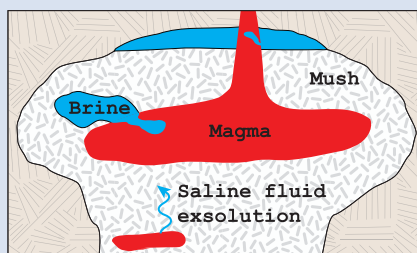# Chlorine isotope ratios record magmatic brine assimilation during rhyolite genesis

E. Ranta[1*], S.A. Halldórsson[1], J.D. Barnes[2], K. Jónasson[3], A. Stefánsson[1]

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Abstract

Magmatic volatile phases within crustal silicic magma domains influence key volcanic processes such as the build up to eruptions and formation of magmatic-hydrothermal ore deposits. However, the extent and nature of fluid-melt interaction in such environments is poorly understood, as geochemical signals in volcanic rocks originating from pre-eruptive volatile processes are commonly overprinted by syn-eruptive degassing. Here, we use $\delta^{37}Cl$ as a conservative tracer of brine-melt interaction on a broad suite of silicic volcanic rocks from Iceland. We find that the $\delta^{37}Cl$ values of silicic rocks are systematically shifted to more negative values compared to associated basalts and intermediate rocks by up to 2.9 ‰. These large shifts cannot be explained by well known processes inherent to silicic magma genesis, including crustal assimilation, mineral-melt fractionation and syn-eruptive degassing. Instead, we show that low $\delta^{37}Cl$ values in silicic rocks can be attributed to assimilation of magmatic brines that are formed and stored in long lived crustal magma mushes. Our results indicate that magmatic brine assimilation is a fundamental, but previously unrecognised part of rhyolite genesis.

Introduction

Magmatic volatiles play a fundamental part during silicic magma genesis and the formation of associated ore deposits. Chlorine is among the most abundant volatile elements in igneous rocks and may become concentrated enough in late stage silicic melts to exsolve and form hydrosaline liquids, *i.e.* high density Cl-enriched aqueous fluids or hydrosaline brines (Webster, 2004). As chlorine is a hydrophile element, its isotopic fingerprint has been used to trace volatile sources in igneous rocks and hydrothermal fluids (Barnes *et al.*, 2008; Li *et al.*, 2015). Lavas associated with subduction zones and oceanic islands have a range of $\delta^{37}Cl$ values from −3 to +3 ‰, likely due to incorporation of subduction fluids, recycled marine sediments and altered oceanic crust into the mantle (John *et al.*, 2010; Barnes and Sharp, 2017). In contrast, the depleted upper mantle (DMM) has a restricted $\delta^{37}Cl$ variability of −0.2 ± 0.3 ‰ (Sharp *et al.*, 2013), reflecting the limited $\delta^{37}Cl$ fractionation from high temperature magmatic processes (Schauble *et al.*, 2003). The majority of chlorine isotope studies on igneous rocks have been conducted on basaltic rocks, whereas published $\delta^{37}Cl$ data for silicic rocks is limited, with 40 out of 44 published analyses coming from a single volcanic system, the Mono Craters, USA (Barnes *et al.*, 2014). This study was designed to explore if and how $\delta^{37}Cl$ systematics can provide new insights into silicic magmatic processes such as assimilation and brine-melt interaction, using Iceland as a test site.

Chlorine Isotope Systematics in Silicic Rocks

We present new $\delta^{37}Cl$ and $\delta^{18}O$ data for a sample set (n = 16) focusing on neovolcanic extrusive silicic (SiO_2 > 65 wt. %) and intermediate (SiO_2 = 52-65 wt. %) rocks from Iceland (Tables S-1, S-2). Together with previously published $\delta^{37}Cl$ and $\delta^{18}O$ data on Icelandic basalts (Halldórsson *et al.*, 2016), the samples represent the full chemical range between subalkaline-tholeiitic rift zone, and transitional to alkaline propagating rift and off-rift magma suites in Iceland (Fig. S-1), spanning a SiO_2 range of 44.4-77.7 wt. % and Cl concentrations between 17 and 3988 ppm (Figs. 1, S-2). The samples cover the main types of silicic rocks in Iceland, *i.e.* dacites and alkaline and subalkaline rhyolites (Jónasson, 2007), and include both obsidians and tephras (*i.e.* products of effusive *vs.* explosive eruptions). All studied volcanoes are situated on land and are free of seawater influence (Halldórsson *et al.*, 2016).

Significant Cl variation is present at any given SiO_2 content in the basaltic (17–1269 ppm), intermediate (130–942 ppm) and silicic (282–3988 ppm) samples (Fig. S-2). These ranges are similar to published Cl concentrations in melt inclusions (MIs) from corresponding locations (Fig. S-3). The $\delta^{37}Cl$ value of all analysed samples (n = 14) vary from −1.9 to +1.3 ‰ (1σ = ±0.2 ‰) (Fig. 1a,b). The basaltic (n = 3) and intermediate (n = 4) samples have $\delta^{37}Cl$ values between −0.4 and +1.3 ‰, overlapping with the known range of Icelandic basalts of −0.6 to +1.4 ‰ (Halldórsson *et al.*, 2016). In contrast, the $\delta^{37}Cl$ values of
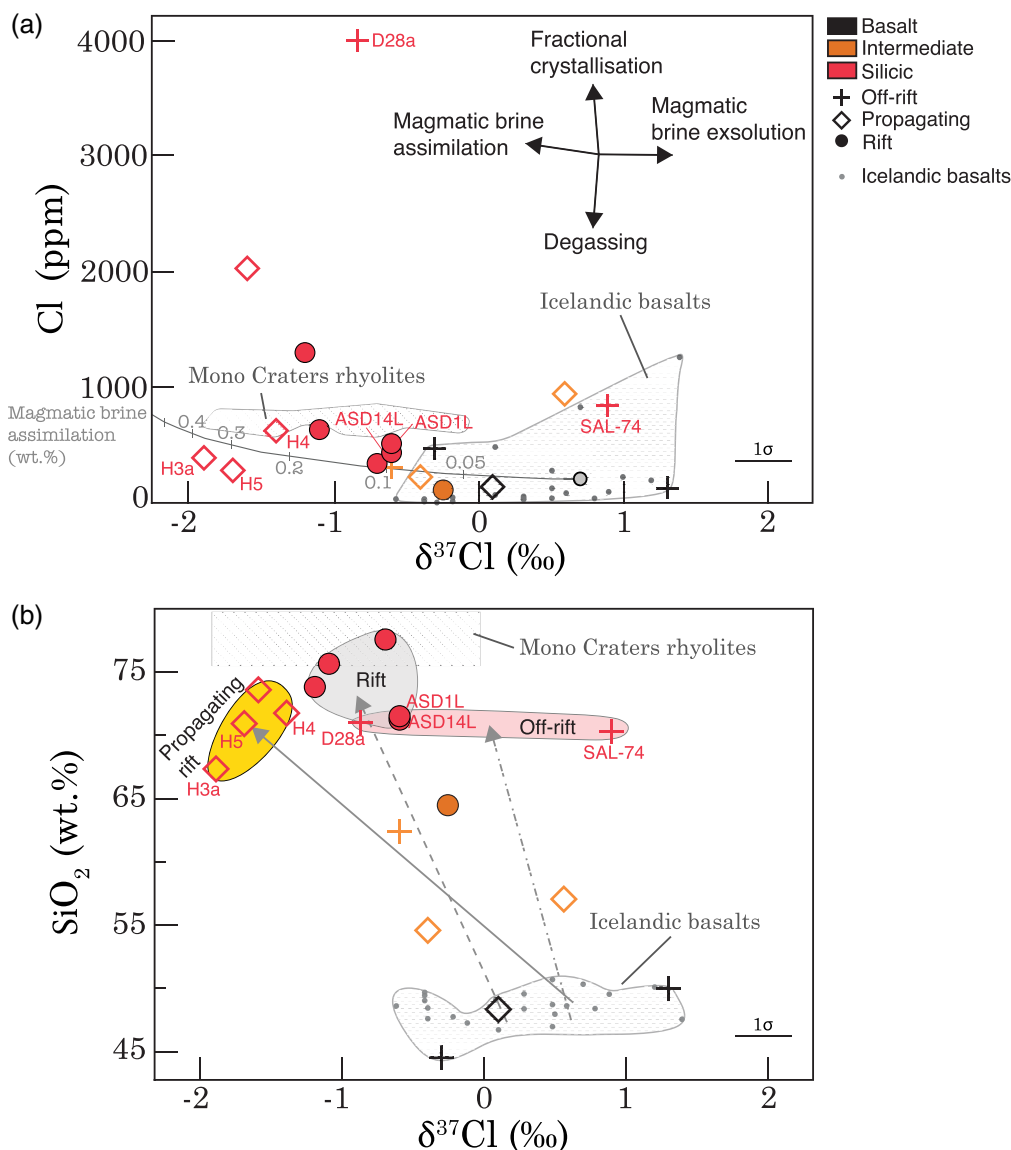
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Figure 1 Chlorine isotope variations *vs.* **(a)** Cl concentrations and **(b)** SiO_2. Silicic rocks in Iceland have lower $\delta^{37}Cl$ values than basalts (data from Halldórsson *et al.*, 2016), overlapping with rhyolites from the Mono Craters, USA (Barnes *et al.*, 2014). Arrows in **(a)** indicate the effects of the small equilibrium isotope fractionations caused by fractional crystallisation and degassing, and the large kinetic isotope fractionation during magmatic brine exsolution (Fortin *et al.*, 2017) and assimilation on the $\delta^{37}Cl$ and Cl composition of silicic melts. The gray curve in **(a)** shows the effect of magmatic brine assimilation (in wt. %) on the Cl-$\delta^{37}Cl$ values of a hypothetical rhyolite melt with an average propagating rift basalt $\delta^{37}Cl$ value of +0.7 ‰. The negative $\delta^{37}Cl$ shifts between silicic rocks and basalts are illustrated in **(b)** by arrows anchored at the average SiO_2 concentrations and $\delta^{37}Cl$ values of the rift, propagating rift and off-rift basalts. The 1σ uncertainty is ±0.2 ‰ for $\delta^{37}Cl$.

the silicic samples from this study (n = 8) and those previously published (n = 3; Halldórsson *et al.*, 2016) deviate from the basaltic-intermediate range towards more negative values of −1.9 to −0.6 ‰ (Fig. 1b), except for a single outlier (SAL-74) with $\delta^{37}Cl$ = +0.9 ‰.

Local $\delta^{37}Cl$ variability in Icelandic rhyolites appears to be small (≤0.5 ‰ for Hekla: H3, H4, H5; and Askja: ASD1L, ASD14L) compared to the large range of −1.9 to 0.0 ‰ reported for the Mono Crater rhyolites (Barnes *et al.*, 2014) (Fig. 1). Rift, propagating rift and off-rift samples define distinct fields in the SiO_2-$\delta^{37}Cl$ and $\delta^{18}O$-$\delta^{37}Cl$ diagrams (Figs. 1b, 2), suggesting a possible correlation between volcano-tectonic setting and $\delta^{37}Cl$ (see Supplementary Information S-2).

Origin of Large $\delta^{37}Cl$ Variability: Sources Versus Processes

Our dataset demonstrates that silicic rocks in Iceland have more negative $\delta^{37}Cl$ values relative to associated basalts and intermediate rocks. Whereas basalts inherit the $\delta^{37}Cl$ signatures of their mantle sources (Halldórsson *et al.*, 2016), the shift to more negative $\delta^{37}Cl$ values in silicic rocks must reflect a process or a combination of processes taking place during rhyolite genesis, such as mineral-melt fractionation, degassing and/or assimilation.

Rayleigh $\delta^{37}Cl$ fractionations between HCl(g), minerals and silicic melt are expected to be small, based on theoretical equilibrium fractionation factors of Schauble *et al.* (2003)
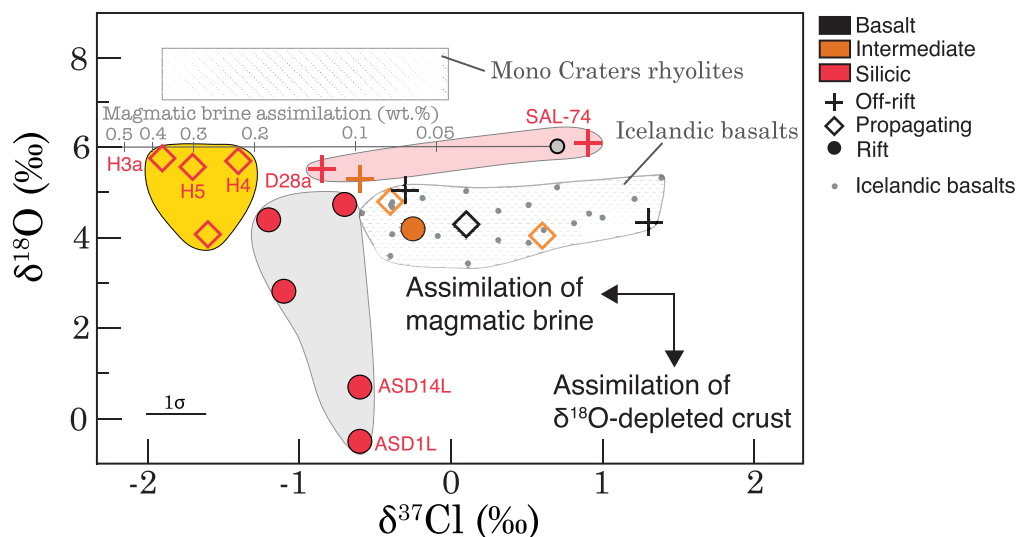
Figure 2 The $\delta^{18}O$-$\delta^{37}Cl$ systematics of silicic rocks. Low $\delta^{18}O$ values of rift-related silicic rocks result from assimilation of hydrothermally altered, $\delta^{18}O$-depleted crust. Lack of correlation between $\delta^{18}O$ and $\delta^{37}Cl$ indicates that negative $\delta^{37}Cl$ values of rhyolites are not caused by crustal assimilation. The gray line shows the effect of magmatic brine assimilation in wt. % (Supplementary Information S-4). Mono Craters field is drawn after data reported in Newman *et al.* (1988) and Barnes *et al.* (2014). The 1σ uncertainty is ±0.2 ‰ for $\delta^{37}Cl$, and smaller than the size of the symbols for $\delta^{18}O$.

extrapolated to magmatic temperatures ($\Delta^{37}Cl_{mineral-melt} \approx \Delta^{37}Cl_{vapour-melt} \approx 0.2$ ‰ at 600 °C). Thus, even extreme cases of 90 % Cl removal by fractional apatite crystallisation or open system degassing of HCl(g) only fractionate the $\delta^{37}Cl_{melt}$ values by about −0.5 ‰. However, modal apatite abundances in our samples are low (<2 %) and similar Cl concentrations in MIs and matrix glasses imply an insignificant degree of syn-eruptive chlorine degassing (Fig. S-3). Therefore, the combined effect of fractional crystallisation and degassing on $\delta^{37}Cl_{melt}$ values of our samples is negligible (<0.2 ‰). Moreover, similar $\delta^{37}Cl$ values of both obsidians and tephras indicate that $\delta^{37}Cl$ fractionation is independent of eruption type and occurs within the crustal magma domain prior to eruptions.

To test if assimilation of altered basaltic crust causes negative $\delta^{37}Cl$ shifts between rhyolites and basalts, we analysed the $\delta^{18}O$ compositions of our samples (Fig. 2). In Iceland, low $\delta^{18}O_{rock}$ values relative to pristine basaltic values (+4.8 to +5.8 ‰; Thirlwall *et al.*, 2006) are used to recognise assimilation (or partial melting) of altered crust, which has been shifted to low $\delta^{18}O$ signatures (≤+2 ‰) by hydrothermal alteration with low $\delta^{18}O$ meteoric water (Gautason and Muehlenbachs, 1998). We note that basalts and intermediate rocks from all three volcanic settings display $\delta^{18}O$ values between +3.4 and +5.2 ‰ (Fig. 2), typical for Icelandic basalts (Thirlwall *et al.*, 2006). Silicic rocks from the propagating rift and off-rift zones have basalt-like $\delta^{18}O$ values of +4.0 to +6.1 ‰, whereas the lower and more variable $\delta^{18}O$ values from −0.5 to +4.7 ‰ in the rift zone rhyolites (Fig. 2) indicate variable degrees of crustal assimilation.

However, there is no correlation between $\delta^{37}Cl$ and $\delta^{18}O$ (Fig. 2). For example, silicic samples with the most negative (H3a) and positive $\delta^{37}Cl$ values (SAL-74) have normal $\delta^{18}O$ values, while the two samples with the lowest $\delta^{18}O$ values (ASD1L, ASD14L) show relatively small $\delta^{37}Cl$ shifts. This indicates that the negative $\delta^{37}Cl$ shifts in Icelandic rhyolites are not caused by assimilation of $\delta^{18}O$-depleted altered crust, but by an additional process. Conversely, this suggests that hydrothermally altered crust in Iceland has a basalt-like $\delta^{37}Cl$ range, consistent with the basalt-like $\delta^{37}Cl$ values in Icelandic hydrothermal fluids (Stefánsson and Barnes, 2016) and the lack of $\delta^{37}Cl$ fractionation resulting from hydrothermal alteration (Cullen *et al.*, 2019). In

contrast, boron another fluid-mobile element, displays anomalous positive $\delta^{11}B$ values in Icelandic silicic rocks that correlate with decreasing $\delta^{18}O$, and that have thus been explained by crustal assimilation (Rose-Koga and Sigmarsson, 2008).

Extensive previous work on the Hekla volcano demonstrates that for non-volatile element stable isotope systems studied thus far, fractionations between rhyolites and basalts are either negligible or can be explained by fractional crystallisation (Supplementary Information S-4). Our silicic Hekla samples (H3a, H4, H5) display the largest $\delta^{37}Cl$ shifts (up to −2.9 ‰) compared to corresponding basalts (Fig. 1). This comparison highlights that $\delta^{37}Cl$ selectively records a process relating to the pre-eruptive volatile history of silicic magmas that is not recorded by other, non-volatile stable isotope systems. Indeed, a complicated pre-eruptive volatile history is also reflected by high Cl variability in Icelandic propagating rift and rift rhyolites (50 to 2600 ppm) (Fig. S-2), likely reflecting a combination of fractional crystallisation, partial melting, accumulation of fractional melts from volatile heterogeneous sources as well as episodic exsolution and resorption of magmatic volatile phases, including magmatic brines (Webster *et al.*, 2019; Supplementary Information S-3; Fig. 3a).

Chlorine isotope systematics provide a strict constraint on the nature of a potential assimilant, which must have a negative $\delta^{37}Cl$ and elevated concentrations of Cl compared to the rhyolites. These criteria best match a fluid assimilant with high Cl concentrations ($Cl_{assimilant}/Cl_{rhyolite} \gg 1$) and low $\delta^{37}Cl$ (<−3 ‰) (Fig S-4). Magmatic hydrosaline fluids have by definition high Cl concentrations and may acquire highly negative $\delta^{37}Cl$ values during exsolution from dacitic (and more silicic) melts due to kinetic diffusion effects, that cause considerable fractionation of up to $\Delta^{37}Cl_{fluid-melt} = -5$ ‰ even at high temperatures (Fortin *et al.*, 2017) (Fig. 3b). Therefore, in terms of predicted Cl-$\delta^{37}Cl$ values, magmatic brine is an assimilant that near-perfectly matches the observed $\delta^{37}Cl$ shifts in Icelandic rhyolites (Fig. S-4). Anomalously negative $\delta^{37}Cl$ values of down to −5.6 ‰ have been reported for saline fluid inclusions in porphyry copper and iron oxide-copper-gold deposits, showing that low $\delta^{37}Cl$ brines do exist in magmatic-hydrothermal environments (Gleeson and Smith, 2009; Nahnybida *et al.*, 2009).
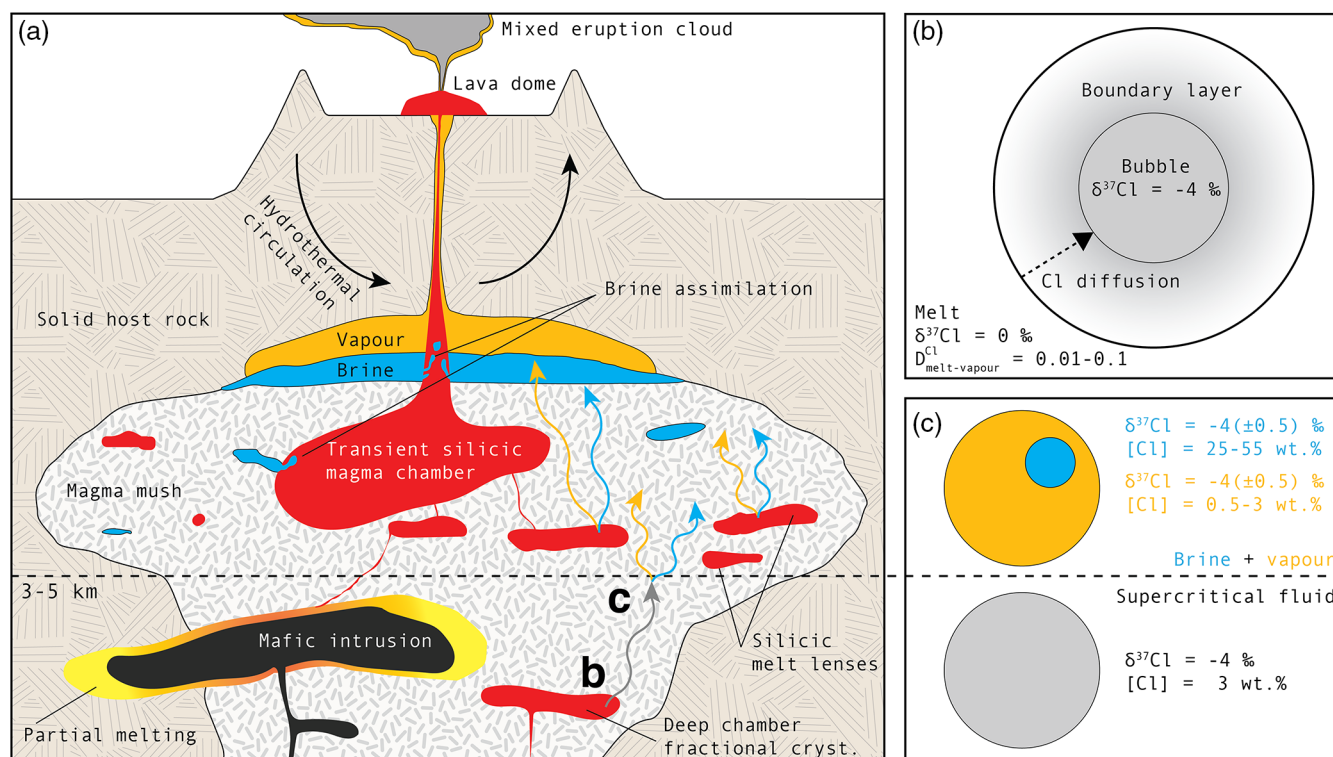
Figure 3   **(a)** A model of magmatic brine formation and assimilation in a long lived upper crustal magma mush. **(b)** Magmatic fluids exsolve from silicic melts during late stage crystallisation and acquire negative $\delta^{37}Cl$ values through kinetic fractionation (Fortin *et al.*, 2017). **(c)** Decompression-driven phase separation of a supercritical fluid produces a NaCl-rich brine and a NaCl-poor vapour with a maximum fractionation of $\Delta^{37}Cl_{liquid-vapour} = \pm0.5$ ‰ (Liebscher *et al.*, 2006).

Assimilation of Magmatic Brines

The presence of magmatic brine is a widely reported phenomenon associated with silicic and intermediate magmas in the upper crust. For example, brines are found in magmatic fluid inclusions and are implicated in the formation of magmatic-hydrothermal ore deposits globally (Audétat *et al.*, 2008), including in Iceland (Kremer and Bird, 2018). Crystallisation of silicic melts that stall in the crust lead to late stage exsolution of magmatic brines or hydrosaline fluids. Magmatic brines may form by direct exsolution from melts with moderate Cl/H_2O ratios (>0.05 for granitic melts; Webster, 2004) at pressures below about 1.5 kbar, by phase separation of a magmatic fluid into low NaCl vapour and a high NaCl brine (up to NaCl > 85 wt. %) during decompression (Fig. 3c), or by condensation of magmatic vapour (Webster and Mandeville, 2007). Magmatic brines are less dense and stable to lower temperatures compared to melts, and once formed, may accumulate in pore space or pool in roof zones of magma mushes forming lenses (Fig. 3a) that can stay stable for over 1 Myr (Blundy *et al.*, 2015; Afanasyev *et al.*, 2018; Edmonds and Woods, 2018). Individual accumulations of silicic melts form over short time scales (0.01 to 1 kyr time scales) compared to the long lifetimes of the silicic magma mushes that they are part of (100 kyr – 1 Myr time scales) (Padilla *et al.*, 2016; Cooper, 2019). Thus, cycles of silicic melt production and crystallisation lead to repeated production and accumulation of magmatic brines in long lived magma mushes.

Our samples are chlorine undersaturated, similar to the majority of felsic melt inclusions globally (Webster *et al.*, 2019). We envision that such chlorine undersaturated melts may, prior to or during eruptions, assimilate ambient low $\delta^{37}Cl$ magmatic brines that have been formed by previous generations of silicic

intrusions within the same, long lived silicic magma mush (Fig. 3a). Our bulk assimilation model shows that modest amounts (*ca.* 0.5 wt. %) of addition of magmatic brines with $NaCl_{equivalent} = 16.5$ wt. % and $\delta^{37}C_{fluid} = -4$ ‰ is sufficient to explain the maximum observed $\delta^{37}Cl$ shift of -2.9 ‰ between silicic rocks and basalts in our samples (Figs. 1b, S-4, S-5). Assimilation of brines has been previously demonstrated to take place in submarine basalts, that may directly assimilate seawater-derived brines (Kendrick *et al.*, 2013), and in silicic melts, where surplus Cl contents have been interpreted as assimilation of hydrosaline fluids of unknown origin (Webster *et al.*, 2019).

The common association of silicic magmas with brines and the dominantly negative $\delta^{37}Cl$ signatures observed in silicic volcanic rocks that are difficult to reconcile with other known magmatic processes suggest that magmatic brine assimilation may be a fundamental process in silicic, long lived magma mushes. Our results highlight that little is still known about the storage and evolution of hydrosaline liquids in magma mushes. The details of physical and chemical interactions between brines and melts should be a fruitful target of future research aiming to improve our understanding of silicic magmatism. Finally, we note that low $\delta^{37}Cl$ magmatic vapours and/or liquids residing in the roof zones of magma mushes may become incorporated in eruption clouds or shallow hydrothermal systems (Fig. 3a). This process could, instead of direct degassing of magmatic Cl, offer an alternative explanation to the association of volcanic activity with negative $\delta^{37}Cl$ signatures in thermal springs and fumaroles in Guadeloupe, Martinique (Li *et al.*, 2015) and the Izu-Bonin-Mariana arc (Barnes *et al.*, 2008) as well as volcanic gases in Stromboli, Italy (Liotta *et al.*, 2017).

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Additional Information

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