

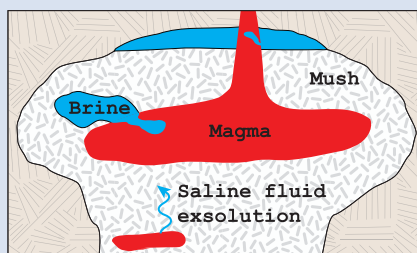
# Chlorine isotope ratios record magmatic brine assimilation during rhyolite genesis

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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  $\delta^{37}\text{Cl}$  as a conservative tracer of brine-melt interaction on a broad suite of silicic volcanic rocks from Iceland. We find that the  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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.

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## 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  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  variability of  $-0.2 \pm 0.3$  ‰ (Sharp *et al.*, 2013), reflecting the limited  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  data for a sample set ( $n = 16$ ) focusing on neovolcanic extrusive silicic ( $\text{SiO}_2 > 65$  wt. %) and intermediate ( $\text{SiO}_2 = 52\text{--}65$  wt. %) rocks from Iceland (Tables S-1, S-2). Together with previously published  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  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  $\text{SiO}_2$  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 tephra (*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  $\text{SiO}_2$  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  $\delta^{37}\text{Cl}$  value of all analysed samples ( $n = 14$ ) vary from  $-1.9$  to  $+1.3$  ‰ ( $1\sigma = \pm 0.2$  ‰) (Fig. 1a,b). The basaltic ( $n = 3$ ) and intermediate ( $n = 4$ ) samples have  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  values of

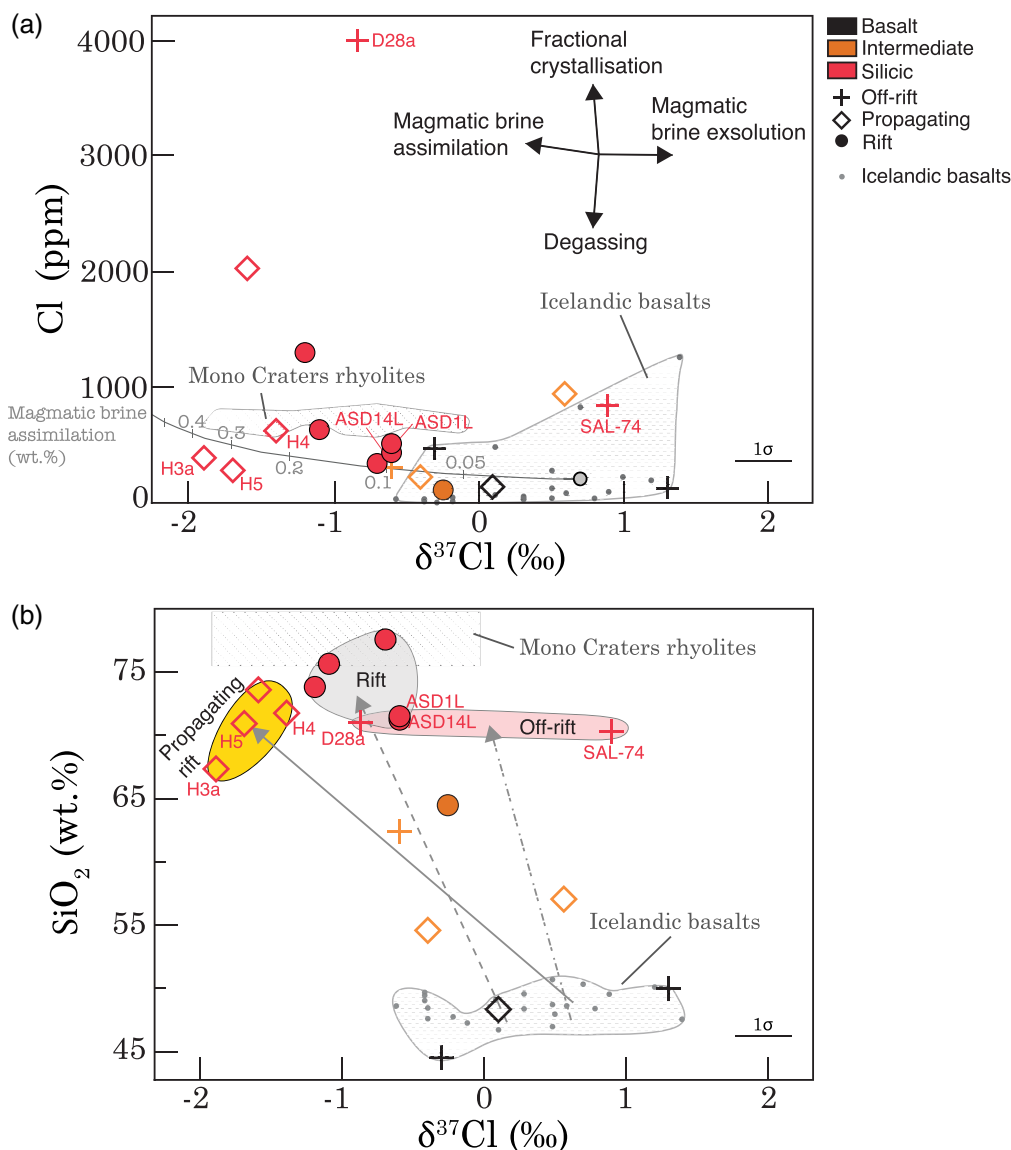
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**Figure 1** Chlorine isotope variations vs. (a) Cl concentrations and (b)  $\text{SiO}_2$ . Silicic rocks in Iceland have lower  $\delta^{37}\text{Cl}$  values than basalts (data from Halldórsson *et al.*, 2016), overlapping with rhyolites from the 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  $\delta^{37}\text{Cl}$  and Cl composition of silicic melts. The gray curve in (a) shows the effect of magmatic brine assimilation (in wt. %) on the Cl- $\delta^{37}\text{Cl}$  values of a hypothetical rhyolite melt with an average propagating rift basalt  $\delta^{37}\text{Cl}$  value of  $+0.7$  ‰. The negative  $\delta^{37}\text{Cl}$  shifts between silicic rocks and basalts are illustrated in (b) by arrows anchored at the average  $\text{SiO}_2$  concentrations and  $\delta^{37}\text{Cl}$  values of the rift, propagating rift and off-rift basalts. The  $1\sigma$  uncertainty is  $\pm 0.2$  ‰ for  $\delta^{37}\text{Cl}$ .

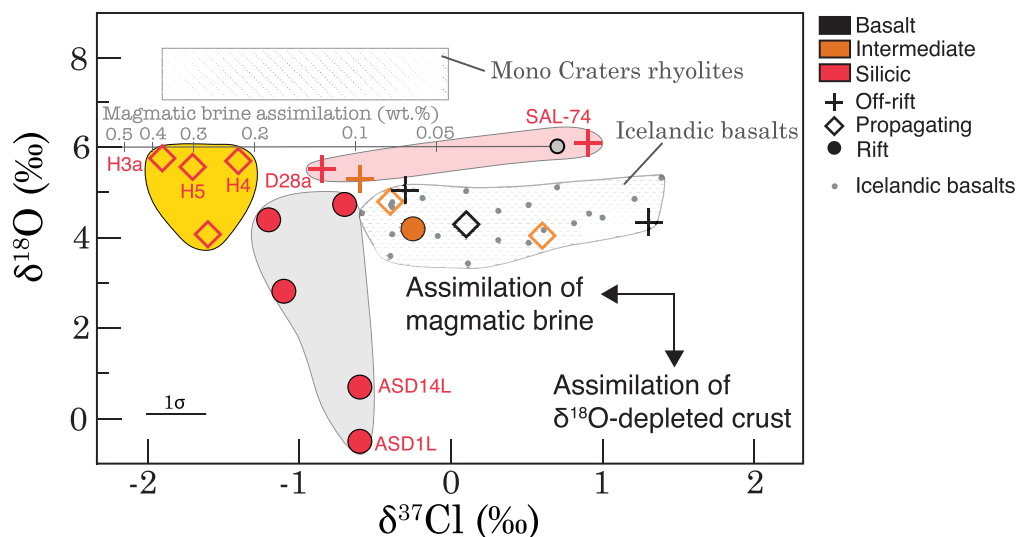
the silicic samples from this study ( $n = 8$ ) and those previously published ( $n = 3$ ; Halldórsson *et al.*, 2016) deviate from the basaltic-intermediate range towards more negative values of  $-1.9$  to  $-0.6$  ‰ (Fig. 1b), except for a single outlier (SAL-74) with  $\delta^{37}\text{Cl} = +0.9$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

Local  $\delta^{37}\text{Cl}$  variability in Icelandic rhyolites appears to be small ( $\leq 0.5$  ‰) 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  $\text{SiO}_2$ - $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$ - $\delta^{37}\text{Cl}$  diagrams (Figs. 1b, 2), suggesting a possible correlation between volcano-tectonic setting and  $\delta^{37}\text{Cl}$  (see Supplementary Information S-2).

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

Our dataset demonstrates that silicic rocks in Iceland have more negative  $\delta^{37}\text{Cl}$  values relative to associated basalts and intermediate rocks. Whereas basalts inherit the  $\delta^{37}\text{Cl}$  signatures of their mantle sources (Halldórsson *et al.*, 2016), the shift to more negative  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  fractionations between  $\text{HCl(g)}$ , minerals and silicic melt are expected to be small, based on theoretical equilibrium fractionation factors of Schauble *et al.* (2003)



**Figure 2** The  $\delta^{18}\text{O}$ - $\delta^{37}\text{Cl}$  systematics of silicic rocks. Low  $\delta^{18}\text{O}$  values of rift-related silicic rocks result from assimilation of hydrothermally altered,  $\delta^{18}\text{O}$ -depleted crust. Lack of correlation between  $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$  indicates that negative  $\delta^{37}\text{Cl}$  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  $1\sigma$  uncertainty is  $\pm 0.2\text{‰}$  for  $\delta^{37}\text{Cl}$ , and smaller than the size of the symbols for  $\delta^{18}\text{O}$ .

extrapolated to magmatic temperatures ( $\Delta^{37}\text{Cl}_{\text{mineral-melt}} \approx \Delta^{37}\text{Cl}_{\text{vapour-melt}} \approx 0.2\text{‰}$  at  $600\text{ °C}$ ). Thus, even extreme cases of 90 % Cl removal by fractional apatite crystallisation or open system degassing of  $\text{HCl(g)}$  only fractionate the  $\delta^{37}\text{Cl}_{\text{melt}}$  values by about  $-0.5\text{‰}$ . However, modal apatite abundances in our samples are low ( $<2\text{‰}$ ) 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  $\delta^{37}\text{Cl}_{\text{melt}}$  values of our samples is negligible ( $<0.2\text{‰}$ ). Moreover, similar  $\delta^{37}\text{Cl}$  values of both obsidians and tephra indicate that  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  shifts between rhyolites and basalts, we analysed the  $\delta^{18}\text{O}$  compositions of our samples (Fig. 2). In Iceland, low  $\delta^{18}\text{O}_{\text{rock}}$  values relative to pristine basaltic values ( $+4.8$  to  $+5.8\text{‰}$ ; Thirlwall *et al.*, 2006) are used to recognise assimilation (or partial melting) of altered crust, which has been shifted to low  $\delta^{18}\text{O}$  signatures ( $\leq +2\text{‰}$ ) by hydrothermal alteration with low  $\delta^{18}\text{O}$  meteoric water (Gautason and Muehlenbachs, 1998). We note that basalts and intermediate rocks from all three volcanic settings display  $\delta^{18}\text{O}$  values between  $+3.4$  and  $+5.2\text{‰}$  (Fig. 2), typical for Icelandic basalts (Thirlwall *et al.*, 2006). Silicic rocks from the propagating rift and off-rift zones have basalt-like  $\delta^{18}\text{O}$  values of  $+4.0$  to  $+6.1\text{‰}$ , whereas the lower and more variable  $\delta^{18}\text{O}$  values from  $-0.5$  to  $+4.7\text{‰}$  in the rift zone rhyolites (Fig. 2) indicate variable degrees of crustal assimilation.

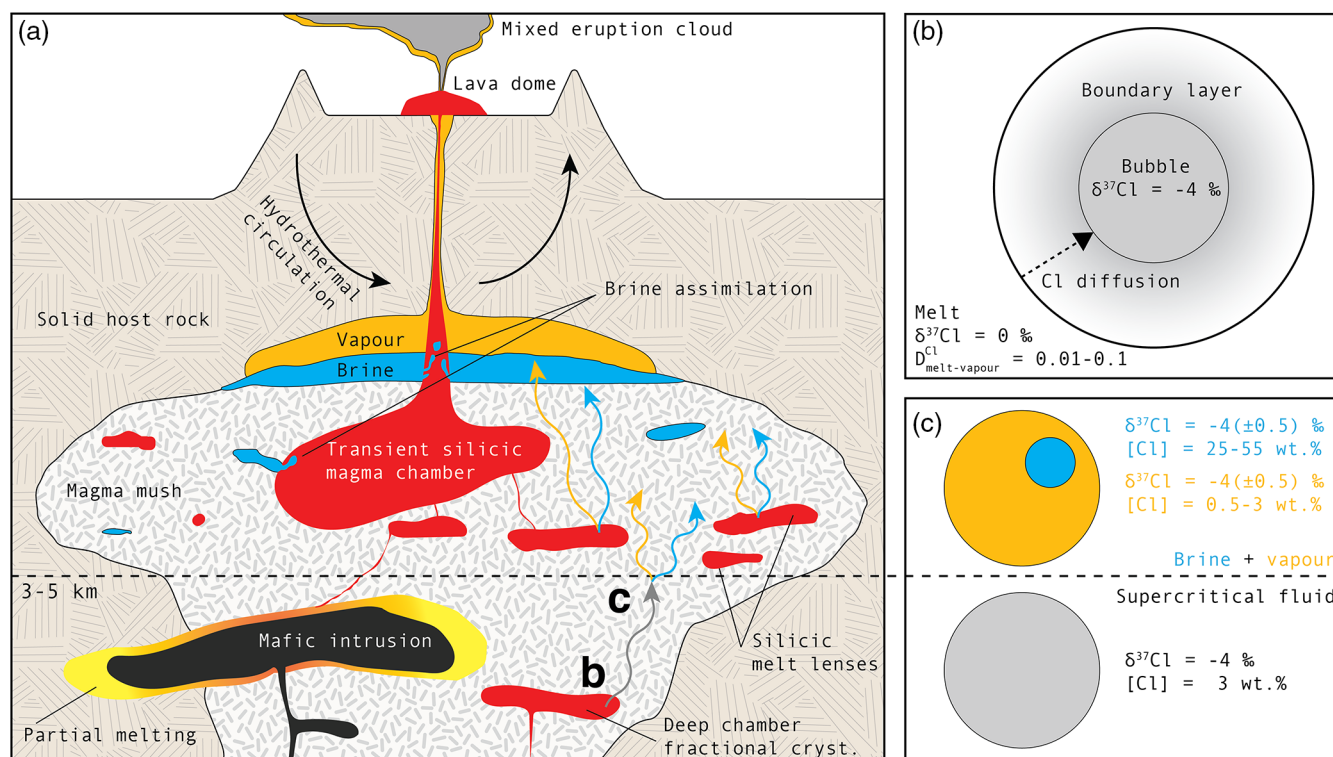
However, there is no correlation between  $\delta^{37}\text{Cl}$  and  $\delta^{18}\text{O}$  (Fig. 2). For example, silicic samples with the most negative (H3a) and positive  $\delta^{37}\text{Cl}$  values (SAL-74) have normal  $\delta^{18}\text{O}$  values, while the two samples with the lowest  $\delta^{18}\text{O}$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

contrast, boron another fluid-mobile element, displays anomalous positive  $\delta^{11}\text{B}$  values in Icelandic silicic rocks that correlate with decreasing  $\delta^{18}\text{O}$ , and that have thus been explained by crustal assimilation (Rose-Koga and Sigmarrsson, 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  $\delta^{37}\text{Cl}$  shifts (up to  $-2.9\text{‰}$ ) compared to corresponding basalts (Fig. 1). This comparison highlights that  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  and elevated concentrations of Cl compared to the rhyolites. These criteria best match a fluid assimilant with high Cl concentrations ( $\text{Cl}_{\text{assimilant}}/\text{Cl}_{\text{rhyolite}} \gg 1$ ) and low  $\delta^{37}\text{Cl}$  ( $< -3\text{‰}$ ) (Fig. S-4). Magmatic hydrosaline fluids have by definition high Cl concentrations and may acquire highly negative  $\delta^{37}\text{Cl}$  values during exsolution from dacitic (and more silicic) melts due to kinetic diffusion effects, that cause considerable fractionation of up to  $\Delta^{37}\text{Cl}_{\text{fluid-melt}} = -5\text{‰}$  even at high temperatures (Fortin *et al.*, 2017) (Fig. 3b). Therefore, in terms of predicted Cl- $\delta^{37}\text{Cl}$  values, magmatic brine is an assimilant that near-perfectly matches the observed  $\delta^{37}\text{Cl}$  shifts in Icelandic rhyolites (Fig. S-4). Anomalous negative  $\delta^{37}\text{Cl}$  values of down to  $-5.6\text{‰}$  have been reported for saline fluid inclusions in porphyry copper and iron oxide-copper-gold deposits, showing that low  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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  $\Delta^{37}\text{Cl}_{\text{liquid-vapour}} = \pm 0.5\text{ ‰}$  (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<sub>2</sub>O 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  $> 85\text{ wt.}\%$ ) 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  $\delta^{37}\text{Cl}$  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  $\text{NaCl}_{\text{equivalent}} = 16.5\text{ wt.}\%$  and  $\delta^{37}\text{Cl}_{\text{fluid}} = -4\text{ ‰}$  is sufficient to explain the maximum observed  $\delta^{37}\text{Cl}$  shift of  $-2.9\text{ ‰}$  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  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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  $\delta^{37}\text{Cl}$  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

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2101>.



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## Chlorine isotope ratios record magmatic brine assimilation during rhyolite genesis

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### Supplementary Information

The Supplementary Information includes:

- S-1: Samples and Methods
- S-2: Geological Setting
- S-3: Chlorine Contents in Icelandic Melt Inclusions
- S-4: Bulk Assimilation Model
- S-5: Quantifying Magmatic Brine Formation in the Crust
- Tables S-1 to S-3
- Figures S-1 to S-5
- Supplementary Information References

### S-1: Samples and Methods

A total of 16 volcanic rocks from Iceland were analysed in this study (Tables S-1, S-2). New  $\delta^{37}\text{Cl}$  data are reported for 14 of these samples (Table S-2). Together with the samples analysed by Halldórsson *et al.* (2016), they cover the main neovolcanic zones of Iceland, *i.e.*, the rift, propagating rift and rift zones, as well as the full geochemical range within these zones, *i.e.*, tholeiitic, transitional and alkaline magma suites (Fig. S-1, S-2). The basaltic ( $n = 3$ ) and intermediate ( $n = 4$ ) rocks are subglacial (HNAUS-1) or subaerial lavas. The silicic samples from this study ( $n = 8$ ) and Halldórsson *et al.* (2016) ( $n = 3$ ) are tephra ( $n = 5$ ) and obsidians ( $n = 6$ ). All material extracted from the samples for chemical analysis was chosen to be as fresh as possible and free from visible alteration. Therefore, any secondary low-T chlorine isotopic fractionation induced by hydrothermal or surface alteration of the rocks is considered unlikely. For all samples,

except for HNAUS-1, ASD1L and ASD14L, major element data has been published previously; by Óskarsson *et al.* (1982) for samples A-THO, A-ALK, B-ALK, D28a (same as SNS-32), I-DAC, I-ICE and SAL-76; by Jónasson (2007) for KER-3 and H-6; by Sverrisdóttir (2007) for H3a, H4 and H5. The samples are Holocene (< 10 ka) in age except for A-THO, D28a, KER-3, H-6, SAL-74 and SAL-76 that are Upper Pleistocene (< 0.8 Ma).

Major element, Cl and S concentrations for the obsidian glasses A-THO, A-ALK, D28a, H-6 and KER-3 were analysed at the Institute of Earth Sciences (IES), University of Iceland using a JEOL JXA-8230 SuperProbe electron probe microanalyser (EPMA). Major elements for the subglacial glass HNAUS-1 were determined with an ARL-SEM-Q EPMA at IES, University of Iceland, using a setup described in Halldórsson *et al.* (2008). For this sample, the chlorine concentrations were analysed by secondary ion mass spectroscopy (SIMS) at the Department of Terrestrial Magnetism, Carnegie Institution of Washington, using methods described in Hauri *et al.* (2002). Major element composition of samples ASD1L and ASD14L were analysed at IES by inductively coupled plasma optical emission spectrometry (ICP-OES) using methods described in Momme *et al.* (2003), and the Cl concentrations with X-Ray fluorescence spectrometry (XRF) with analytical details described in Sigvaldason and Óskarsson (1976). For the five obsidians (A-THO, A-ALK, H-6, KER-3, D28a), the H<sub>2</sub>O and CO<sub>2</sub> concentrations were determined by Fourier transform infrared spectroscopy (FTIR) at IES on 50–380 µm thick, doubly polished glass wafers. The H<sub>2</sub>O and CO<sub>2</sub> concentrations were calculated with Beer-Lambert's law

$$C = \frac{100MA}{\rho h \epsilon} \quad \text{Eq. S-1}$$

where M is the molar weight of the species [g/mol], A is the absorbance, ρ is density [g/L], h is the thickness of the glass wafer [cm] and ε is the absorptivity coefficient [L mol<sup>-1</sup>cm<sup>-1</sup>]. For the H<sub>2</sub>O peak at 3500 cm<sup>-1</sup>, a value of ε = 93.1 L mol<sup>-1</sup>cm<sup>-1</sup> was used, determined experimentally for an Icelandic tholeiitic series rhyolite sample (KRA-045-2; McIntosh *et al.*, 2017). The CO<sub>2</sub> concentrations were below detection limit (c. 10 ppm) for all samples.

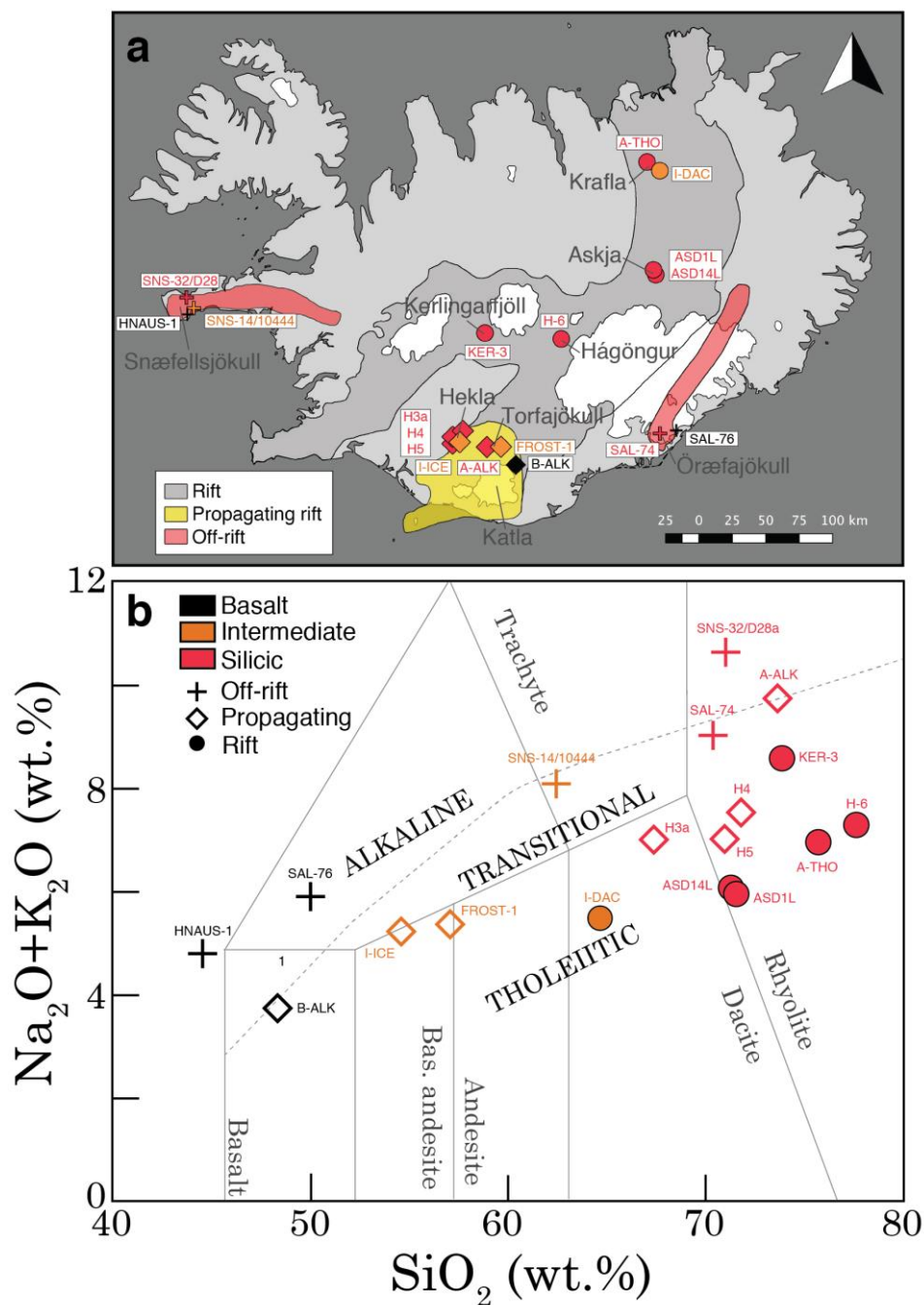
Chlorine and oxygen isotope ratios were measured at the University of Texas at Austin using methods described in the supplement of Halldórsson *et al.* (2016). For chlorine isotope analysis, 200–600 mg of sample powder was washed five times in 18 MΩ deionised water. Chloride ions were released by pyrohydrolysis, trapped in an aqueous solution and converted to AgCl. The AgCl was reacted with CH<sub>3</sub>I to produce CH<sub>3</sub>Cl. The CH<sub>3</sub>Cl was purified on-line in a series of cryogenic traps and a gas chromatograph before introduction into a ThermoElectron MAT 253 isotope ratio mass spectrometer (IRMS). The reported error of 1σ = 0.2 ‰ is based on a long-term average of internal standards.

Oxygen isotope ratios for samples D28a, H-6, HNAUS-1, KER-3, and SAL-76 were determined on chips of ≈ 2 mg of sample by laser fluorination-IRMS using a CO<sub>2</sub> laser in a BF<sub>5</sub> atmosphere. The extracted O<sub>2</sub> was purified in a series of cryogenic traps before introduction into a ThermoElectron MAT 253 IRMS. Full methodology is described by Sharp (1990). An error of 1σ = 0.07 ‰ is based on the long-term reproducibility of δ<sup>18</sup>O values of the San Carlos olivine (δ<sup>18</sup>O = 5.25 ‰), Lausanne-1 quartz (δ<sup>18</sup>O = 18.1 ‰) and UWG-2 garnet (δ<sup>18</sup>O = 5.8 ‰) (Valley *et al.*, 1995) standards.



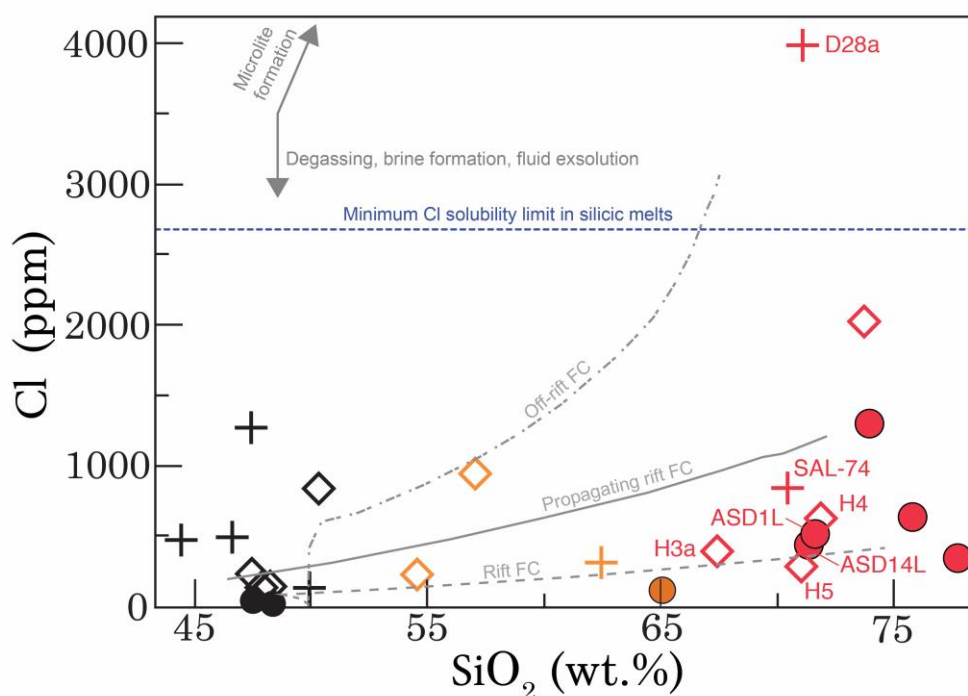


Oxygen isotope ratios for ASD1L, ASD14L, H3a, H4 and H5 were analysed from whole rock samples by Geochron Laboratories, Inc., Cambridge, Mass., in 1996 with conventional methods and have an analytical uncertainty of  $1\sigma = 0.2\text{‰}$ .



**Figure S-1** (a) Sample map and classification. The neovolcanic zones in Iceland are indicated by grey field. Locations of samples used in this study are indicated by black (basalts), orange (intermediate) and red (silicic) circles (rift), diamonds (propagating rift) and crosses (off-rift). (b) Total alkali vs.  $\text{SiO}_2$  diagram showing the geochemical range of the samples. The samples cover the Icelandic alkaline, transitional and tholeiitic magmatic suites.





**Figure S-2** Chlorine concentrations show an overall increase from low to high concentrations with increasing SiO<sub>2</sub> contents, compatible with isobaric fractional crystallisation models (using MELTS, c.f. Fig. S-3) for the different volcano-tectonic settings. Propagating rift and off-rift samples have generally higher Cl concentrations than the rift samples. However, the large spread in chlorine concentrations at a given SiO<sub>2</sub> content even within similar settings probably indicates the combined effect of different source concentrations, chlorine loss by degassing and fluid exsolution, increase during microcline formation upon cooling, and chlorine addition by assimilation of magmatic brines. Notably, all except one sample (D28a) plot below the estimated minimum Cl solubility limit in silicic melts (Metrich and Rutherford, 1992; Webster, 1997). Symbols as in Figure S-1.

## S-2: Geological Setting

Rhyolites are rare in most oceanic islands but constitute up to 10 % of the crust of Iceland (Jónasson, 2007). Genesis of rhyolites in Iceland is favored by prolonged melt evolution in long-lived magmatic reservoirs beneath central volcanoes that sit on top of an unusually thick, up to 40 km, oceanic-type crust, which in turn is the result of excessive melt generation beneath Iceland. Icelandic rhyolite genesis is often seen as a modern analogue for how the first silicic continental crust on the planet may have emerged before the onset of plate tectonics (Willbold *et al.*, 2009; Reimink *et al.*, 2014).

Prevailing ideas suggest that silicic melts in Iceland have been created by (1) partial melting of hydrated basaltic crust, (2) fractional crystallisation of mantle-derived basaltic melts or (3) a combination of (1) and (2) (Nicholson *et al.*, 1991; Sigmarsson *et al.*, 1992; Gunnarsson *et al.*, 1998; Martin and Sigmarsson, 2010; Schattel *et al.*, 2014). Moreover, (1) and (2) are generally thought to dominate at two end-member volcano-tectonic settings: partial melting is favored at rift

zones where the geothermal gradient is high (*e.g.*, Askja, Krafla) (Martin and Sigmarsson, 2007; Kuritani *et al.*, 2011; Schattel *et al.*, 2014), whereas fractional crystallisation from basaltic parental melts seems to be the dominant rhyolite forming process at the off-rift volcanoes (Snæfellsjökull, Öraefajökull) that are situated on top of colder crust (Prestvik *et al.*, 2001; Martin and Sigmarsson, 2010). An intermediate setting is represented by the non-rifting South Iceland Volcanic Zone (*e.g.*, Hekla, Torfajökull), which is the southward-propagating tip of the Eastern Rift Zone and is marked by high magma production rates and high frequency of rhyolitic eruptions, whose genesis is likely a combination of (1) and (2) (Gunnarsson *et al.*, 1998; Martin and Sigmarsson, 2010; Chekol *et al.*, 2011).

### Possible correlation between volcano-tectonic setting and $\delta^{37}\text{Cl}$ – implications for magmatic brine formation

The negative  $\delta^{37}\text{Cl}$  shifts in silicic rocks observed in this study seem to be larger at propagating rift and rift settings, but smaller or absent at off-rift settings (Figs. 1b and 2). This apparent correlation may be explained by considering how the volcano-tectonic setting is likely to influence how magmatic brine formation and assimilation take place. Silicic magma genesis below rift and propagating rift central volcanoes in Iceland takes place in hot (Martin and Sigmarsson, 2010; Schattel *et al.*, 2014) and dynamic mush systems that are maintained by frequent injections of fresh basaltic magma from underlying mafic domain or impinging rift dikes, which stimulate partial melting of wall rock and remobilisation of previously formed silicic segregations (Gunnarsson *et al.*, 1998; Jónasson 2007; Gurenko *et al.*, 2015). Such conditions promote magmatic brine formation. The off-rift systems reside in a colder crust, experience longer intervals without activity and are characterised by silicic magma generation that more closely resembles closed-system fractional crystallisation (Martin and Sigmarsson, 2010; Schattel *et al.*, 2014). In such environment, mushes are likely to be less developed, melts interact less with their surroundings, and the conditions for magmatic brine assimilation are suboptimal.

## S-3: Chlorine Contents in Icelandic Melt Inclusions

Glassy melt inclusions (MI) potentially record the pre-eruptive volatile contents of the melts from which they crystallised and may hold information about the de- and regassing history of Cl within the crustal magma storage domain (Webster *et al.*, 2019). We compiled volatile concentration data in melt inclusions (MIs) in olivine, clinopyroxene and plagioclase in Icelandic basalts and rhyolites published before July 2020 with the aim of assessing degassing relationships between  $\text{H}_2\text{O}$  and Cl (Fig. S-3; Table S-3). Where available, the database includes data for paired matrix glass (MG) or whole-rock analyses, as well as MI major and trace element data. Values corrected for post-entrapment crystallisation are plotted as published.

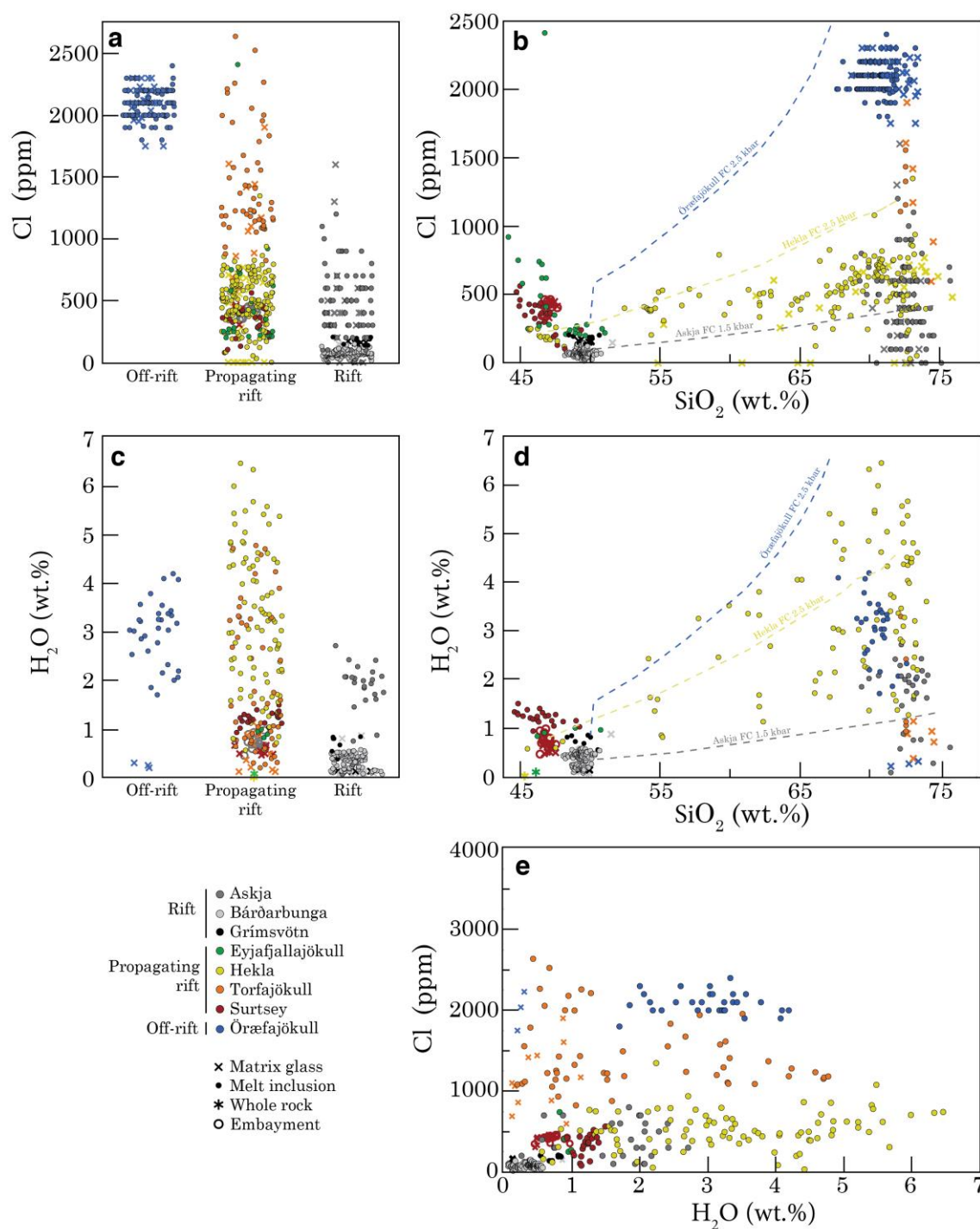
MI and matrix glass Cl concentrations in Icelandic silicic rocks are similar (Fig. S-3a), suggesting that insignificant amount of syn-eruptive Cl degassing takes place, presumably caused by the slow diffusion of Cl compared to  $\text{H}_2\text{O}$  from melt into vapor bubbles (Baker and Balcone-Boissard, 2009; Barnes *et al.*, 2014). Chlorine concentrations in the silicic MIs are generally lower than predicted by fractional crystallisation (Fig. S-3b), and the wide range of Cl concentrations in silicic MIs suggests that Cl is affected by other pre-eruptive processes. In the case of rift and propagating rift samples, low and variable Cl concentrations may be explained by their formation mechanism which involves partial melting of



altered crust with low Cl contents. Melt Cl concentrations can also increase through assimilation of Cl-rich material such as brines (Webster *et al.*, 2019) and decrease by exsolution of hydrosaline fluids or assimilation of Cl poor material. Exsolution of a Cl-rich brine is not indicated by the MI data, because the Cl concentrations are lower than the solubility limit of Cl at the pressure range of the model of Webster *et al.* (2015) (up to 7 kbar) and below the lower end of solubility limits of Cl in rhyolitic melts in general of 2200-2700 ppm at 1 bar (Metrich and Rutherford, 1992; Webster, 1997). Chlorine may also be lost by partitioning to an aqueous vapor phase (Shinohara, 2009). Essentially, the Cl/H<sub>2</sub>O ratio of the melt controls whether a melt will exsolve a hydrosaline fluid or a Cl-bearing aqueous vapor upon reaching saturation (Webster, 2004). About half of the silicic Icelandic MIs record Cl/H<sub>2</sub>O ratios above 0.05, which is the approximate threshold for hydrosaline liquid exsolution in granitic melts (Webster, 2004).

In conclusion, the published MI and matrix glass volatile data available for Icelandic volcanic systems demonstrates that Cl concentrations in MIs are highly variable and indistinguishable from the matrix glasses (Fig. S-3a). Furthermore, Cl concentrations are also decoupled from the MI H<sub>2</sub>O concentrations (Fig. S-3e), which in turn are essentially controlled by magma storage depths and degassing during eruptions (Schattel *et al.*, 2014). The pre- and syn-eruptive processes that affect Cl systematics of silicic rocks in Iceland and elsewhere, *e.g.*, at Mono Craters, USA (Barnes *et al.*, 2014) seem to be complex compared to H<sub>2</sub>O and not fully understood at present (Webster *et al.*, 2019).





**Figure S-3** (a)-(e) Compilation of published melt inclusion H<sub>2</sub>O and Cl data from Iceland. The basaltic samples from different volcanic systems have variable Cl and H<sub>2</sub>O concentrations depending on the degree of partial melting and, possibly, source volatile concentrations (Nichols *et al.*, 2002). This results in rift basalts with relatively low Cl and H<sub>2</sub>O concentrations (Bárðarbunga, Grímsvötn) compared to alkaline basalts of Surtsey. Fractional crystallisation paths were calculated with the rhyolite-MELTS software (Gualda *et al.*, 2012; Ghiorso and Gualda, 2015). The total range in Cl contents of rhyolitic MIs from rift and propagating rift settings is large (< 50 to 2600 ppm) compared to Örfajökull (1700-2400 ppm), the only rhyolitic off-rift volcano with available MI data. We take this difference to reflect the two different modes of rhyolite genesis in Iceland: at off-rift settings the pre-eruptive volatile history with respect to Cl is



seemingly simple and controlled by fractional crystallisation (Martin and Sigmarsson, 2010), while partial melting, assimilation as well as fluid exsolution and resorption processes at rift and propagating rift settings amount to a complex volatile history. The data was compiled from Moune *et al.* (2007), Sharma *et al.* (2008), Brounce *et al.* (2012), Moune *et al.* (2012), Portnyagin *et al.* (2012), Owen *et al.* (2013), Schattel *et al.* (2014), Lucic *et al.* (2016), Schipper *et al.* (2016) and Bali *et al.* (2018).

## S-4: Bulk Assimilation Model

Bulk assimilation can be simulated with a binary mixing model (*e.g.*, Albarède, 1995). A binary mixture of a melt and an assimilant will attain the concentration  $C$  of element  $A$  of

$$C_{\text{mix}}^A = C_{\text{assimilant}}^A f_{\text{assimilant}} + C_{\text{melt}}^A (1 - f_{\text{assimilant}}) \quad \text{Eq. S-2}$$

where  $f_{\text{assimilant}}$  is the fraction of the assimilant. The mixture will have an isotopic ratio  $R$  of

$$R_{\text{mix}}^A = \rho_{\text{melt}}^A R_{\text{melt}}^A + \rho_{\text{assimilant}}^A R_{\text{assimilant}}^A \quad \text{Eq. S-3}$$

where the mixing parameters  $\rho_{\text{melt}}^A$  and  $\rho_{\text{assimilant}}^A$  are defined as

$$\rho_{\text{melt}}^A = \frac{C_{\text{melt}}^A (1 - f_{\text{assimilant}})}{C_{\text{assimilant}}^A f_{\text{assimilant}} + C_{\text{melt}}^A (1 - f_{\text{assimilant}})} \quad \text{Eq. S-4}$$

$$\rho_{\text{assimilant}}^A = \frac{C_{\text{assimilant}}^A f_{\text{assimilant}}}{C_{\text{melt}}^A (1 - f_{\text{assimilant}}) + C_{\text{assimilant}}^A f_{\text{assimilant}}} \quad \text{Eq. S-5}$$

For chlorine and oxygen, the isotopic ratios are converted to standard delta notation as

$$\delta^A = \frac{R_{\text{mix}}^A - R_{\text{standard}}^A}{R_{\text{standard}}^A} \times 1000 \text{ ‰} \quad \text{Eq. S-6}$$

The isotopic ratios used for the international standards for chlorine (SMOC = Standard Mean Ocean Chloride) and oxygen (VSMOW = Vienna Standard Mean Ocean Water) were

$$R_{\text{SMOC}}^{\text{Cl}} = (^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}} = 0.3188962681$$

$$R_{\text{VSMOW}}^{\text{O}} = (^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}} = 0.002005171$$

We performed assimilation modeling using the following hypothetical end-member compositions:



(1) Pristine rhyolite melt: Cl = 200 ppm, O = 48 wt.%,  $\delta^{37}\text{Cl} = 0 \text{ ‰}$ ,  $\delta^{18}\text{O} = 6.0 \text{ ‰}$  (the low Cl concentrations and the basalt-like  $\delta^{18}\text{O}$  values are typical for Hekla rhyolites; Table S-2).

(2) Saline pore water (*e.g.*, mix of magmatic brine and meteoric-derived hydrothermal water): Cl = 20,000 ppm (NaCl equivalent = 3.3 wt.%), O = 83.1 wt.%,  $\delta^{18}\text{O} = -10 \text{ ‰}$ ,  $\delta^{37}\text{Cl} = -4.0 \text{ ‰}$  (the low  $\delta^{18}\text{O}$  value representing high-latitude precipitation (Árnason, 1976)).

(3) Magmatic brine: Cl = 100,000 ppm (NaCl<sub>equivalent</sub> = 16.5 wt.%), O = 62.2 wt.%,  $\delta^{18}\text{O} = 6.0 \text{ ‰}$ ,  $\delta^{37}\text{Cl} = -4.0 \text{ ‰}$  (the  $\delta^{18}\text{O}$  is assumed to be similar to pristine rhyolite melt).

(4) Hydrothermally altered crust: Cl = 500 ppm, O = 48 wt.%,  $\delta^{18}\text{O} = -10.0 \text{ ‰}$ ,  $\delta^{37}\text{Cl} = -4.0 \text{ ‰}$  (the Cl concentration is at the upper end of altered oceanic crust (Barnes and Cisneros, 2012) and the  $\delta^{18}\text{O}$  value is at the lower end of altered crust in Iceland (Gautason and Muehlenbachs, 1998)).

Our choice of  $\delta^{37}\text{Cl} = -4 \text{ ‰}$  for magmatic brine and saline pore fluid is less negative than the possible  $\delta^{37}\text{Cl} = -5 \text{ ‰}$  demonstrated by Fortin *et al.* (2017). The model demonstrates that assimilation of hydrothermally altered basalt, even if ascribed a relatively high Cl concentration (500 ppm; Barnes and Cisneros, 2012) and an unrealistically low  $\delta^{37}\text{Cl}$  value of  $-4 \text{ ‰}$  (see main text), is unable to explain the observed data (Fig. S-4) because unrealistically high degrees of assimilation ( $> 40 \text{ wt.}\%$ ) would be required to explain the observed negative  $\Delta^{37}\text{Cl}_{\text{rhyolite-basalt}}$  shifts.

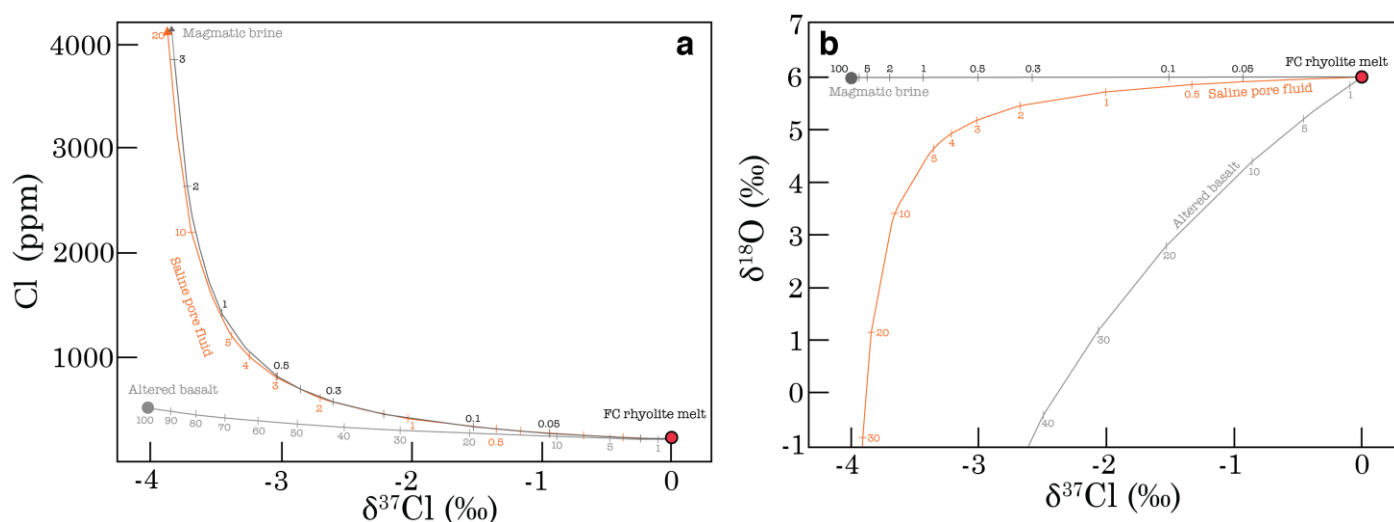
Other globally known materials with distinctly negative  $\delta^{37}\text{Cl}$  values include marine sediments ( $-3.0$  to  $+0.7 \text{ ‰}$ ; Barnes and Sharp, 2017) and marine pore fluids ( $-7.8$  to  $+0.3 \text{ ‰}$ ; Ransom *et al.*, 1995; Bonifacie *et al.*, 2007), but are not widespread in the Icelandic crust, which has not significantly interacted with seawater (Halldórsson *et al.*, 2016). Potential assimilation of clays with negative  $\delta^{37}\text{Cl}$  values cannot readily explain the negative  $\Delta^{37}\text{Cl}_{\text{rhyolite-basalt}}$  shifts as their Cl concentrations are generally similar to rhyolites ( $< 2000 \text{ ppm}$ ; Barnes *et al.*, 2008). Negative  $\delta^{37}\text{Cl}$  values found in arc basalts (Barnes and Straub, 2010; Chiaradia *et al.*, 2014; Manzini *et al.*, 2017; Bouvier *et al.*, 2019) and some recycled mantle components (John *et al.*, 2010) are most likely related to Cl sourced from subducted slabs. While incorporation of recycled sediments in the Icelandic mantle has been suggested to explain the  $\delta^{37}\text{Cl}$  variability of Icelandic basalts (Halldórsson *et al.*, 2016), it can not explain the negative  $\delta^{37}\text{Cl}$  values of silicic rocks relative to the basalts.

Instead, all negative  $\delta^{37}\text{Cl}$  values in this study can be explained by up to 0.5 wt.% assimilation of a magmatic brine (Fig. S-4). Notably, the  $\delta^{18}\text{O}_{\text{rhyolite}}$  values resulting from fluid assimilation are relatively insensitive to the  $\delta^{18}\text{O}$  value of the assimilant, because only low degrees of assimilation are required, and because the oxygen concentrations of melts and fluids are of the same order (Fig. S-4b). For example, 2.5 wt.% assimilation of the saline pore fluid end member required for the maximum  $\delta^{37}\text{Cl}$  shift of  $-2.9 \text{ ‰}$  leads only to a minor ( $-0.7 \text{ ‰}$ ) shift of the  $\delta^{18}\text{O}$  value of the silicic melts despite a very low hypothetical  $\delta^{18}\text{O} = -10 \text{ ‰}$  (Fig S-4b).

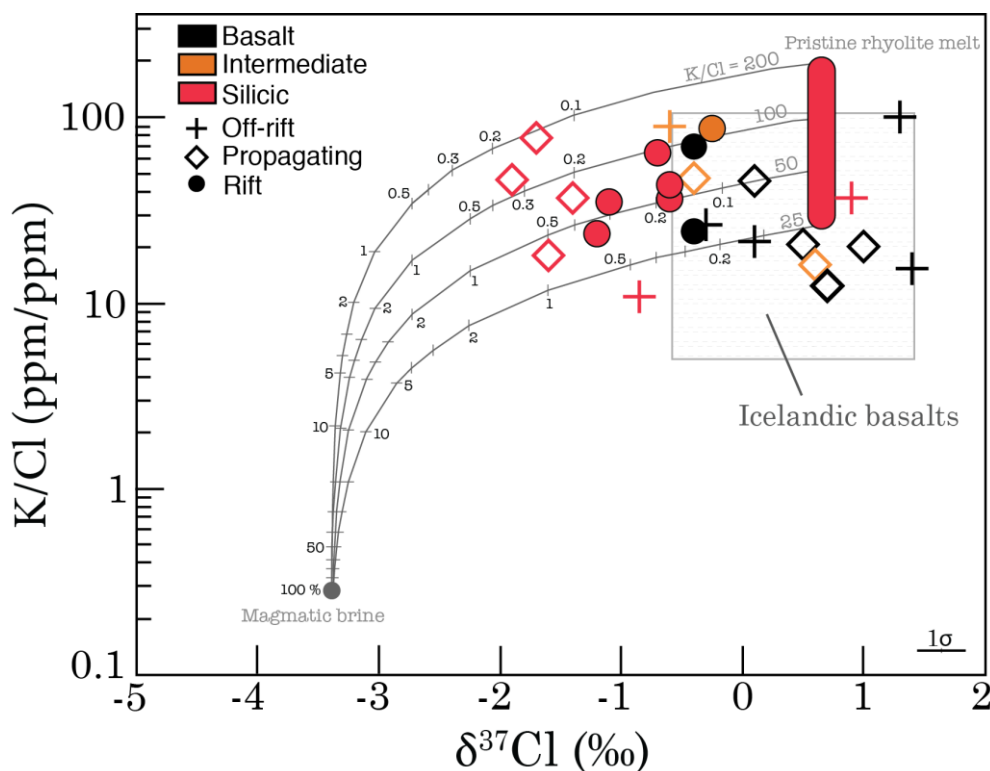


Lowered K/Cl ratios have been used to trace brine assimilation in mid-ocean ridge basalts (e.g. Kendrick et al. 2013, 2017) as K/Cl ratios are low in saline fluids and brines ( $\ll 1$ ) compared to the pristine basaltic melts (c. 10-100), and because the K/Cl ratio is not fractionated during fractional crystallisation of basalts. Compared to basaltic MIs (K/Cl  $\approx$  5-50), silicic MIs in Iceland show a considerably larger variation of K/Cl ratios at the propagating rift volcano Hekla (13-755) and the rift volcano Askja (16-291). This large variation is caused by the complicated controls on Cl concentrations in silicic melts (see section S-3). Because of the large variability in K/Cl ratios in silicic melts, assimilation of small amounts ( $< 1$  wt.%) of magmatic brine is difficult to demonstrate using K/Cl (Fig. S-5). Figure S-5 demonstrates that  $\delta^{37}\text{Cl}$  is a much more sensitive tracer of magmatic brine assimilation in silicic rocks than K/Cl.

Furthermore, we consider a fluid assimilant the most likely candidate for controlling the  $\delta^{37}\text{Cl}$  signatures of silicic rocks because isotopes of non-volatile elements show that (1) rhyolites in Iceland generally preserve the long-lived radiogenic isotopic (Sr-Nd-Hf-Pb) signatures of corresponding basalts confirming that the source material of the refractory elements is ultimately basalt from the same system (Sigmarsson *et al.*, 1992 ; Kuritani *et al.*, 2011), and (2) extensive previous work on multiple non-volatile stable isotopes in Hekla samples, where the largest  $\Delta^{37}\text{Cl}_{\text{rhyolite-basalt}}$  shifts are seen, conclude that the  $\delta^7\text{Li}$ ,  $\delta^{41}\text{K}$ ,  $\delta^{66}\text{Zn}$ ,  $\delta^{98}\text{Mo}$  and  $\varepsilon^{205}\text{Tl}$  systematics show no difference between rhyolites and basalts from Hekla (Schuessler *et al.*, 2009; Chen *et al.*, 2013; Yang *et al.*, 2015; Prytulak *et al.*, 2017; Tuller-Ross, 2019), or that, in the case of  $\delta^{30}\text{Si}$ ,  $\delta^{49}\text{Ti}$ ,  $\delta^{51}\text{V}$ ,  $\delta^{56/54}\text{Fe}$  and  $\delta^{94/90}\text{Zr}$ , can be fully explained by fractional crystallisation (Schuessler *et al.*, 2009; Savage *et al.*, 2011; Prytulak *et al.*, 2016; Deng *et al.*, 2019; Inglis *et al.*, 2019).



**Figure S-4** (a)-(b) The effects of bulk assimilation of magmatic brine, saline pore fluid and hydrothermally altered crust on Cl,  $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$  values on pristine (unaffected by assimilation) rhyolite melt. See text for the used assimilant compositions.



**Figure S-5** The effect of bulk assimilation of magmatic brine on K/Cl and  $\delta^{37}\text{Cl}$  values of rhyolitic melt. Small amount of magmatic brine assimilation does not generate K/Cl ratios subceeding the K/Cl range of basalts. Grey curves show binary mixing curves between magmatic brine with K/Cl = 0.28 (calculated for a brine with 10 wt.% Cl dissolved as  $\text{Na}_{0.5}\text{K}_{0.5}\text{Cl}$ , comparable to brine inclusions analysed by Audétat and Pettke (2003)) and pristine rhyolite melts with variable K/Cl ratios (25-200), K = 20,000 ppm. The  $\delta^{37}\text{Cl}$  compositions of magmatic brine and pristine rhyolite melt are shifted by +0.7 ‰ compared to the end-member compositions defined in section S-4, so that the value of pristine rhyolite melts reflects the average  $\delta^{37}\text{Cl}$  value of +0.7 ‰ of the propagating rift basalts. Note that binary mixing curves in K/Cl- $\delta^{37}\text{Cl}$  space are linear, but are here plotted on a logarithmic y-axis.

## S-5: Quantifying Magmatic Brine Formation in the Crust

In the following, we assess (1) how much magmatic brine is expected to exsolve from magmatic intrusions, and (2) whether this production would be enough to sustain assimilation of 0.3 wt.% brine in extrusive silicic rocks, which is enough to explain most negative  $\delta^{37}\text{Cl}$  shifts in rhyolites in this study (Fig. S-5).

Our estimate for brine assimilation,  $A = 0.3$  wt.% (mass of assimilated brine/mass of erupted rhyolite), with salinity of Cl = 10 wt.% or NaCl = 16.5 wt.% (see previous section), corresponds to a volume ratio for brine/melt of about 0.006 (using densities of  $\rho_{\text{melt}} = 2260 \text{ kg/m}^3$  and  $\rho_{\text{brine}} = 1200 \text{ kg/m}^3$ ). For a hypothetical cylindrical silicic magma chamber with a thickness of 50 m, this corresponds to an overlaying brine layer with a thickness of c. 0.3 m, or equivalently, a 6 m thick mush layer with 5% porosity that is occupied by brine. This estimate can be compared to a > 1 km thick low-resistivity layer below the Merapi volcano, Indonesia, interpreted as saline fluids of possible magmatic origin residing



in host rock of 15% porosity (Müller and Haak, 2004). To convert A to a maximum brine assimilation rate  $B_a$  (kg of brine assimilated/yr) in Iceland, we use a silicic extrusion rate of  $R_e = 0.004 \text{ km}^3/\text{yr}$  estimated for silicic historic eruptions (Thordarson and Larsen, 2007). Thus,

$$B_a = \rho_{\text{melt}} \times R_e \times A \approx 27 \times 10^6 \text{ kg/yr} \quad \text{Eq. S-7}$$

To estimate how much brine can be produced by magmatic intrusions,  $R_b$  (kg brine/yr) *i.e.*, magma that stalls and crystallises in the crust without erupting, we use

$$R_b = \rho_{\text{melt}} \times R_i \times F \quad \text{Eq. S-8}$$

where F is the mass ratio of exsolved brine/intrusive melt and  $R_i$  is derived from the magmatic intrusion/extrusion production ratio X,

$$X = R_i/R_e \quad \text{Eq. S-9}$$

We choose a value of  $X = 5$ , which is considered plausible for Iceland (White *et al.*, 2006), yielding a silicic intrusion rate for Iceland of  $R_i = 0.02 \text{ km}^3/\text{yr}$ . The most difficult parameter to estimate in Eq. S-8 is F. An effort to estimate fluid/melt ratios and the salinities of exsolved fluids from a global compilation of silicic MIs was recently undertaken by Webster *et al.* (2019). The Cl contents of fluids exsolved from magmas range from 0.3 to up towards 70 wt. % for low fluid/melt ratios of  $F = 2 \times 10^{-3}$  (by mass) and 0.3-11 wt.% for a higher fluid/melt estimate of  $F = 4.7 \times 10^{-2}$ , *i.e.*, lower fluid/melt ratios generate higher salinity fluids (Webster *et al.*, 2019). A brine can alternatively be created from a supersolvus fluid with moderate NaCl concentrations by unmixing to a low-NaCl vapor and a high-NaCl liquid upon hitting a solvus curve at 1.3-1.5 kbar (Webster and Mandeville, 2007; Audétat *et al.*, 2008), or alternatively, by vapor condensation (Audétat *et al.*, 2008; Giggenbach *et al.*, 2003). For example, a supersolvus fluid exsolved from a melt with a relatively high fluid/melt ratio of  $2 \times 10^{-2}$  but a relatively low salinity of NaCl = 2 wt.% would unmix upon decompression from 1.5 kbar to 1 kbar to form vapor with about NaCl = 1 wt.% and a liquid with NaCl = 11 wt.% with vapor/liquid mass proportions of 10. In this case, the effective brine/melt ratio with respect to original melt would be  $2 \times 10^{-3}$ . In the following calculations we use a range of brine/melt ratios of  $F = 2 \times 10^{-3}$  to  $5 \times 10^{-3}$ , which we consider to be a realistic estimate for generating a brine with an average  $\text{NaCl}_{\text{equivalent}} = 16.5 \text{ wt.}\%$  from crystallising intrusions (the concentration used in our assimilation model).

Using these estimates, Eq. S-8 yields magmatic brine production rates of  $90\text{--}226 \times 10^6 \text{ kg/yr}$  from silicic intrusions in Iceland. Thus, the supply of brines from crystallizing intrusions is likely to exceed the amount of brine assimilation required to explain the observed  $\delta^{37}\text{Cl}$  signatures in Icelandic rhyolites by a factor of 3 to 8.



## Supplementary Tables

**Table S-1** Sample information.

Sample	Volcanic system	Location/eruption	Rock type	Class	Setting	Type
ASD1L	Askja	1875 eruption	Rhyolite	Silicic	Rift	Tephra
ASD14L	Askja	1875 eruption	Rhyolite	Silicic	Rift	Tephra
A-THO <sup>a</sup>	Krafla	Hrafninnuhryggur	Rhyolite	Silicic	Rift	Obsidian
I-DAC	Krafla	Hraunbunga	Dacite	Intermediate	Rift	Lava
KER-3	Kerlingarfjöll	Ögmundur	Rhyolite	Silicic	Rift	Obsidian
H-6	Hágöngur	Hágöngur	Rhyolite	Silicic	Rift	Obsidian
SNS-32/D28a	Snæfellsjökull	Mælifell	Rhyolite	Silicic	Off-rift	Obsidian
SNS-14/10444	Snæfellsjökull	Háahraun	Dacite	Intermediate	Off-rift	Lava
HNAUS-1	Snæfellsjökull	Hnausagil	Basanite	Basalt	Off-rift	Subglacial
SAL-74 <sup>a</sup>	Öræfajökull	Kvísker	Rhyolite	Silicic	Off-rift	Obsidian
SAL-76	Öræfajökull	Kálfafellsdalur	Trachybasalt	Basalt	Off-rift	Lava
A-ALK <sup>a</sup>	Torfajökull	Hrafninnusker	Alkali rhyolite	Silicic	Propag. rift	Obsidian
H3a	Hekla	H3	Dacite	Silicic	Propag. rift	Tephra
H4	Hekla	H4	Rhyolite	Silicic	Propag. rift	Tephra
H5	Hekla	H5	Rhyolite	Silicic	Propag. rift	Tephra
I-ICE	Hekla	Hekla 1970	Icelandite	Intermediate	Propag. rift	Lava
B-ALK	Katla	Eldgjá	Fe-Ti Basalt	Basalt	Propag. rift	Lava

<sup>a</sup>Halldórsson *et al.* (2016)



**Table S-2** Sample data.

Sample	$\delta^{37}\text{Cl}$ ‰	$\delta^{18}\text{O}$ ‰	$\text{SiO}_2$ wt. %	$\text{TiO}_2$ wt. %	$\text{Al}_2\text{O}_3$ wt. %	$\text{FeO}_{\text{tot}}$ wt. %	$\text{MnO}$ wt. %	$\text{MgO}$ wt. %	$\text{CaO}$ wt. %	$\text{Na}_2\text{O}$ wt. %	$\text{K}_2\text{O}$ wt. %	$\text{P}_2\text{O}_5$ wt. %	Total wt. %	n (EPMA)	$\text{H}_2\text{O}$ wt. %	$\pm 1\sigma$ (n=6)	$\text{CO}_2$ ppm
ASD1L <sup>b</sup>	-0.6	-0.50	71.62	0.85	12.83	4.32	0.11	0.99	2.96	3.70	2.26	0.20			0.51		
ASD14L <sup>b</sup>	-0.9	0.70	71.35	0.87	12.85	4.30	0.10	0.91	3.11	3.80	2.28	0.25			0.14		
<i>duplicate</i>	-0.3																
A-THO <sup>a</sup>	-1.1	2.82	75.80	0.23	12.19	3.20	0.09	0.09	1.68	4.28	2.68	0.02	100.36	6	0.08	0.01	b.d.
I-DAC <sup>c</sup>	-0.1	4.20	64.68	0.88	15.26	6.02	0.12	1.46	4.83	4.12	1.37	0.21			0.45		
<i>duplicate</i>	-0.4																
KER-3	-1.2	4.40	73.95	0.18	13.13	2.54	0.07	0.06	0.92	4.89	3.71	0.02	99.60	6	0.13	0.004	b.d.
H-6	-0.7	4.74	77.74	0.15	11.57	2.17	0.05	0.00	0.92	4.64	2.66	0.02	99.96	6	0.10	0.02	b.d.
SNS-32/D28a	-0.6	5.37	71.09	0.16	14.06	2.58	0.14	0.05	0.45	5.45	5.21	0.01	99.60	6	0.08	0.02	b.d.
<i>duplicate</i>	-1.1	5.67															
SNS-14/10444 <sup>d</sup>	-0.5	5.3	62.45	0.90	16.15	6.96	0.18	0.70	3.28	4.75	3.35	0.20			0.18		
<i>duplicate</i>	-0.7																
HNAUS-1	-0.3	5.05	44.43	4.23	12.22	14.07	0.30	5.20	10.47	3.30	1.50	0.84			0.12		10
SAL-74 <sup>a</sup>	0.9	6.10	70.44	0.19	14.10	2.93	0.08	0.10	1.14	5.30	3.74	0.01			0.84		
SAL-76	1.2	4.35	49.93	2.56	16.36	11.45	0.22	4.15	7.00	4.33	1.58	0.84			0.48		
<i>duplicate</i>	1.4																
A-ALK <sup>a</sup>	-1.6	4.08	73.72	0.20	12.41	3.08	0.07	0.05	0.39	5.35	4.42	0.02	99.89	6	0.08	0.01	b.d.
H3a <sup>b</sup>	-1.9	5.76	67.42	0.39	14.57	5.07	0.16	0.30	2.95	4.84	2.17	0.07			1.28		
H4 <sup>b</sup>	-1.4	5.70	71.86	0.18	13.02	2.33	0.09	0.07	1.55	4.77	2.78	0.00			2.53		
H5 <sup>b</sup>	-1.7	5.57	71.03	0.47	13.97	4.14	0.12	0.42	2.57	4.38	2.64	0.12					
I-ICE <sup>d</sup>	-0.4	4.8	54.55	2.02	14.50	11.69	0.27	2.95	6.96	3.95	1.28	1.02			0.29		
B-ALK <sup>d</sup>	0.1	4.3	48.25	4.22	12.38	14.52	0.22	5.35	10.00	2.97	0.77	0.56			0.25		

Table S-2 (Continued)

Sample	F	Cl	S	Reference for major and volatile element concentrations
ASD1L <sup>b</sup>	466	513		this study
ASD14L <sup>b</sup>	382	435		this study
duplicate				
A-THO <sup>a</sup>		634	41	this study
I-DAC <sup>a</sup>	350	130		Óskarsson <i>et al.</i> (1982)
duplicate				
KER-3		1298	24	this study
H-6		342	26	this study
SNS-32/D28a		3988	28	this study
duplicate				
SNS-14/10444 <sup>d</sup>	1260	310		Óskarsson <i>et al.</i> (1982)
duplicate				
HNAUS-1	1101	470	52	this study
SAL-74 <sup>a</sup>	1080	840		Óskarsson <i>et al.</i> (1982)
SAL-76	752	130		Óskarsson <i>et al.</i> (1982)
duplicate				
A-ALK <sup>a</sup>		2024	23	this study
H3a <sup>b</sup>	1084	390		Sverrisdóttir (2007)
H4 <sup>b</sup>	1424	624		Sverrisdóttir (2007)
H5 <sup>b</sup>		282 <sup>e</sup>		Sverrisdóttir (2007)
I-ICE <sup>d</sup>	1230	225		Óskarsson <i>et al.</i> (1982)
B-ALK <sup>d</sup>	443	140		Óskarsson <i>et al.</i> (1982)

<sup>a</sup> $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$  data from Halldórsson *et al.* (2016) except for the  $\delta^{18}\text{O}$  value of SAL-74, which is from Condomines *et al.* (1983)

<sup>b</sup> $\delta^{18}\text{O}$  values measured on whole rock by Geochron Laboratories, Inc., Cambridge, Mass.

<sup>c</sup> $\delta^{18}\text{O}$  value from Jónasson (2005)

<sup>d</sup> $\delta^{18}\text{O}$  value from Óskarsson *et al.* (1982)

<sup>e</sup>Cl concentration was determined based on the IRMS peak area and calibrated with internal standards of known Cl concentration.





## Supplementary Data Table

A compilation of published melt inclusion H<sub>2</sub>O and Cl data from Iceland (n = 725) is presented in Table S-3, which can be downloaded as a separate Excel file at <http://www.geochemicalperspectivesletters.org/article2101>. The data was compiled from Moune *et al.* (2007), Sharma *et al.* (2008), Brounce *et al.* (2012), Moune *et al.* (2012), Portnyagin *et al.* (2012), Owen *et al.* (2013), Schattel *et al.* (2014), Lucic *et al.* (2016), Schipper *et al.* (2016) and Bali *et al.* (2018).

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