Magma hybridisation and diffusive exchange recorded in heterogeneous glasses from Soufrière Hills Volcano, Montserrat

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ABSTRACT
Arc volcanoes commonly show evidence of mixing between mafic and silicic magma. Melt inclusions and matrix glasses in andesite erupted from Soufrière Hills Volcano include an anomalously K₂O-rich population which shows close compositional overlap with residual glass from mafic inclusions. We suggest that these glasses represent the effects of physical mixing with mafic magma, either during ascent or by diffusive exchange during the formation of mafic inclusions. Many glasses are enriched only in K₂O, suggesting diffusive contamination by high-K mafic inclusion glass; others are also enriched in TiO₂, suggesting physical mixing of remnant glass. Some mafic inclusion glasses have lost K₂O. The preservation of this K-rich melt component in the andesite suggests short timescales between mixing and ascent. Diffusive timescales are consistent with independent petrological estimates of magma ascent time.

INTRODUCTION
Many arc volcanoes are dominated by interaction between mafic and silicic magmas. Recharge by hotter, more mafic material is frequently cited as an eruption trigger, and
transfer of volatiles may be important in both promoting mixing (e.g. Eichelberger, 1980) and advecting heat into, and remobilising, the overlying crystal-rich silicic magma (Bachmann and Bergantz, 2006). Magma mingling (incomplete mixing) produces quenched magmatic enclaves, crystal clusters and other clear disequilibrium textures (Anderson, 1976; Bacon, 1986; Clynne, 1999). Recognising the products of magma hybridisation (complete mixing) is important for understanding the relative proportions and compositions of the end-member magmas, the likely impact of repeated recharge, and the processes causing mass transfer between magmas.

Recent studies have shown that microlites of anomalously An-rich plagioclase (as well as clinopyroxene and Mg-rich orthopyroxene) in intermediate arc magmas originate in mafic magmatic enclaves or ‘mafic inclusions’ (Martel et al., 2006; Humphreys et al., 2009a). The microlites are transferred into the andesite either during mixing in the chamber (Martel et al. 2006) or by physical break-up and disaggregation of mafic inclusions by shearing during ascent (Humphreys et al., 2009a). This physical transfer of crystals will increase magma viscosity in the conduit and therefore has implications for eruption dynamics, as well as the potential to be used as a tracer of the mafic component. With effective mixing, one might also expect to see a mafic melt component. Melt inclusions and matrix glasses are commonly used to track magma evolution paths and assess magma storage conditions (e.g. Sisson and Layne, 1993; Wallace et al., 1995; Blundy et al., 2006), so it is vital to determine whether melt derived from the mafic magma is entering the andesite, and if so, in what proportions and with what chemical signature. Quantifying the extent and timescale of interaction between andesitic and mafic magma, which is thought to drive the eruption, would also be invaluable for volcano monitoring and hazard assessment. Here we examine evidence that magma mingling does involve transfer of mafic-derived melt, preserved as heterogeneity in plagioclase-hosted melt inclusions and matrix glasses.

**GEOLOGICAL BACKGROUND AND SAMPLES STUDIED**

The Soufrière Hills Volcano on Montserrat lies in the Lesser Antilles subduction zone and has been active for approximately ~300 ka (Harford et al., 2002). The most recent eruption started in 1995, with a series of pulses of dome growth and explosive activity, interrupted by long pauses when no magma was erupted. Major dome

Products from the current eruption are porphyritic andesite, with phenocrysts of hornblende, plagioclase, orthopyroxene and Fe-Ti oxides plus rhyolite glass or groundmass. Disequilibrium crystal textures are common, including rare, resorbed quartz phenocrysts, oscillatory zoning in plagioclase and hornblende, reversely zoned orthopyroxene and sieve-textured plagioclase (Murphy et al., 2000). The groundmass contains microlites of plagioclase, orthopyroxene, clinopyroxene and Fe-Ti oxides as well as rhyolitic glass, and may show extensive crystallisation, incipient devitrification and deposits of cristobalite. Macroscopic mafic inclusions have been described in detail (Murphy et al., 1998; 2000) and contain plagioclase, clinopyroxene, orthopyroxene, Fe-Ti oxides and rhyolitic interstitial glass; larger inclusions also crystallise pargasitic amphibole (Murphy et al., 1998). Many of the microlites in the andesite are derived from mafic inclusions, as are crystal clusters, i.e. mafic-derived fragments that can be recognised by texture and mineral compositions (Humphreys et al., 2009a).

RESULTS

We analysed plagioclase-hosted melt inclusions, matrix glass and residual mafic inclusion glass from 23 samples erupted between July 2001 and July 2008 (see supplementary table 1). Most of the samples represent typical andesite. Sample MVO1532d is a heterogeneous mixture of nearly microlite-free rhyolite glass containing euhedral quartz, plagioclase and hornblende, with fine-grained, crystal-rich patches with very little remaining glass. Sample preparation and analytical methods, together with the procedure used to correct for post-entrapment crystallisation (PEC) of melt inclusions, are described in the auxiliary material.

Melt inclusions

Melt inclusions are rhyolitic, with 71-79 wt% SiO₂ (see supplementary data table 2; figures show PEC-corrected values, normalised to 100% anhydrous). Compositions are similar to those reported by Edmonds et al. (2001), Harford et al. (2003) and Buckley et al. (2006). Two populations can be distinguished on the basis of K₂O...
Most inclusions have 2–3 wt% K$_2$O, increasing with SiO$_2$ and Cl contents, but a minority of inclusions has up to 6 wt% K$_2$O. For the low-K population, Al$_2$O$_3$, CaO and Na$_2$O show a scattered negative relationship with SiO$_2$. FeO, MgO and TiO$_2$ subtly increase with SiO$_2$, and also correlate with each other (e.g. figure 1d). The high-K inclusion population has lower CaO than the low-K glasses, and slightly lower Cl (figure 1). Two inclusions have high TiO$_2$ but low K$_2$O (figure 2). High-K glasses were not present in pumiceous samples.

**Matrix glasses**

Matrix glass was analysed in samples without significant groundmass crystallisation (supplementary table 1). Matrix glasses are rhyolitic, clustering at the SiO$_2$-rich end of the melt inclusion trends (75-79 wt% SiO$_2$, figure 1). There are four groups of matrix glasses: (i) high-K, low-Ti, (ii) low-K, low-Ti, (iii) high-K, high-Ti, and (iii) low-K, high-Ti compositions (figure 2). High-K matrix glasses extend to lower CaO contents than low-K glasses (figure 2). Some glasses have anomalously low MgO. High-K glasses were not present in the pumice samples.

**Mafic inclusion glass**

Residual mafic inclusion glasses are also rhyolitic (72-78 wt% SiO$_2$). In Si, Al, Fe and Na composition they are indistinguishable from the melt inclusions. However, they have distinctive high-Ti, high-K compositions (figure 2) and also show low CaO contents, similar to the other high-K glasses. Many of the residual glasses also have low MgO contents. Cl concentrations are variable but tend to be lower than in the melt inclusions (figure 1).

**DISCUSSION**

In general, the negative correlations of Al$_2$O$_3$, CaO and Na$_2$O with SiO$_2$ in the melt inclusions indicate decompression crystallisation dominated by plagioclase (e.g. Buckley et al., 2006). The positive correlation between FeO and MgO, and slight increase of both MgO and FeO with SiO$_2$ suggests minor crystallisation of orthopyroxene or hornblende as observed in the andesite. Ti-Fe variations are consistent with crystallisation of minor Ti-magnetite. The low-K matrix glasses follow mainly the same compositional trends as the low-K melt inclusions but tend towards higher K$_2$O and higher SiO$_2$, as K is enriched in the melt during groundmass
crystallisation (Harford et al., 2003). Low-K matrix glasses show decreasing MgO
with increasing SiO₂, consistent with groundmass crystallisation of orthopyroxene.
The trend of decreasing Cl with increasing K₂O in the matrix glass (figure 1f)
indicates degassing of Cl during decompression crystallisation (Edmonds et al., 2001;
Harford et al., 2003; Humphreys et al., 2009b).
The low-Ca, low-Mg compositions of the mafic inclusion residual glasses are
consistent with significant crystallisation of clinopyroxene in the mafic inclusions.
The very high K₂O contents of mafic inclusion glasses are consistent with the lower
proportions of amphibole in the mafic inclusions and their lower bulk SiO₂ contents
relative to the andesite; their high TiO₂ may be related to the high TiO₂ of the bulk
mafic inclusions.

Origin of high-K glass
While the main compositional characteristics of the glass suite are consistent with
near-surface processes (see above), the K-rich signature of some glasses is not. The
occasional high TiO₂, high-K₂O, low MgO and low CaO contents are also seen in
previously reported matrix glasses (Edmonds et al., 2001; 2002; Harford et al., 2003;
Buckley et al., 2006; see figure 1). These compositional features are largely shared by
the residual mafic inclusion glasses.

The anomalous glass compositions cannot be caused by boundary layer effects
during melt inclusion entrapment (Baker, 2008) because only slowly diffusing
incompatible elements should be enriched in the melt boundary layer, whereas K⁺
diffusivities are rapid (Jambon, 1983). Similarly, post-entrapment crystallisation of
host plagioclase should result in coupled increases of MgO, TiO₂ and K₂O with
decreasing CaO, which are not observed, and cannot account for anomalous matrix
glass compositions.

K-rich glasses or crystalline products have been ascribed to grain-boundary
partial melting of mafic cumulate nodules (Dungan and Davidson, 2004; Heliker,
1995) or assimilation of biotite-rich cumulates (Reubi and Blundy, 2008), with K-rich
and host melts mixing during subsequent nodule break-up. However, cumulate
nodules are relatively rare in Soufrière Hills andesite and were not observed in any of
the samples studied, while the high-K glasses are texturally indistinguishable from
‘normal’ glasses and their host crystals are not obviously xenocrystic. Finally, K-rich
glasses are also found in mafic inclusions, which are widely agreed to form by rapid
quenching against a cooler host (e.g. Wager and Bailey 1953; Yoder 1973).

*Buckley et al.* (2006) ascribed the high-K compositions to hornblende
breakdown during slow magma ascent and mixing between more- and less-evolved
melts. Mass balance between the dissolving hornblende and the observed rims (cpx +
opx + plag + oxides) indicated that melts modified by hornblende breakdown should
thus be compositionally variable, with high TiO₂ and MgO but low SiO₂ and FeO.
The melts should all have high K₂O, Na₂O and Cl (*Buckley et al.*, 2006). Neither of
their predicted trends fits with all the observed compositional variations (figure 1).

Interstitial melts in hornblende breakdown rims (*Buckley et al.*, 2006) actually show
both high-K and low-K compositions (figure 1a), not just high-K compositions as
expected. We therefore conclude that decompression breakdown of hornblende cannot
adequately describe the high-K glasses.

**Magma hybridisation and diffusive contamination**

We propose that the K-rich melts are derived from, or affected by mixing with
intruding mafic magma. The K-rich compositions are similar to those of mafic
inclusion residual glass, and incorporation of K-rich melt into the host matrix is
consistent with transfer of microlites into the andesite groundmass by disaggregation
of mafic inclusions (*Humphreys et al.*, 2009a). However, K₂O-TiO₂ concentrations
demonstrate the presence of four distinct glass compositions (see earlier; figure 2): (i)
low-K, low-Ti; (ii) low-K, high-Ti; (iii) high-K, high-Ti; and (iv) high-K, low-Ti.
This indicates that the mafic inclusion glasses are, for the most part, not being
transferred unmodified into the host andesite, and suggests diffusive modification.

Breaking open partially crystalline mafic inclusions would allow interaction between
host (rhyolite) melt from the andesite and residual rhyolite from the interior of the
mafic inclusions. Similarly, complete disaggregation of mafic inclusions would result
in physical transfer of K-rich, Ti-rich residual rhyolite, which can be modified by
diffusive re-equilibration with the host melt. Diffusion of TiO₂ is much slower than
that of K₂O (see later), so residual mafic glass that has lost K₂O by diffusion still
retains its high-Ti signature, whereas the high-K host rhyolite cannot gain TiO₂ by
diffusion (figure 2). The result is anomalously K-rich (but Ti-poor) host rhyolite melt,
and K-poor (but Ti-rich) residual mafic inclusion glasses. This process explains the
lack of ubiquitous Ti-enrichment of high-K melt inclusions and matrix glasses
compared with mafic inclusion glass. Once a pocket of K-rich melt is present in the matrix of the andesite, it can be incorporated into melt inclusions by sealing of proto-inclusions during ascent-driven crystallisation (see Humphreys et al., 2008, figure 11).

**Timescales of between mixing and eruption**

The glass compositions and distribution can give further insight into the physical processes involved in transfer of material. For example, the lack of K-rich glasses in pumiceous samples (see earlier) implies that K-enrichment occurs during slow ascent. Many of the K-rich compositions are matrix glass, with relatively few high-K melt inclusions. This also suggests that transfer occurs primarily during low-pressure ascent and crystallisation, and could be explained by lower shear stresses in the conduit during rapid ascent of less viscous, less crystalline magma (e.g. Melnik and Sparks 2005) compared with the highly viscous, strongly crystalline magma that erupts slowly during dome growth.

Elemental diffusivities can be used to assess the timescales of this process (Sparks et al. 1977; Baker, 1991). Alkali and alkaline earth diffusivities ($D$) in anhydrous rhyolite are $D_{Na} \sim 1.6 \times 10^{-6}$ cm$^2$/s, $D_{K} \sim 8.9 \times 10^{-8}$ cm$^2$/s, and $D_{Ca} \sim 4.0 \times 10^{-10}$ cm$^2$/s at 900 °C (Jambon 1983). A first-order approximation of timescales ($t$) can be made, ignoring the effects of possible differences in melt H$_2$O content, from $x \sim 2\sqrt{Dt}$, where $x$ is the diffusion lengthscale, here taken to be 1 cm. Diffusive timescales are 43 hours ($Na^+$), 32 days ($K^+$) and 20 years ($Ca^{2+}$). In other words, alkaline earth diffusion is slow relative to alkalis; diffusion of highly charged ions (e.g. Ti$^{4+}$) should be even slower than the alkaline earths (Henderson et al. 1985). Diffusive contamination of alkalis should therefore be rapid, but modification of other elements would be prohibitively slow (Baker, 1991). The K-enrichment of the rhyolite matrix of the host andesite must therefore have occurred ~1 month or less prior to eruption of the magma at the surface, in order to preserve the high-K signature. This is consistent with timescales estimated by preservation of Fe-Ti oxide zoning (Devine et al. 2003) and decompression breakdown rims on hornblende (Rutherford and Devine 2003). The few high-Ti, low-K glasses, and the wide range of K$_2$O contents of residual mafic inclusion glasses (figure 2) may reflect a spread to longer timescales, allowing complete or partial re-equilibration of K$_2$O with the host rhyolite. We also note that the K$_2$O contents of mafic inclusion and high-K host melts
are similar, whereas a diffusion couple should give slightly lower K$_2$O contents in the host melt. There are two possible explanations for this: (i) the mafic inclusion glasses are already diffused and their observed compositions are not primary, or (ii) the high K$_2$O in the host rhyolite represents an uphill diffusion ‘spike’ similar to that observed in experimental diffusion couples (Bindeman and Davis 1999; van der Laan et al. 1994). In either case, this observation reinforces the short timescales between mixing and eruption.

The estimated diffusion timescales also suggest that Na$_2$O contents would quickly be homogenised by diffusion between host andesite and mafic inclusions, while original CaO contents should be preserved. We would also anticipate rapid diffusion of volatiles (e.g. CO$_2$ and H$_2$O), particularly in more H$_2$O-rich melt (Baker et al. 2005). It is difficult to assess the effects of mixing and diffusion on Ca and Na as these elements are compatible in the crystallising assemblage and therefore strongly affected by fractionation of plagioclase, whereas K is strongly incompatible. However, the K-enriched glasses are slightly depleted in CaO relative to the normal glasses, as is the mafic inclusion residual glass. The different diffusivities of CaO and K$_2$O are not consistent with diffusive contamination of both elements: timescales long enough for significant Ca diffusion would also eliminate any K$_2$O signature. The lower CaO contents cannot be produced by crystallisation of quartz, or diffusion gradients around growing plagioclase or pyroxene grains, as discussed earlier. We suggest that the lower CaO might be related to continued crystallisation of plagioclase.

CONCLUSIONS

Glass compositional heterogeneity from Soufrière Hills Volcano, Montserrat, is interpreted as the result of mingling between hotter, mafic magma and the host andesite. High-K$_2$O melt inclusions and matrix glasses in the andesite overlap with the compositions of residual glass from mafic inclusions. However, K$_2$O and TiO$_2$ contents are decoupled: many high-K melt inclusions do not show high Ti as seen in residual mafic inclusion glasses. This can be explained by diffusive exchange between disaggregated mafic inclusion melt and host matrix melt. The host rhyolite gains K$_2$O from mafic inclusions, but the original low TiO$_2$ contents are unchanged. Conversely, high-Ti glasses with normal K$_2$O contents probably represent residual mafic inclusion glass that has lost K$_2$O by diffusion. The preservation of such heterogeneity can be
used to estimate the timescales between mingling and magma ascent to the surface. The timescales necessary to preserve K heterogeneity are on the order of a month, which is consistent with magma ascent times estimated from hornblende breakdown and Fe-Ti oxides.

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**Figures**

Figure 1

Compositions of melt inclusions, matrix glasses and mafic inclusion residual glasses. Melt inclusions (diamonds) and matrix glasses (circles) are divided into high-K (open symbols) and low-K (filled symbols) compositions. Crosses represent mafic inclusion glasses. Grey symbols represent previously published glasses from Soufrière Hills (pluses, Edmonds et al., 2001, 2002; squares, Harford et al., 2003; triangles, Buckley et al., 2006). Grey dashes: glasses in hornblende breakdown rims (Buckley et al., 2006). Large arrows indicate the schematic effects of hornblende breakdown reactions (reactions 2 and 3, Buckley et al., 2006), or the effect of 5% post-entrapment crystallisation of plagioclase (pl).

Figure 2

Decoupled compositional variations in K$_2$O and TiO$_2$ for all glasses. Thick grey arrows indicate how diffusive contamination of K$_2$O affects melt compositions. TiO$_2$ is unaffected because of its very low diffusivity. Symbols as for figure 1.
Figure 2

End-member 1 (rhyolite MI & mg from host andesite)

Gain of K$_2$O by host rhyolite

Diffusive loss of K$_2$O from mafic inclusion glass

End-member 2 (residual glass from mafic inclusions)