Local redox gradients induced during magma mixing

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Abstract. We present an experimental study described in detail in Fiege et al. (in review). Diffusion-couple timeseries experiments between a crystal-bearing basaltic andesite and a mostly aphyric dacite (both compositions taken from Quizapu volcano, Chile) were performed to investigate the physiochemical processes at the mixing interface. In particular, we explore the evolution of redox gradient at the interface as the compositionally distinct melts move towards equilibrium. A (meta)stable gradient in fO₂ of > 1.5 log units persists in all time series experiments. We suggest that this redox gradient is the result of (1) ferrous iron liberation during cpx- and opx-dissolution in the basaltic andesite and diffusion into the dacite and (2) the formation of a charge imbalance as charged ions diffuse across the interface.

Keywords: Magma mixing, oxygen fugacity, elemental diffusion

1 Introduction

Magma mixing is ubiquitous in arc magmatic systems with intermediate compositions. However, a rigorous assessment of the various physiochemical processes during magma-magma equilibration is yet to be developed. Only a few experimental studies have explored these processes at temperatures at which at least one magma is crystal-bearing (e.g., Watson, 1982; Johnston and Wyllie, 1988). Here, we present an experimental study using magma compositions from Quizapu volcano (Chile, Ruprecht et al., 2012) to investigate the complex interplay of diffusion and phase changes at sub-liquidus conditions of two compositionally distinct magmas. In particular, we focus on elucidating redox processes at the interface between a basaltic andesite (recharge magma) and a dacite (host magma). As diffusive mass transfer is taking place, redox sensitive elements are exchanged potentially leading to a boundary layer that becomes oxidized or reduced. Significantly, the transport of iron, due to its variable valence states that are dependent on not just oxygen fugacity but also melt composition, pressure, and temperature, may induce a redox gradient as magmas mix; e.g., between a dacitic host magma and an intrusive basalt in an arc magma chamber.

We combine micro X-ray absorption near-edge structure (µ-XANES) spectroscopy at Fe K-edge (cf. Wilke et al., 2005) with two-oxide oxybarometry (cf. Ghiorso and Evans, 2008) to measure redox profiles in the run products of the diffusion-couple experiments. We evaluate the µ-XANES and oxybarometry datasets and demonstrate that redox gradients during magma mixing and partial melting may develop and may modulate mass transfer across that interface of other redox sensitive elements, such as sulfur.

2 Method, Results

2.1 Methods

Two compositions from recent eruptions at Quizapu volcano, Chile, a basaltic andesite (VQ-22A) and a dacite (VQ-37D; Ruprecht et al., 2012), were used as starting material. After separately fusing them in a 1-atm. furnace, volatile (H₂O, Cl, S) bearing glass cylinders were synthesized at 900 °C (dacite) and 1030 °C (basaltic andesite) in vertical rapid-heat rapid-quench cold-seal TZM pressure vessels at 150 MPa with intrinsic redox conditions of log(fO₂/bar) = QFM+4 ± 0.5. Finally, basaltic andesite and dacite were reloaded into the TZM (150 MPa; QFM+4) as a diffusion-couple and heated to an intermediate mixing temperature (1000 °C), which resulted in (near-) volatile saturated conditions for both compositions. The diffusion-couple experiments were rapidly heated and run for 1, 10, and 79 h before isobaric rapid-quench.

We measured glass and mineral compositions (Fe-Ti oxides, pyroxenes) via electron probe microanalyses (EPMA). X-ray maps were taken to document the changing phase assemblage near the interface. Iron µ-XANES spectra were collected on each of the experimental dactitic glasses from the three diffusion-couple experiments via line transsects from the magma-magma interface into the dacite. Spectra were collected in fluorescence mode at high spatial resolution (2 x 2 µm spot analyses). Pre-edge Fe peak fitting from ~7082 to ~7119 eV followed the procedure described in Cottrell et al. (2009). The diffusion-couple glass measurements were evaluated for Fe²⁺/ΣFe.

2.2 Results

Major element concentration profiles show a diffusion-like exchange between mafic and felsic end-members. Felsic components such as Si, Na, and K decrease in the dacitic melt near the interface. Simultaneously, mafic components such as Mg and Fe increase near the interface. During mixing, the crystallinity near the interface on the basaltic andesite side decreases continuously and slowly with time.
The crystallinity in the basaltic andesite away from the interface remains largely unaffected throughout the experiments. The dacite end-member contains minor amounts of spl. Phase assemblage maps show that cpx is the first mineral that is fully dissolved during the mixing process, followed by opx (Figure 1). Plagioclase while being dissolved continues to constitute a rigid crystal network in the basaltic andesite end-member.

Redox-sensitive rhombohedral oxides (here: il) and spinel (spl) show compositional variations associated with potential changes in redox conditions near the interface. The TiO$_2$ content of il and spl in all experiments decreases from the far field of the andesite to near the interface. The far field oxide compositions are similar to those in the starting basaltic andesite. The length scales of the variations within the basaltic andesite are significantly larger than the measured changes in crystallinity in the basaltic andesite (Figure 1), indicating that the observed redox gradient is largely decoupled from the crystal dissolution rate.

The XANES analyses on the diffusion-couple experiments reveal significant changes in Fe oxidation state, where the Fe$_3+$/$\Sigma$Fe decreases from the far field in the dacite to the interface most dramatically in the 1 h and 10 h experiments (~20 % change). In the far field, the profiles remain at a constant Fe$_3+$/$\Sigma$Fe. The longest duration experiment shows a more moderate gradient in Fe$_3+$/$\Sigma$Fe. The Fe$_3+$/$\Sigma$Fe correlates spatially with total FeO and other melt constituents.

3 Redox evolution near the interface

Results from Fe $\mu$-XANES and two-oxide oxybarometry reveal a zigzag redox trend in all run products (Figure 2). We infer fO$_2$ in the experimental charges by applying the models of Moretti (2005) and Ghiorso and Evans (2008) to the Fe $\mu$-XANES data obtained for the melt on the dacitic side and the oxide compositions in the basaltic andesite, respectively. Oxide equilibration is fast, given their small size (typically < 5 $\mu$m). In the far field at large distance away from the interface both redox trends (XANES and two-oxides) match within error the intrinsic redox of the TZM vessel (~QFM+4) and of the starting basaltic andesite dacite, providing independent constraints that the calculated variations in fO$_2$ are accurate. The relative variations within one sample are accurate to within ± 0.25 log units fO$_2$ (2 $\sigma$) as they mostly depend on the analytical uncertainties of the Ti and Fe determinations in the oxides. An absolute redox gradient at the interface of about 1.8 log units fO$_2$ is observed in all three run products and remains steady for several days and possibly weeks to months. We suggest that two mechanisms control the gradients in fO$_2$. First, mineral dissolution (in order of: cpx $\rightarrow$ opx $\rightarrow$ plag $\rightarrow$ ox)) in the basaltic andesite liberates Fe and other compatible elements (e.g., Mg). In this process, Fe with a low Fe$_3+$/$\Sigma$Fe ratio (opx: only Fe$_2^+$; cpx: low Fe$_3^+$/$\Sigma$Fe) is delivered to the melt and then diffuses preferentially along the Fe concentration gradient into the dacite establishing a gradient in Fe$_3^+$/$\Sigma$Fe in the dacite melt. The observed Fe diffusion profiles in the dacite are consistent with known Fe diffusivity in dacite melts therefore providing further evidence that release of ferrous Fe to the melt is important. However, this mechanism only partially explains the inferred redox profiles. Another mechanism is required to account for the mirrored redox gradient (i.e., oxidation) within the basaltic andesite. Thus, a second, probably dominating, mechanism that we have identified as a potential “driving force” for the observed gradient in fO$_2$ stems from the mass transfer across the interface. As ions diffuse across the interface, they introduce a charge imbalance that may lead to a net oxidation on the basaltic andesite side and net reduction on the dacite side. Hence, the observed redox gradients are probably induced during mixing between a felsic and a mafic magma because melt
constituents (such as Fe) can only follow the overall chemical gradients.

4 Implications

4.1 Magma mixing

Our experiments show that a redox gradient (> 1.5 log units) can form during magma mixing between mafic and felsic magmas. The maximum net gradient, the stability of the gradient, as well as the spatial extent of the gradient is probably significantly affected by the (pre-) mixing pressure and temperature conditions as well as compositions and fO$_2$ of the two mixing magmas. Whether the described effect of local, magma reduction/oxidation is of importance during magma evolution depends on the time scale of fractionation of such melts and the extent of mafic-felsic interfaces. While mafic enclaves provide ample surface area to develop locally reduced magma layers, they are also intricately mixed with the host felsic magma. More importantly, if the boundary layer melts are entrapped as melt inclusions, they may be responsible for some scatter in redox determined for natural samples.

4.2 Porphyry Ore deposits

Mixing-induced redox gradients have important implications for the transport of S from the mafic to the felsic magma. Mafic magmas are thought to be the main source of S in arc volcano eruptions (Keppler, 1999). Also in porphyry Cu deposits the S and most of the Cu is probably derived from mafic magmas (Halter et al., 2005; Simon and Ripley, 2011). Notably, S changes its valence state in the silicate melts from sulfide (S$^2-$) to sulfate (S$^6+$) over a narrow redox range. Thus, the observed redox gradient of > 1.5 log units across the interface can change the S speciation in the melt from almost fully oxidized to almost fully reduced, depending on the initial fO$_2$. This can cause a dramatic decrease in S solubility in the melt. Hence, sulfide phases may precipitate near the interface, limiting the transfer of S and chalcophile metals via diffusion through the melt from a mafic to a felsic magma. However, this hypothesis cannot be tested based on the experiments performed here because the fO$_2$ of the TZM runs (~QFM+4) was far above the S$^2-$ to S$^6+$ transition.

4.2 Melting of mafic precursors

To a first order, the diffusion-couple experiments can also be interpreted in light of partial melting in mafic material. Here, our experiments show that melts formed, e.g., by dehydration melting of mantle material can be characterized by Fe$_3^+$/ΣFe ratios that correspond to a ~1.5 log units lower fO$_2$ than that prevailing in the parental magma. Of course, the results from the diffusion-couple experiments are not direct analogs to mantle melting during which olivine is the most refractory phase followed by opx. Whether the melts can re-equilibrate with respect to fO$_2$ depends on the time scale of melt extraction; however, we observe metastable conditions near the interface, thus, potentially enabling the formation of a long-term oxidation gradient during melting. Regardless, non-equilibrium fO$_2$ conditions in the melt may have been underappreciated since melt extraction in the mantle or mafic cumulates occurs commonly at low melt fractions.

5 Concluding remarks

The physicochemical nature of magma-magma interaction represents a complex interplay of diffusive equilibration of the participating melts as well as crystal dissolution and precipitation near the interface. Our results show that during such equilibration processes a primary intrinsic variable, oxygen fugacity, may not be constant. Instead, large gradients of almost two orders of magnitude in fO$_2$ emerge over a lengthscale of hundreds of microns to millimeters potentially affecting (1) the fidelity of trapped melts as recorders of melt evolution in crustal magmatic
systems and during partial melting as well as (2) mass transfer of redox sensitive elements across the mixing interface. This contribution is currently in review elsewhere and future reference of this study should be to Fiege et al. (in review).

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**References**


