complex than the simple relationships described above, therefore the potential importance of the role of Cl in altering the \( \text{Fe}^{3+}/\Sigma\text{Fe} \) via changing the melt NBO/T is still an open question.

**Implications for Ore-Forming Processes and Cl-Rich Arc Magmas:**

It has been proposed that onset of magnetite crystallization plays a critical role in modulating the onset of Fe-Cu sulfide saturation in arc magmas (Jenner et al. 2010). In this way, the suppressing effect of Cl on magnetite saturation may help keep the sulfide in Cl-enriched arc magmas under-saturated until an exsolved volatile phase has removed a significant quantity of Cl from the melt. From the perspective
of ore deposit formation, the timing of sulfide saturation controls the total metal budget of the causative magma; it is therefore critical that the role of Cl is understood in the context of how it alters the stability of ferric iron-bearing minerals.

Additionally, the equilibrium $\text{Fe}^{3+}/\Sigma \text{Fe}$ of the melt is significantly affected by the presence of Cl. This relationship may be the effect of two different but complimentary mechanisms - the formation of ferrous-chloride complexes in the melt as well as the formation of alkali chloride species. In either case, the removal of Cl from the melt will result in the stabilization of FeO$_{1.5}$ at the expense of FeO, provided that the system is open with respect to oxygen (or H$_2$, as the case may be). Though this initial work hints at the important relationship between Fe and Cl in felsic-intermediate melts, much more work is required to fully appreciate and understand the extent to which Cl may alter the fundamental redox behavior and phase equilibria of arc magmas.

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References


Bell, A.S., and Simon, A. (2011) Experimental evidence for the alternation of $\text{Fe}^{3+}/\Sigma \text{Fe}$ of silicate melt caused by chlorine rich aqueous volatiles. Geology


### Table 1

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<tr>
<th>MagLiq Series</th>
<th>T °C</th>
<th>Pressure (MPa)</th>
<th>Duration (Hours)</th>
<th>pH2 (bar)</th>
<th>log fO2</th>
<th>wt % Cl</th>
<th>wt % FeO</th>
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</tr>
</tbody>
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*The EPMA determined Fe contents of both the MagLiq series glasses and the SRD glasses are reported by convention as wt% “FeO”. The locations of the EPMA analytical spots used to determine the Fe and Cl concentrations in these experiments were distributed randomly throughout the melt volume of the experimental charge from portion of the melt directly adjacent to the magnetite, to the distal portions of the melt at the opposite end of the charge. The values listed in the table are the mean of 15-20 spot analyses; the ± values following the mean are the 1σ standard deviation for the population of EPM analyses.

*The values reported for the MagLiq Failed experiment are the ranges of Cl and Fe contents that were observed in the EPMA transect across the melt of the experimental charge. The approximate location of the analytical transect that produced these values is shown in Fig. 1a.

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Figure 1. The image in Figure 1a schematically shows the location of the EPMA analytical transect from the MagLiq Failed experiment (see Table 1). The experimental charge shown in the BSE image is comprised of two phases, glass (the light grey phase) and magnetite powder (the bright white phase). Figure 1b shows a plot of FeO and Cl concentrations measured along the length of the transect that is shown in Figure 1a. Distance 0.00 on the x-axis of the plot corresponds to the point labeled “Start” on the BSE image.
Figure 2 is an In-In plot of the XANES measured Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratios of the SRD Series experiments vs. the experimental $f_{O_2}$ values. The dashed line represents the slope of the homogenous ferric-ferrous equilibrium as predicted by the Kress and Carmichael equation (1991) which is shown as a frame of reference. The deviation from the predicted slope systematically becomes larger as $f_{O_2}$ increases.