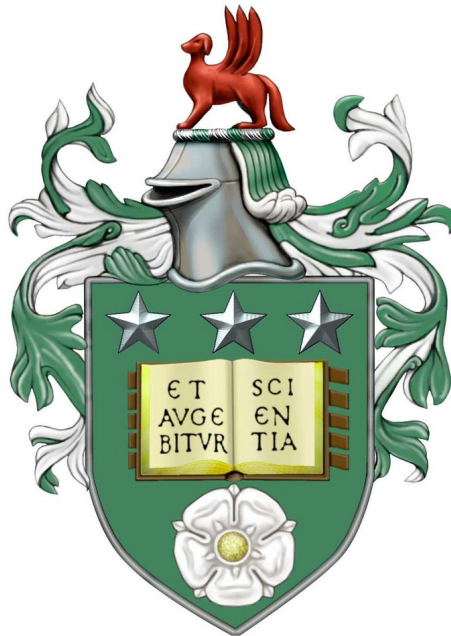


Volcanic Emissions of Environmentally Reactive Trace Elements at the Fagradalsfjall 2021-2023 Eruptions, Iceland

Laura Rose Wainman



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Doctor of Philosophy

The University of Leeds
School of Earth and Environment

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Declaration of Authorship

I confirm that the work submitted is my own, except where work which has formed part of jointly authored publications has been included. My contribution and that of the other authors to this work has been explicitly indicated below. I confirm that appropriate credit has been given within the thesis where reference has been made to the work of others.

Chapter 3 is published as Wainman et al., (2024) in *Geochemistry, Geophysics, Geosystems*:

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I conceptualised and led the study, including data collection in 2022 and 2023, data analysis and visualisation, and preparation of the manuscript, with supervisory input from Evgenia Ilyinskaya, Melissa Pfeffer, and Penny Wieser. Data collection in 2021 was led by Evgenia Ilyinskaya and FTIR data was collected and processed by Melissa Pfeffer and Samuel Warren-Scott. All other co-authors aided with fieldwork logistics and/or technical sample analysis, as well as editing of the manuscript.

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I led data collection in 2022 and performed sample extractions, data analysis and visualisation, and preparation of the manuscript, with supervisory input from Evgenia Ilyinskaya, Melissa Pfeffer, and Penny Wieser. Data collection in 2021 was led by Evgenia Ilyinskaya and snow data was collected by Martin Voigt and processed initially by Abigail Symonds and Evgenia Ilyinskaya. All other co-authors aided with fieldwork logistics and/or technical sample analysis,

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I conceptualised the study and led data collection in 2023 at the Litli-Hrútur eruption. I also performed the sample extractions and conducted microscopy analysis with the help of technical staff at LEMAS. I led data analysis, visualisation, and the preparation of the manuscript, with supervisory input from Evgenia Ilyinskaya, Melissa Pfeffer, and Penny Wieser. All other co-authors aided with fieldwork logistics and/or technical sample analysis, as well as editing of the manuscript.

Additional publications arising from my time as a PhD student:

1) **Wainman, L., Marshall, L.R. and Schmidt, A., 2024.** *Utilising a multi-proxy to model comparison to constrain the season and regionally heterogeneous impacts of the Mt Samalas 1257 eruption. Climate of the Past, 20(4), pp.951-968.*

2) **Wainman, L., 2024.** *Using drones to sample volcanic plumes. Nature Reviews Earth and Environment, 5(7), pp.484-484.*

3) **Wainman, L., Karki, N., Quinn, C., Gregory, L. and Geary, M., 2026.** *Evaluating the use of community co-creation approaches to develop the Disaster Ready! boardgame for DRR education in Nepal. Earth Science, Systems and Society, pp.esss2025-011.* <https://www.lyellcollection.org/doi/full/10.1144/esss2025-011>

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For John,
a dearly missed friend and mentor, who would have been enormously proud.

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Abstract

Effusive basaltic eruptions are one of the most significant natural sources of trace elements to the atmosphere. Trace elements are transferred from deep within the Earth to the surface, where they can serve as essential nutrients for life or as harmful pollutants. Understanding the emission sources, downwind transport processes, and depositional mechanisms of volcanic trace elements is therefore vital for constraining and mitigating against potential environmental and health hazards, as well as for gaining deeper insight into fundamental volcanic and bio-geochemical processes.

This thesis explores the behaviour of volcanic trace elements at the Fagradalsfjall 2021-2023 eruptions on the Reykjanes Peninsula in Iceland. Cutting-edge UAV (Uncrewed Aerial Vehicle) sampling was used to collect in-situ samples of the at-vent and downwind volcanic plume, including major gases and particulate matter, which were analysed for an array of trace elements. Sampling above lava flows at discrete distances from the vent revealed that the composition of lava flow outgassing evolves downflow as the lava cools and ages, driven by fractional degassing of S, Cl, and F species, respectively. This has implications for understanding population exposure downflow and for re-evaluating total trace element degassing inventories for effusive eruptions. In-situ sampling of the downwind volcanic plume also demonstrated heterogeneous deposition of volatile trace elements depending on background meteorological conditions. The resulting mechanistic framework can be applied to interpreting ice core records of volcanic aerosols and raises the possibility of seasonally dependent delivery of trace elements to surface reservoirs. Mixing between volcanic and wildfire emissions during a compound volcanic-wildfire event was also explored, where scavenging and agglomeration processes generated “hybrid” particulate matter with altered physicochemical properties. Interactions between emissions therefore provide alternative depositional and transport pathways for trace elements compared to a standalone volcanic eruption. Continued global warming and growing urbanisation make compound volcanic air pollution events a clear direction for future work.

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List of Abbreviations

AQ	Air Quality
BSE	Backscattered Electrons
CCN	Cloud Condensation Nuclei
EDS	Energy Dispersive X-ray Spectroscopy
EF	Enrichment Factor
EELS	Electron Energy Loss Spectroscopy
FIB	Focussed Ion Beam
FTIR	Fourier Transform Infrared Spectroscopy
FP	Filter Pack
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
INP	Ice Nucleating Particle
OPS	Optical Particle Spectrophotometer
PM	Particulate Matter
REE	Rare Earth Elements
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UAV	Uncrewed Aerial Vehicle
WAF	Weighted Ash Fraction

Chapter 1

Introduction

1.1 Motivation

Volcanoes are one of the most important natural sources of metal and metalloid trace elements to the atmosphere and facilitate the transfer of these elements from deep magmatic reservoirs to the surface environment (Nriagu, 1989; Edmonds et al., 2022). The emission of these trace elements can provide insight into underlying magmatic processes occurring at depth; however, when released at the surface, these elements can also accumulate in terrestrial and aquatic reservoirs where they may be environmentally reactive and harmful to human health (Martin et al., 2010; Mather et al., 2012; Calabrese et al., 2015; Carrera-Beltrán et al., 2024; Sauzéat et al., 2025 and references therein). Constraining the emission sources, transport processes, and depositional mechanisms of trace elements in volcanic environments is therefore critical to understanding and mitigating one of the major environmental and health hazards associated with volcanic activity.

Alongside major gases (H_2O , CO_2 , SO_2 , H_2S , HCl , HF) volcanic emissions contain an array of different trace elements, with over 50 having been identified in volcanic emissions to date (Stoiber and Rose, 1974; Symonds et al., 1987; Symonds et al., 1992; Taran et al., 1995). Some of these elements, such as Fe, Mn, Cu, and Zn can act as essential nutrients in land and ocean ecosystems (Duggen et al., 2007; González-Santana et al., 2024), but induce phytotoxicity at high concentrations (Mohamed et al., 2025), whilst others, such as Pb, As, Cd, and Hg are classified as hazardous “metal pollutants” by health protection agencies (World Health Organisation, 2007). During periods of intense eruptive activity, the emission rates of these trace elements can

be comparable to or greater than anthropogenic emission rates for entire regions or countries (Ilyinskaya et al., 2021). Emissions can result from discrete eruptive events or from prolonged activity and can span days to weeks (e.g., the Fagradalsfjall 2022-2023; Caracciolo et al., 2025 and Svartsvengi 2024-2025; Matthews et al., 2024 eruptions on the Reykjanes Peninsula in Iceland), months (e.g., Fagradalsfjall (Geldingadalir) 2021; Halldórsson et al., 2022; Pfeffer et al., 2024 and Holuhraun 2014-2015; Gauthier et al., 2016; Ilyinskaya et al., 2017; Pfeffer et al., 2018), decades (e.g., Masaya 1993–present; Moune et al., 2010 and Kīlauea 1983–2018; Mather et al., 2012; Ilyinskaya et al., 2021; Mason et al., 2021), or potentially up to centennial or thousand-year timescales considering long-term eruptive cycles (e.g., the Reykjanes Fires; Sæmundsson et al., 2020) or ancient flood basalt eruptions (Self et al., 2005). Looking forward, growing industrial emissions and urbanisation in proximity to active volcanoes (Chester et al., 2000) means that the volcanic emission of trace elements is no longer an isolated geological phenomenon, but is a dynamic process at the intersection of human and planetary systems.

In this thesis, I use in-situ multi-element sampling of volcanic emissions at the Fagradalsfjall 2021-2023 eruptions to investigate the behaviour of trace elements in effusive volcanic environments. By utilising cutting-edge uncrewed aerial vehicle (UAV) sampling technologies to access the volcanic plume, I present new constraints on the additional contribution of degassing lava flows to overall trace element fluxes and provide insights into the underlying mechanisms controlling heterogeneous and meteorologically dependent trace element deposition from the volcanic plume during downwind transport. I also consider how volcanic emissions may interact with additional emission sources in the environment and present the first case study on the air quality impacts of a compound volcanic-wildfire event. The work presented in this thesis has directly contributed to informing public health hazard decisions during the Fagradalsfjall 2021-2023 eruptions and the ongoing Reykjanes Fires, and lays the groundwork for future investigations into the behaviour of trace elements in volcanic and volcanic-adjacent environments.

1.2 Volcanic Emissions of Trace Elements

1.2.1 Element Outgassing and Aerosol Formation

A broad array of metal and metalloid elements is outgassed from volcanoes directly into the atmosphere, both as silicate material (e.g., ash or tephra) or in the gas phase (Symonds et al., 1987; Hinkley, 1991). For basaltic magma, a typical gas composition is $\sim 90 - 95\%$ H_2O , $\sim 2-8$

% CO_2 , $\sim 1\text{-}2\%$ SO_2 , $< 1\%$ trace gases such as HCl , HF , and H_2S , with trace elements at ppm - ppb concentrations (See Supplementary Material for full list of 50+ analysed trace elements). Emissions of silicate material are classified as a primary aerosol as they are generated directly at the vent by magma fragmentation (e.g., gas bubbles bursting on the magma surface, which produce silicate microspheres) or swept up during conduit wall erosion (Martin et al., 2008). The primary silicate aerosol phase contributes the coarsest particle size fraction in the volcanic plume ($> 2.5\text{ }\mu\text{m}$ diameter), consistent with being predominantly formed of mechanically generated particles (Whitby, 1978). A secondary volcanic aerosol phase is also present in the volcanic plume and starts to form immediately post emission through rapid gas-to-particle conversion processes (e.g., experiments at Kilauea showed less than 10% of metals are present in the gas phase beyond 8 m of the volcanic vent; Hinkley, 1991). Gas-to-particle conversion can occur via nucleation, where molecular clusters aggregate to form new, stable particles, or through droplet condensation, where low-volatility vapours, formed by gas-phase reactions, condense onto existing aerosol surfaces, causing them to grow (Whitby, 1978; Hinkley, 1991; Mather et al., 2003; Pfeffer, Rietmeijer, et al., 2006). These gas-to-particle conversion processes result in characteristically smaller particle sizes (< 0.01 to $2\text{ }\mu\text{m}$; Mather et al., 2003; Martin et al., 2008; Martin et al., 2012) than the primary silicate aerosol phase and are consistent with the characteristic diameter ranges outlined by Whitby (1978) based on different particle formation processes: 1) the ‘nucleation’ mode ($D < 0.1\text{ }\mu\text{m}$): generated by nucleation of high temperature magmatic gases as they cool upon mixing with the ambient atmosphere; 2) the ‘accumulation’ mode ($0.1\text{ }\mu\text{m} < D < 2\text{ }\mu\text{m}$): formed from the condensation of low volatility vapours and through the agglomeration and growth of particles in the nucleation mode during downwind transport in the volcanic plume.

Size-aggregated sampling of volcanic aerosols (e.g., using Cascade impactors) has shown that trace elements in the volcanic plume are characteristically distributed between coarser and finer particle size fractions (corresponding to the primary and secondary aerosol phases, respectively; Martin et al., 2008; Martin et al., 2012; Mather et al., 2012; Ilyinskaya et al., 2021). Elements such as Cd, Se, As, Pb, and Te are predominantly collected in the finest resolved particle size fraction ($D < 0.25\text{ }\mu\text{m}$), indicative of being transported by volatile magmatic gases at depth (Hinkley, 1991; Zelenski et al., 2021). By contrast, elements such as Al, Ca, Mg, and the REE are found mostly in the coarser size fraction ($> 2\text{ }\mu\text{m}$), associated with the primary silicate aerosol phase formed through magma fragmentation and conduit wall erosion (Martin et al.,

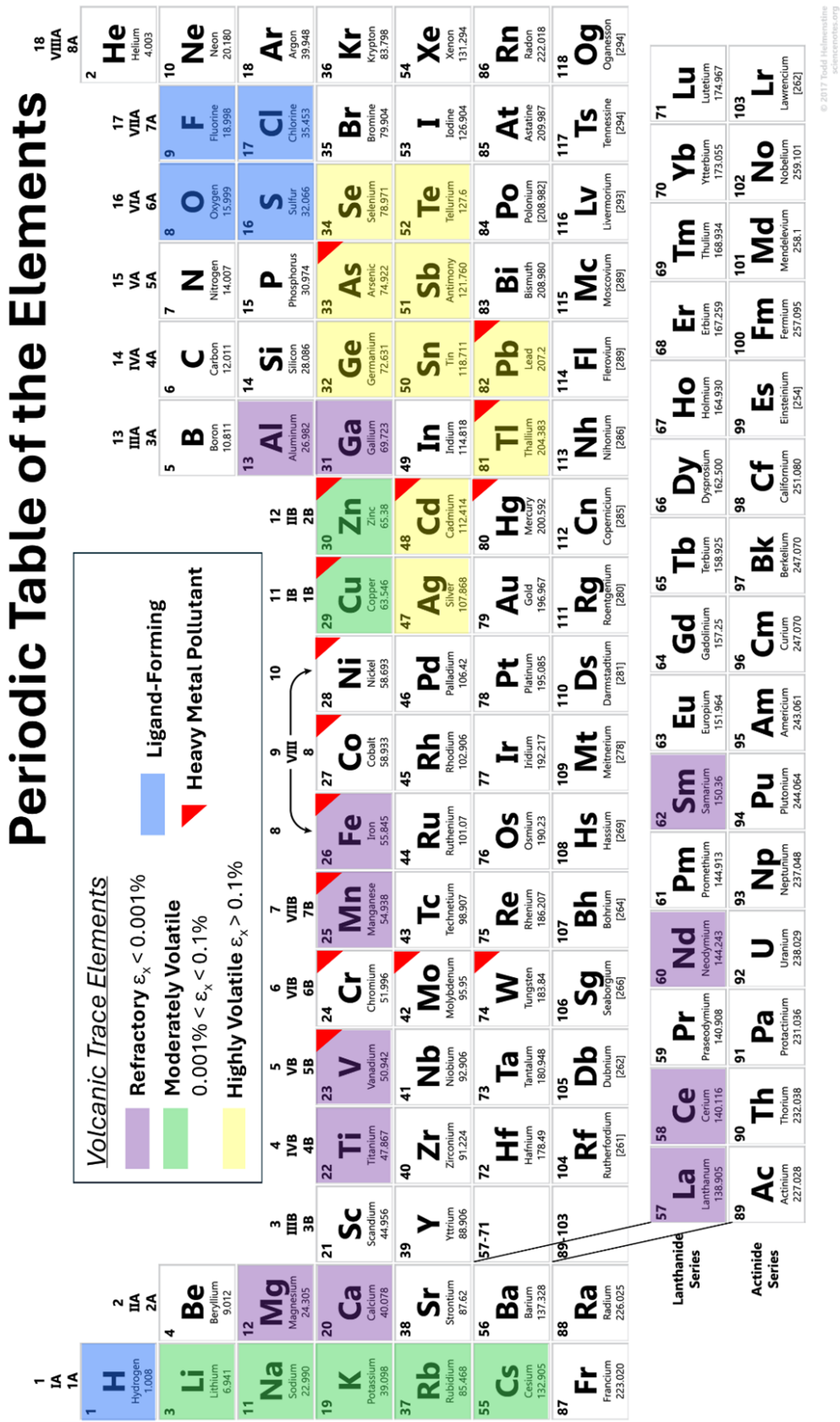


Figure 1.1: Periodic Table of Volcanic Trace Elements. Elements are coloured by their relative volatilities as described by their emanation coefficients calculated in Chapter 4 and Mason et al. (2021) Ligand-forming elements are also highlighted in blue, and metal pollutants, as defined by World Health Organisation (2007), are denoted by red triangles.

2008). The distribution of an element across this particle size spectrum is a critical parameter for subsequent aerosol properties, including sedimentation rate and scavenging efficiency, both of which directly control element atmospheric residence times (Section 1.3), as well as respiratory penetration depth (see Section 1.4.3).

The characteristic distribution of elements between the coarser primary silicate phase and the secondary volatile aerosol phase can be explained by relative differences in their volatilities, where an element's volatility controls how readily it partitions from the silicate melt into a coexisting exsolved magmatic volatile phase (Mather, 2015; Zelenski et al., 2021). Elements with very low volatilities (the refractory elements; such as REE, Mg, and Fe) tend to remain in the melt and thus are erupted in the primary silicate phase during magma fragmentation, whilst elements which are more volatile (e.g., Te, Se, S, Cl) tend to readily partition into the exsolved volatile phase and thus are erupted as magmatic gases which then form the secondary aerosol phase. Element volatilities have been quantified using a range of approaches at many volcanoes globally. This includes using gas-melt partition coefficients (Kd ; Zelenski et al., 2021), calculated by directly comparing the concentrations of elements in volcanic gases to those in melt inclusions or whole rocks (eq. 1.1), emanation coefficients (ϵ_X), which quantify the proportion of the element that was released from the magma into the gas phase (eq. 1.2 and 1.3; Lambert et al., 1985; Pennisi et al., 1988), or enrichment factors (EF), which are a more general approach to describe the extent to which an element is enriched in one phase compared to another, typically normalised to a refractory reference element (eq. 1.4). All three approaches are commonly used to describe trace element volatility and, given their close relationship to one another, generally produce consistent results for the relative volatilities of different trace elements.

$$Kd^* \simeq Kd = \frac{C_X^{fl}}{C_X^{melt}} \quad (1.1)$$

Gas-Melt Partition Coefficient: Kd is the equilibrium partition coefficient, which assumes the silicate melt – volcanic gas system is in equilibrium, whereas Kd^* is the effective (observed) partition coefficient. For all but the most volatile elements (Se and Te) $Kd \approx Kd^*$ (Zelenski et al., 2021) during near-surface degassing. C_X^{fl} is the element concentration in the fluid/gas phase, whereas C_X^{melt} is the element concentration in the melt.

$$\epsilon_X = ([X]_i - [X]_f)/[X]_i \quad (1.2)$$

$$\epsilon_X = ([X/Y]_{plume} * Y_{degassed})/([X/Y]_{plume} * Y_{degassed} + [X]_{MG}) \quad (1.3)$$

Emanation Coefficients: Calculated in eq 1.2 by comparing the initial concentration of an element in the melt $[X]_i$, often from melt inclusions, with the final degassed concentration $[X]_f$, from matrix glass. Calculating emanation coefficients using eq 1.2 for intermediately volatile elements, where there is relatively small amount of change between initial and final concentrations, can however result in a high degree of uncertainty (Rubin, 1997). In this thesis, I calculate emanation coefficients according to equation 1.3 instead, using in-plume $([X]/[Y]_{plume})$ and matrix glass $([X]_{MG} = [X]_f)$ concentrations, where Y is the concentration of S degassed during subaerial eruption and calculated by comparing melt inclusion and matrix glass compositions. X_{MG} is the measured concentration remaining in the degassed matrix glass. These emanation coefficients are calculated using plume composition data which has been corrected to remove the contribution of silicate ash. During the correction for ash and silicate dust (WAF; Supplementary A, Note 1), the refractory elements Mg, Fe, Mn and Ti are assumed only to be present in the silicate phase, and are therefore defined as having emanation coefficients of zero. However, they may actually partition into the gas phase to a limited extent. Thus, in this thesis $\epsilon_X = 0$ describes a completely non-volatile element, whereas $\epsilon_X = 100 \%$ suggests that the element is completely volatilized from the erupting magma. Moderate to highly volatile elements are defined as having $\epsilon_X > 0.05 \%$ (Rubin, 1997) and are shown on Figure 1.1.

$$EF = (C_X/C_R)_{gas}/(C_X/C_R)_{rock} \quad (1.4)$$

Enrichment Factors: A more general calculation used in environmental science to determine the relative enrichment of an element in one phase compared to another (e.g., gas vs solid), normalised to a conservative non-volatile reference element (Eq. 1.4; Zoller et al., 1983). EF calculations are particularly useful when multiple sources are likely to be contributing to overall element concentrations. The reference element is then chosen as it is known to be characteristically enriched in a certain source, and thus can be used to apportion out the other elements

which are also derived from the same source; e.g., Al has been used to determine the contribution of solid matter (e.g., ash or dust) and Na has been used as a reference element to determine the component from sea spray aerosol (Mather et al., 2012). However, when considering relative element volatilities in volcanic systems the choice of reference element often varies between studies based on available data (Al; Aiuppa et al., 2003, Mg; Gauthier et al., 2016, Be; Moune et al., 2010, Br; Allard et al., 2000, and Sc; Mandon et al., 2019). The lack of a common reference element can thus limit the usefulness of comparing EF between studies and different volcanic systems (whereas ϵ_X are more readily comparable, as presented in Chapter 4 of this thesis).

1.2.2 Element Chemical Speciation

When emitted in the gas phase, volcanic trace elements are released either in their elemental form, or more commonly they are complexed with major gas species as oxides, halides, sulfides, hydrides, or hydroxides (Symonds et al., 1987; Moune et al., 2010; Mandon et al., 2019; Zelenski et al., 2021; Mandon et al., 2025). The preference of an element to bond with S, Cl, F, O, and OH ligands or to remain in its elemental form is described as its "speciation behaviour" and depends on temperature, pressure, oxygen fugacity, and melt composition (Zelenski et al., 2021, Mason et al., 2021). Element speciation behaviour in volcanic environments has been inferred using a variety of methods, including correlation analysis of different trace elements and ligands (Aiuppa et al., 2003; Moune et al., 2010), experimental fumaroles to artificially produce sublimates in silica glass tubes from analogue melt compositions (Scholtysik and Canil, 2018; Scholtysik and Canil, 2020; Scholtysik and Canil, 2021), and thermodynamic modelling (Gerlach, 2004; Martin et al., 2006). Thermodynamic modelling is one of the most frequently applied approaches as it can be used to constrain element speciation using directly measured plume compositions and conditions for a specific volcano (e.g., White Island and Yasur, Mandon et al., 2019; Kīlauea, Mason et al., 2021; Fagradalsfjall 2021-2023, this thesis; Wainman et al., 2024). Thermodynamic modelling is commonly performed using the HSC Chemistry software (version 9.9.2, Outotec Research Oy, Finland) which uses Gibbs Free Energy minimisation and experimentally determined thermodynamic parameters (Gibbs energy (ΔG), enthalpy (ΔH), entropy (S), and heat capacity (C_p)) to determine the equilibrium speciation for a given element under specific temperature and pressure conditions (example model input conditions outlined in the Electronic Supplement Sheet A6).

Recent thermodynamic modelling approaches at different global volcanoes have shown clear

distinctions in element speciation behaviour between arc and hotspot volcanic settings (Mandon et al., 2019; Mason et al., 2021). At arc volcanoes, such as Yasur and White Island, Mandon et al. (2019) highlighted the importance of Cl as a ligand forming element, with key trace elements such as Cu, Fe, Zn, and Pb being modelled as forming $CuCl_{(g)}$, $FeCl_{2(g)}$ and $Fe(OH)_{2(g)}$, $ZnCl_{2(g)}$, and $PbCl_{4(g)}$ and $PbCl_{(g)}$ complexes, respectively. By contrast, modelling of the Kīlauea 2018 eruption plume by Mason et al. (2021), which is a hotspot volcano, showed that the same elements Cu, Zn, and Pb, formed $CuCl_{(g)}$ and $Cu_{(g)}$, $PbS_{(g)}$, and $Zn_{(g)}$ species, respectively. These differences in speciation between tectonic settings can be related to underlying melt compositions (discussed below) and are likely to have profound effects on the dispersion and transport behaviour of trace elements in the volcanic plume, where for example, speciation is known to be a key control on element water solubility (Mather et al., 2012; Ilyinskaya et al., 2021).

Experiments using artificial fumaroles have shown that the volatile trace elements can be broadly grouped by their speciation behaviour according to if they preferentially complex with S (Zn, As, Pb, $\pm$ Cd, $\pm$ Bi) or Cl (Rb, Cs, Ag, $\pm$ Cd, $\pm$ Bi), although these groupings are dependent on melt composition, temperature, and oxygen fugacity (Scholtysik and Canil, 2021). The role of these two groupings, based on element speciation with S or Cl, is explored throughout this thesis as a control on element outgassing, transport, and deposition behaviour. In Chapter 3, element speciation is determined via thermodynamic modelling using directly measured compositions from the Fagradalsfjall 2021-2023 eruptions inputted into the HSC Chemistry software. This work contributes an additional element speciation dataset for a basaltic mid-ocean ridge type volcano, which was previously limited to arc and hotspot tectonic settings (Edmonds et al., 2018; Mason et al., 2021). In Chapter 3, I use this thermodynamic modelling to compare element speciation between volcanic vent and outgassing lava flow emissions, and in doing so present new insights into how trace element speciation may vary both between tectonic settings and also within a single volcanic environment.

1.2.3 Geochemical Fingerprints and Global Context

Comparisons between different global volcanoes have revealed characteristic differences in trace element volatility and overall fluxes between volcanoes in arc and hotspot tectonic settings (Edmonds et al., 2018). Emissions from hotspot volcanoes, such as the Kīlauea 2018 eruption in Hawai'i and the Holuhraun 2014-2015 in Iceland, generally have lower overall emission fluxes

of trace elements (< 100 kg/day) and produce emissions which are more enriched in chalcophile elements such as Se, Te, Cd, and Pb (Edmonds et al., 2018; Gauthier et al., 2016; Mason et al., 2021). Volcanoes in arc volcanic settings by contrast, have consistently higher overall trace element fluxes (up to $10^3 - 10^4$ kg/day) and are characteristically more enriched in elements such as Cu, Tl, and Zn (Edmonds et al., 2018; Mandon et al., 2019).

These differences can be explained by differences in melt compositions between tectonic settings and the interplay between melt composition, ligand availability, element speciation behaviour, and relative element volatilities. Magmas at hotspot volcanoes generally have relatively lower concentrations of Cl, with higher S/Cl mass ratios (e.g., Kīlauea S/Cl = 32-35; Mason et al., 2021, Holuhraun 2014-2015 = 30-110; Pfeffer et al., 2018). Volcanoes in arc settings, by contrast, generally have higher magmatic Cl concentrations (as well as F and Br) and lower S/Cl mass ratios (e.g., Yasur $\sim$ 6-13; Mandon et al., 2019, Mt Etna $\sim$ 0.1-6.8; Aiuppa et al., 2004). This is due to the additional input of slab derived fluids and fluid mobile elements to the mantle wedge (Edmonds et al., 2018). Higher H_2O concentrations can also enhance the halogen melt-vapour partition coefficients and thus further increase the availability of halide ligands in arc settings (Hogg et al., 2023). The availabilities of Cl and S ligands in different tectonic settings are therefore a key control on element gas-melt partition coefficients and the extent to which trace elements are volatilized from the melt. This was demonstrated by Zelenski et al. (2021) who showed that trace elements with an affinity to be transported as halides in the gas phase have higher partition coefficients in arc settings, whereas elements which preferably form sulfides, hydrides and free atoms, have higher partition coefficients in rift/hotspot settings that are more sulfur-rich, suggesting a shallow degassing control on element volatility.

Edmonds et al. (2018) propose that differences in metal volatilisation between arc and hotspot volcanoes can also be explained by a deeper control due to differences in the timing of sulfide saturation relative to vapour saturation. At relatively oxidised, water and chlorine-rich arc volcanoes, sulfide saturation is suppressed, which promotes the partitioning of trace elements into a saline aqueous fluid phase that is then outgassed during magma ascent and eruption at the surface. At relatively reduced, water and chlorine-poor hotspot and rift volcanoes, by contrast, Edmonds et al. (2018) propose that if sulfide saturation occurs prior to vapour saturation, trace elements will partition into the denser sulfides and be sequestered into cumulates, effectively scrubbing trace elements from the silicate melt–aqueous fluid system. If these sulfides become

unstable due to degassing at low pressure, sulfide dissolution and resorption may then release these elements to the silicate melt-vapour system to be erupted, thus explaining the relative enrichments of chalcophile elements (Se, Te, Cd) observed at hotspot volcanoes (Edmonds et al., 2018; Wieser et al., 2020).

Whilst degassing from the main volcanic vent(s) has been the primary focus of much previous research into volcanic trace element emissions (Martin et al., 2008; Moune et al., 2010; Mather et al., 2012; Ilyinskaya et al., 2017; Mandon et al., 2019), the extensive lava flows generated during basaltic eruptions can be an additional source of gas and trace element emissions (e.g., Thordarson and Self, 2003; Simmons et al., 2017; Donovan et al., 2023), although have received comparatively little attention. Toutain et al. (1990) investigated trace element outgassing from lava flows at Piton de la Fournaise volcano and found a fractionation in the trace element compositions of down-flow sublimates. They demonstrated that further down-flow, sublimates were dominated by chlorides and fluorides but lacked sulfides, sulfates or oxides, which they hypothesised to be degassed more rapidly closer to the vent. Studies of major gas fractionation in outgassing lava flows at the Holuhraun 2014-2015 eruption in Iceland mirrored the degassing dynamics observed by Toutain et al. (1990), with decreasing S/Halogen ratios at increasing distances down flow (Sigmarsson et al., 2020; Donovan et al., 2023). Aiuppa (2009) similarly concluded that lower SO_2/HCl and SO_2/HF ratios are characteristic of the late stages of volcanic degassing and cooling lavas. The observed transition from sulfur to halogen dominated regimes can be explained by Rayleigh degassing and the decreasing availability of S in the crystallizing magma. The higher solubilities of the halogens in basaltic melt ($S < Cl < F$; Carroll and Webster, 1994) mean they are retained in the melt for longer and thus continue to degas to a greater extent down flow. In Chapter 3 of this thesis, I combine this framework of fractional degassing presented by Sigmarsson et al. (2020) with thermodynamic modelling of element speciation over varied lava flow temperatures to explore how trace element outgassing evolves as lava flows age and cool away from the vent. I also present an updated inventory of trace emissions from the Fagradalsfjall 2021 eruption, compared with other global volcanoes and anthropogenic emissions in Iceland for the same year, accounting for the additional and non-negligible contribution of lava flow outgassing to overall trace element fluxes to the troposphere and surrounding environment.

1.3 Atmospheric Transport and Deposition of Trace Elements

1.3.1 Atmospheric Transport in Volcanic Plumes

Following release at the vent, the volcanic plume (comprised of major gases, ash, and non-silicate PM) rapidly mixes with the ambient atmosphere and is transported downwind according to the prevailing wind strength and direction. Whilst eruption style would not be expected to change the distinctive element enrichment patterns observed between different global volcanoes (discussed in section 1.2.3), it is a key parameter for controlling the absolute fluxes of trace elements, and their likely transport pathways in the atmosphere. Effusive-dominant activity is commonly associated with basaltic eruptions (e.g., Kīlauea 2018) and persistently degassing volcanoes (such as Masaya, Nicaragua). This style of activity generally produces gas-rich, ash-poor plumes that are confined to the troposphere and dispersed on local and regional scales ($\sim < 100$ km; Cassidy et al., 2018; Ilyinskaya et al., 2021). Explosive activity, by contrast, which is more frequent at arc or ice-covered volcanoes (e.g., Mt Pinatubo in Indonesia or Eyjafjallajökull, Iceland) more frequently results in ash-rich plumes capable of reaching stratospheric altitudes (> 15 km). Whilst these larger explosive eruptions are more commonly associated with planetary-scale climatic and environmental impacts (Robock, 2000), sufficiently large or long-lived effusive eruptions can also result in planetary/hemispheric-scale climate forcing effects (e.g., Laki 1783–1784; Thordarson and Self (2003) if sufficient SO_2 is injected/transported into the stratosphere.

Previous studies have suggested that trace element concentrations in ice cores may be used as markers of historic volcanic activity (alongside the more commonly used sulfate spikes) and as a means to constrain far-field element transport (Mason et al., 2022; Edmonds et al., 2022). For example, the Summit ice core in Greenland preserves volatile metal concentrations (Pb, Cd, Cu, Zn) that are related to the fallout from the 1783–1784 Laki eruption cloud, highlighting widespread regional dispersion (Hong et al., 1996; Thordarson and Self, 2003). Ice core records from the West Antarctic ice sheet have also been linked to a chemical signature related to the 17.7-ka eruption of Mount Takahe, where a range of trace volatile metal concentrations (e.g., Bi) showed a correlation with a strong Cl signal throughout the period of the eruption but were uncorrelated with the refractory lithophile elements that are associated with a volcanic ash phase. This fractionation has been hypothesised to represent an early localised deposition of aerosol particulates from a halogen-rich volcanic plume whilst sulfate aerosol PM was transported further afield (McConnell et al., 2017; Edmonds et al., 2022). The long-term influence of persistent

tropospheric degassing on total atmospheric metal budgets was also asserted by Matsumoto and Hinkley (2001) based on pre-industrial ice core concentrations of volatile trace elements, which they suggest to have been from predominantly volcanic origins. Further use and interpretation of volcanic trace element signatures in ice cores will, however, be enhanced by an improved understanding of the long-range transport processes and controls on trace element atmospheric residence times (e.g., Mason et al., 2022; Hutchison et al., 2024). Chapter 4 of this thesis explores the potential for meteorologically dependent element deposition behaviour from the volcanic plume, and demonstrates that wet and dry processes in the near-vent plume can result in the heterogeneous deposition of volatile trace elements to the surface.

1.3.2 Wet and Dry Deposition

Dry Deposition

The deposition of trace elements from volcanic plumes can occur via both wet and dry processes. Dry deposition is a continuous process and is the direct, non-aqueous transfer of gases and particles from the atmosphere to the surface of the earth (e.g., soil, water, and vegetation; Wesely and Hicks, 2000). Dry deposition occurs in the absence of precipitation and is driven by wind, gravity, and diffusion, and is highly dependent on the physical characteristics of the receiving surface as well as the particle size fraction within the volcanic plume (Wesely and Hicks, 2000; Mather et al., 2003). For the smallest particles ($< 0.1 \mu\text{m}$) and gases, turbulent eddies drive them toward the surface layer, where Brownian diffusion then causes them to diffuse across the laminar boundary layer to the surface layer, where they are collected (Wesely and Hicks, 2000; Mather et al., 2003). Particles in the 2-20 μm size range are instead removed by direct impaction, where they directly collide with and adhere to surfaces due to their inertia, whilst the very largest particles ($> 20 \mu\text{m}$) are predominantly removed via gravitational sedimentation, as described by Stokes' Law of particle settling. The nucleation ($< 0.1 \mu\text{m}$) and coarse ($> 2 \mu\text{m}$) mode particle size fractions (as defined by Whitby (1978)) are thus efficiently removed from the volcanic plume via Brownian diffusion and gravitational sedimentation, respectively. The removal mechanisms for particles in the accumulation mode (0.1 – 2 μm), which is formed through the condensation of low volatility magmatic vapours and the agglomeration and growth of particles from the nucleation mode during downwind transport, are by contrast relatively inefficient (Mather et al., 2003). This means that the PM and volatile trace elements hosted in this intermediary size fraction have the most extended atmospheric lifetimes and thus the

greatest potential for wide-reaching atmospheric and environmental effects.

An additional, indirect mechanism for the dry deposition of trace elements from volcanic plumes is via scavenging by silicate ash (Rose, 1977; Óskarsson, 1980; Mather et al., 2003; Witham et al., 2005; Delmelle et al., 2007; Delmelle et al., 2018). Volcanic volatiles, such as sulfur, chlorine, and fluorine, as well as trace element complexes, are adsorbed onto the surface of silicate ash particles as water-soluble salts, as shown by volcanic ash leachate studies (Varekamp et al., 1984; Varekamp et al., 1986; Witham et al., 2005). The delivery of volcanic volatile species to the ash surface has been hypothesized to occur via different mechanisms in three separate temperature-dependent reaction zones: 1) sulfate and halide salts formed through homogeneous nucleation at magmatic temperatures (600 - 1200 °C) are deposited directly as sublimates onto the ash surface (Taylor and Stoiber, 1973; Smith et al., 1983); 2) chemisorption of gaseous SO_2 , HCl or HF onto the ash particle surfaces between 800 - 190 °C (Delmelle et al., 2018); 3) low temperature reactions (below 190–200 °C) where ash particles act as condensation nuclei for volcanic acids which can then react with and dissolve the ash leading to the precipitation of sulfate and halide salts (Rose, 1977; Delmelle et al., 2007). In explosive eruptions, which produce very ash-rich plumes, scavenging by ash is considered one of the primary sinks for volatile species. For example, previous work has shown that up to 30–40% of sulphur and 10–20% of chlorine emitted during an explosive eruption may be scavenged by ash and thus removed from the plume more rapidly due to the faster gravitational settling of the larger ash particles (Rose, 1977; Varekamp et al., 1984; Textor et al., 2003; Delmelle et al., 2007; Brown et al., 2012).

In Chapters 4 and 5 of this thesis, I explore the transport, deposition, and in-plume interactions of silicate particles at the effusive Fagradalsfjall 2021-2023 eruptions. This is relatively under-researched compared to ash-rich explosive eruption plumes because effusive plumes are more commonly associated with gas-rich ash-poor plumes. In Chapter 4, I consider silicate PM as a pathway for the very near-vent deposition of refractory trace elements, which are hosted directly in the ash phase, and also as a sink for volatile trace elements via scavenging and surface adsorption processes. In Chapter 5, particulate scavenging processes are considered in the context of a compound volcanic-wildfire event, where scavenging and agglomeration processes between volcanic and wildfire PM produce a unique atmospheric transport and deposition pathway compared to stand-alone volcanic eruptions.

Wet Deposition

When precipitation interacts with the volcanic plume (i.e. rain or snowfall) trace elements and PM can also be removed from the atmosphere via wet depositional processes (Kawaratani and Fujita, 1990; Van Eaton et al., 2015; Cheng et al., 2021). Elevated concentrations of volatile species (SO_4 , Cl, and F) and volcanic trace elements have been recorded in precipitation samples around several volcanoes globally; this includes during rainfall episodes at the Holuhraun 2014–2015 eruption (Stefánsson et al., 2017), around Mt Nyiragongo (Cuoco et al., 2013), at Mt Vesuvius and Vulcano Island (Madonia and Liotta, 2010), at Stromboli (Liotta et al., 2006), at Mt Etna (Aiuppa et al., 2006; Calabrese et al., 2011), and on Montserrat (Edmonds et al., 2003), as well as during a snowfall event at the Hekla 2000 eruption (Moune et al., 2010). Wet deposition can occur via rainout (in-cloud scavenging), where particles and gases are either incorporated into existing cloud droplets and ice crystals (e.g., via diffusion), or can act as cloud condensation nuclei (CCN) or ice nucleating particles (INP) themselves (Kawaratani and Fujita, 1990; Textor et al., 2003; Maters et al., 2020; Sanchez-Marroquin et al., 2020; Cheng et al., 2021). These cloud droplets and ice crystals subsequently fall out of the atmosphere as precipitation. Wet deposition from the volcanic plume can also occur via washout (below-cloud scavenging; Kawaratani and Fujita, 1990; Zhang et al., 2013). This is where falling precipitation (rain or snow) passes through the plume and captures the particulates via impaction. The efficiency of impact scavenging is strongly dependent on particle diameter, where larger particles are more likely to be impacted and thus removed via falling precipitation (Zhang et al., 2013; Cheng et al., 2021).

The role of element solubility in controlling wet deposition efficiency is, however, less well understood in volcanic or other atmospheric environments, but has been hypothesised to play a role in modulating in-cloud scavenging processes (Pfeffer, Langmann, and Graf, 2006; Cheng et al., 2021; Mason et al., 2021; Mason et al., 2022). In volcanic environments, the role of solubility in the wet deposition of gaseous SO_2 and HCl is better understood than for trace element complexes. For example, measurements at Mt Sakurajima volcano and simulations using the ATHAM plume model both suggest that HCl gases are scavenged by precipitation (ice and rainfall) with greater efficiency than SO_2 or H_2S gases, primarily due to the higher solubility of HCl in water (Kawaratani and Fujita, 1990; Textor et al., 2003). The water solubilities of trace elements in the volcanic plume have been estimated by several previous studies (Mather et al.,

2012; Ilyinskaya et al., 2021), where the more volatile elements, when hosted in the secondary non-silicate aerosol phase, are generally more water soluble than the more refractory elements, which are hosted in the larger silicate ash fraction (Mather et al., 2012; Ilyinskaya et al., 2021).

This difference in water solubility between refractory and volatile trace elements was invoked by Ilyinskaya et al. (2021) to explain the preferential loss of the more volatile trace elements from the Kīlauea 2018 volcanic plume compared to the more refractory elements. Ilyinskaya et al. (2021) suggested that the more volatile elements (e.g., Cd, Te, Se), which form the more soluble complexes, were lost preferentially in high-humidity conditions due to in-cloud scavenging processes. This observation is an advancement on previous studies that have assumed elements are deposited homogeneously and thus that measured element ratios in the deposited samples reflect those in the airborne plume (Moune et al., 2010). The study presented in Chapter 4 of this thesis explores this further by directly measuring the heterogeneous deposition of trace elements from the Fagradalsfjall 2021-2022 eruption plumes under varied meteorological conditions and examining the interplay between particle size distribution, speciation behaviour, and water solubility in controlling wet and dry depositional processes.

1.3.3 Interactions with Emissions from Additional Non-Volcanic Sources

As volcanic plumes are transported downwind and mix with the ambient atmosphere, they are also likely to encounter emissions from other natural and/or anthropogenic sources. Sea-salt spray aerosol and wind-borne remobilised dust particles are two of the most important natural sources of PM and trace elements to the atmosphere in Iceland (Bertram et al., 2018; Baldo et al., 2020). Biogenic sources, such as from plants and wetlands, can also contribute significant proportions of some trace elements such as Se, Cu, Zn and As, as can biomass burning during wildfire events (such as the Litli-Hrútur 2023 moss wildfires, which are explored in Chapter 5 of this thesis; Nriagu, 1989).

It remains largely unconstrained, however, how volcanic trace elements may behave upon mixing with gaseous and PM emissions from other natural or anthropogenic sources. The emission sources outlined above all have distinct geochemical compositions that are enriched in a characteristic array of trace metals and reactive gas species. It is therefore highly probable that both chemical reactions and mechanical interactions may occur upon mixing between volcanic emissions and those from additional external sources downwind. The study presented in Chap-

ter 5 of this thesis focuses on mechanical scavenging and agglomeration interactions between volcanic and wildfire emissions at the Litli-Hrútur 2023 eruption and lava-ignited wildfires, and demonstrates the formation of hybrid PM upon mixing between emission sources.

1.4 Impacts on Air Quality, the Environment, and Human Health

1.4.1 Particulate Matter and Air Quality

As outlined in Section 1.2.1, volcanic emissions are extremely rich in particulate matter (PM; defined broadly as microscopic solid and liquid particles suspended in the air, the particles and air combined form an “aerosol” phase). Measuring PM is particularly useful in the context of assessing population exposure to air pollution and is studied across the fields of atmospheric science and air quality, as well as being routinely reported as part of operational air quality (AQ) monitoring activities (Heal et al., 2012; Fuzzi et al., 2015). PM concentrations are commonly measured and reported according to several designated size fractions: PM_{10} (all particles with a diameter of less than or equal to 10 μm), $PM_{2.5}$ (particles with diameter $\leq 2.5 \mu\text{m}$), and PM_1 (particles with diameter $\leq 1 \mu\text{m}$).

The size-resolved distribution of trace elements in volcanic aerosols (described in Section 1.2.1) can be partially mapped onto the PM size fractions described above (PM_{10} , $PM_{2.5}$, PM_1). PM_{10} , being composed of both primary silicate PM and the smaller non-silicate PM, contains a mixture of refractory and volatile trace elements. $PM_{2.5}$ and PM_1 , by contrast, are mostly comprised of the smaller secondary aerosol phase formed from magmatic gas-to-particle conversion, and so host mostly volatile trace elements (Whitty et al., 2026). The PM size distribution of trace elements is a key parameter when considering their likely health impacts, where PM size fraction controls the respiratory penetration depth of PM in the human body; e.g., PM_{10} is considered inhalable and deposits primarily in the upper respiratory tract, whereas $PM_{2.5}$ can travel deeper into the lungs, and PM_1 , which is the finest particle mode, can reach the bloodstream and travel throughout the body to reach vital organs including the brain (Polichetti et al., 2009; Sturm, 2020).

Continuous monitoring of PM concentrations has been applied at several recent eruptions to assess air quality, population exposure, and environmental risks (Kīlauea 2018: Crawford et al., 2021; Whitty et al., 2020, Masaya: Whitty et al., 2022; Montserrat: Lewis et al., in prep). In

Chapter 5 of this thesis, PM_{10} and $PM_{2.5}$ concentrations were monitored at several locations around the Litli-Hrútur 2023 eruption and wildfires using an Optical Particle Spherometer (OPS – TSI3330), which is a reference-grade instrument that meets international monitoring standards. Similar reference grade instruments are often used in permanent air quality monitoring stations, such as the regulatory municipal air quality (AQ) network maintained by the Environment Agency of Iceland, and utilised by Whitty et al. (2026) to assess the air pollution impacts of the Fagradalsfjall 2021 eruption across the Reykjanes Peninsula. Permanent, reference-grade AQ stations are, however, mostly situated in urban locations and therefore far from areas of volcanic activity, or may be too sparsely located to sufficiently measure PM concentrations at the spatial resolution needed to capture variable population exposures (Crawford et al., 2021; Whitty et al., 2026). Monitoring during periods of volcanic activity, therefore, often relies on installing a network of semi-permanent low-cost sensors that may be calibrated to a reference grade instrument (Whitty et al., 2020; Crawford et al., 2021; Whitty et al., 2022; Whitty et al., 2026; Lewis et al., in prep).

Air quality thresholds for PM_{10} and $PM_{2.5}$ have been published by national (DEFRA; Department for Environment, Food & Rural Affairs, UK) and international (WHO/UN) agencies for annual and 24-hour averages (Department for Environment, Food and Rural Affairs (DEFRA), 2025; World Health Organisation (WHO), 2026). Whilst these can be useful in informing exposure assessments, they are often not readily transferable to volcanic environments where exposure is commonly acute (minutes to hours), and very high in concentration. In Chapter 5 of this thesis, we therefore assess PM_{10} and $PM_{2.5}$ concentrations relative to published 1-hour thresholds from the Icelandic Environment Agency (Table 2 in Supplementary C). These thresholds are the most locally relevant for the Fagradalsfjall 2021-2023 eruptions, and the shorter times better reflect the likely window of exposure for tourists visiting the eruption site.

1.4.2 Environmental Delivery of Trace Elements

Upon deposition to the surface, volcanic trace elements may be delivered to both terrestrial and hydrological reservoirs. Although the surface delivery and post-depositional environmental processing of volcanic trace elements is not the primary focus of this thesis, the work presented here is critical for understanding the parameters and processes that control the delivery of trace elements and their behaviour in the surface environment, including as catalysts for primary production and in microbe-mediated cycles (Chen et al., 2022). Biomonitoring has also been

demonstrated as a useful tool for investigating the regional scale transport and dispersion process of trace elements in volcanic environments, and thus, a brief overview of these approaches and processes is presented below.

Several studies have investigated the surface delivery of trace elements using the vegetation surrounding active volcanoes: grass samples around Masaya and Kīlauea were analysed for key volatile volcanic trace elements by Martin et al. (2010) and Mather et al. (2012), respectively, where the grasses take up the trace elements from the soil which acts as a reservoir for deposited volcanic species (Graham and Stangoulis, 2003; Delmelle et al., 2003). Nonetheless, uptake of trace elements from soils can lead to significant uncertainties due to existing heterogeneity in soil composition and the potential for fractionated uptake by plants of different trace metals (i.e., measured ratios in biological material may reflect complex terrestrial processing pathways, rather than a readily interpretable signature of volcanic delivery). Moss-based biomonitoring has therefore been employed as a simpler and more effective tool, both in volcanic environments, such as around Mt Etna, Stromboli, Nyiragongo, and Vulcano (Arndt et al., 2014; Calabrese et al., 2015; Arndt et al., 2017), as well as for monitoring environmental heavy metal pollution from anthropogenic sources around mines and smelting operations (e.g., Steinnes et al., 2003; Olise et al., 2019). Moss-based biomonitoring is advantageous as the mosses directly take up trace elements from the air via wet and dry processes and thus avoid the complexity of soil heterogeneity and intermediary processing during uptake from soils (Varela et al., 2023). These studies found that the spatial distribution of element enrichment patterns showed a dependence on prevailing wind/plume directions (Martin et al., 2010; Mather et al., 2012; Arndt et al., 2014) and that there was a potential topographic dependence which controlled localized rainfall patterns and thus preferential wash out of volatile trace elements in certain areas (Mather et al., 2012). The work presented in Chapter 4 of this thesis considers how meteorologically dependent deposition of trace elements from the volcanic plume may lead to seasonally variable deposition of volcanic trace elements and fractionation in the surface delivery of trace elements in the surrounding environment due to variable delivery pathways. In Chapter 5 of this thesis, I also explore the role of scavenging and agglomeration processes between volcanic aerosols and burnt vegetation particulates as a novel pathway for the atmospheric transport and environmental delivery of volcanic trace elements during compound volcanic-wildfire events.

Volcanic trace elements such as Cu, Fe, Mn, and Zn can act as essential nutrients that are

critical for plant growth and are for microbially-mediated cycles crucial for bio-transformation (Chen et al., 2022). However, these metals can also induce phytotoxicity if accumulated in high concentrations (Aller et al., 1990; Ciriminna et al., 2022). The net impact of volcanic emissions on terrestrial environments, whether natural ecosystems, anthropogenic farmland or urban environments, is an area of ongoing research, although most work to date has focussed on the impact of volcanic ash, rather than the more volatile trace elements hosted in the non-silicate aerosols phase (Ayrís and Delmelle, 2012; Ciriminna et al., 2022; Ligot et al., 2024; Carrera-Beltrán et al., 2024). The delivery and accumulation of these volatile trace elements in volcanic environments is likely to depend on a multitude of factors, some of which are explored in this thesis, including at-source emissions (e.g., Chapter 3 explores how lava flows may be an additional, diffuse source of trace elements), background meteorological conditions (and their impacts on heterogeneous trace element deposition, explored in Chapter 4), and plant/crop specific characteristics.

Once delivered to the surface, volcanic trace elements can also accumulate in hydrological environments, including lakes, rivers, groundwater, and stored drinking water reservoirs (Tomašek et al., 2022; García-Gil et al., 2023). Delivery to these hydrological reservoirs can occur via the direct wet deposition of trace elements from the volcanic plume (e.g., via wash-out and rain out processes outlined in Section 1.3.2) or via leaching by surface waters from contaminated soils or ash fall deposits (Ayrís and Delmelle, 2012; Tomašek et al., 2022). At Mt Etna, elevated concentrations of As, Cd, Tl, and Te were found in rainfall up to 80 km from the volcanic vent, highlighting the far-field hazard potential of volcanic trace elements (Brugnone et al., 2020). From a hazard perspective, understanding the pathways by which volcanic trace elements can be delivered to and accumulate in hydrological surface reservoirs is particularly important in regions such as the Democratic Republic of Congo where rainwater is the primary supply of drinking water (Liotta et al., 2017; Balagizi et al., 2017) or for example around Mt. Meru (Tanzania, along the East African Rift) where elevated concentrations of volcanic trace elements were found in ground water samples with concentrations of U and Mo exceeding permissible safe drinking water limits (Tomašek et al., 2022). Along with the transfer of volcanic trace elements, the dissolution of acidic gases in the volcanic plume such as SO_2 and HCl can lead to acidification of falling precipitation by releasing H^+ ions, often reducing the $pH \ll 4$ (Parnell and Burke, 1990). This can also lead to enhanced ash dissolution and the release of additional heavy metals in surface environments (Delmelle, 2003). Similar to anthropogenic acid rain, the delivery

of acidic species can leach essential soil nutrients, reduce the soil’s natural buffering capacity, and mobilise naturally occurring heavy metals in the soil, such as Al (Parnell and Burke, 1990; Singh and Agrawal, 2007). Nonetheless, where volcanic emissions are transported to the ocean, they can also form a key part of trace element biogeochemical cycles (particularly for Fe and Mn) and act as key fertilising nutrients for primary production (Frogner et al., 2001; Langmann et al., 2010; Duggen et al., 2010; Olgun et al., 2011; Longman et al., 2022) highlighting the complex role that volcanic emissions of trace elements play in global biogeochemical cycles.

1.4.3 Human Exposure and Health Hazards

Exposure to volcanic emissions (SO_2 , PM, heavy metal pollutants) has been linked to a range of negative health outcomes in humans and animals (Stewart et al., 2021). Exposure can occur via direct inhalation of the airborne volcanic plume or indirectly via ingestion of contaminated food, soil, or drinking water (Calkins and Delmelle, 2021). Exposure may also be chronic or acute depending on the length and style of eruption, prevailing background conditions (which may, for example locally concentrate the plume in certain areas), and the specific interactions of the volcanic emissions with human activity (e.g., if emissions reach permanent human settlements such as towns or cities or if tourists are temporarily visiting the eruption site). The primary pathway of exposure can also vary by demographic and socio-economic status within a single exposed population. For example, around Masaya volcano in Nicaragua, Calkins and Delmelle (2021) showed that air inhalation and accidental soil ingestion were the predominant fluoride exposure pathways in children, whereas water consumption dominated fluoride intake in adults. Chapter 4 of this thesis explores how trace elements may be heterogeneously removed from the volcanic plume via wet and dry depositional processes, respectively, with crucial implications for understanding if certain exposure pathways (e.g., airborne, aqueous, food) are likely to be more enriched in certain trace elements.

The health impacts associated with generalised exposure to volcanic smog (“vog”) and ash at a macro level have been more extensively studied than the health impacts associated with exposure to specific volcanic trace elements (Stewart et al., 2021 and references therein). Vog exposure has been associated with more frequent medical visits due to aggravated acute respiratory illnesses during periods of eruptive activity, particularly for vulnerable populations with pre-existing conditions (Kīlauea, 2008; Longo et al., 2010; Holuhraun, 2014-2015; Carlsen et al., 2021). Persistent degassing, at volcanoes such as Ambrym, Vanuatu, and Masaya, has also

been associated with additional health effects such as dental fluorosis in exposed populations (Stewart et al., 2021). The specific health effects related to volcanic trace element exposure are, however, relatively poorly constrained, although due to their health impacts in other settings, many elements (such as Pb, Hg, Cd, As, Cr) are classified as metal pollutants by national and international environmental and health protection agencies (World Health Organisation, 2007; Department for Environment (DEFRA), 2025). Exposure to metal pollutants has been associated with increased risk of respiratory problems, certain cancers, cardiovascular diseases and neurocognitive and behavioural disorders in children (Jaishankar et al., 2014; Al Osman et al., 2019), although there is no guarantee these health impacts translate to volcanic environments due to potential differences in element speciation and oxidative chemistry. Some recent studies have suggested exposure to volcanic heavy metals may be linked to specific health effects, including an increased incidence of thyroid cancer (Vigneri et al., 2017) and fertility issues (in mice; Sauzéat et al., 2025), although determining clear links between exposure to volcanic trace elements and health-related consequences remains highly challenging due to exposure to volcanogenic metals often occurring over long periods of time, over wide geographic areas, and in combination with exposure to many other environmental pollutants. This makes it difficult to constrain the extent and severity of population exposure or to conclusively link subsequent whole-body health impacts to volcanogenic pollution exposure (Stewart et al., 2021). The work presented in Chapter 5 of this thesis considers how interactions between volcanic and wildfire emissions may result in PM with altered physicochemical characteristics. This work is directly applicable to future toxicological studies (which have been used previously to constrain the effect of co-exposure in human epithelial tissues to combined volcanic and vehicle exhaust emissions; Tomasek et al., 2016).

1.5 The Fagradalsfjall 2021-2023 Eruptions

The Geldingadalir, Meradalir, and Litli-Hrútur fissure eruptions, which occurred on the Reykjanes Peninsula in 2021, 2022, and 2023 respectively, form the three central case studies presented in this thesis. These eruptions all occurred within the Fagradalsfjall volcanic system, which is one of six volcanic systems in the Reykjanes Volcanic Zone on the Reykjanes Peninsula in Iceland (Einarsson and Sigurgeirsson, 2019) and are henceforth in this thesis referred to collectively as the Fagradalsfjall 2021-2023 eruptions. Exact details of each eruption are presented in Chapter

3 of this thesis and detailed in other publications (e.g., Halldórsson et al., 2022; Barsotti et al., 2023). Here, I therefore present a more general overview of the Fagradalsfjall eruptions and provide an outline of work that has emerged from them, spanning many different research fields, and towards which this thesis contributes.

Recent activity on the Peninsula began in 2019 with an intense week-long earthquake swarm at the southern margin of Mount Fagradalsfjall, thought to be related to the intrusion of a magmatic sill, followed by several episodes of surface inflation centred on the neighbouring Svartsengi volcanic system (Sigmundsson et al., 2022). This marked the end of 6,000 years of quiescence for the Fagradalsfjall volcanic system and 800 years of dormancy on the wider Reykjanes Peninsula (Sæmundsson et al., 2020). The timing of reactivation in 2019 (with the first surface eruption of lava in 2021) is in keeping with previous cycles of activity on the Peninsula which have occurred intermittently for roughly 100–200-year periods every 800 years over the past 4000 years, with the last “Reykjanes Fires” ceasing at the end of the 13th Century (See Figure 1.2; Sæmundsson et al., 2020).

The Fagradalsfjall 2021-2023 lavas are characterised as olivine tholeiite basalts, although the composition of the magma changed both throughout and between eruptions. In the first several weeks of the 2021 eruption, the magma underwent a large compositional shift in K_2O/TiO_2 and La/Yb ratios, both increasing by a factor of 2 over the first 50 days of the eruption (Halldórsson et al., 2022). This is interpreted as mantle-derived variability and an increase in the contribution from deeply generated mantle melts that are enriched in incompatible trace elements into the 2021 eruption (Halldórsson et al., 2022). Based on thermobarometry constraints, this magma is thought to derive from magma bodies at near-Moho depths at around 15 km (Halldórsson et al., 2022; Marshall et al., 2024). Magma compositions in 2022 and 2023 showed considerably less variability than in 2021 and had enriched compositions consistent with those erupted at the end of the 2021 eruption. This suggests these eruptions were also sourced from a near-Moho magma domain at ~ 15 km, with inputs of deeply derived mantle melts (Caracciolo et al., 2025).

Eruptive activity during the Fagradalsfjall 2021-2023 eruptions was predominantly effusive in style owing to the low volatile contents and low viscosity of the basaltic magmas (Halldórsson et al., 2022). All three eruptions followed a similar pattern of an initial long fissure (~ 1 km in length in 2023, multiple fissures in 2021) rapidly localising into a single volcanic vent that was subsequently built up through intermittent spattering and fire-fountaining activity. During

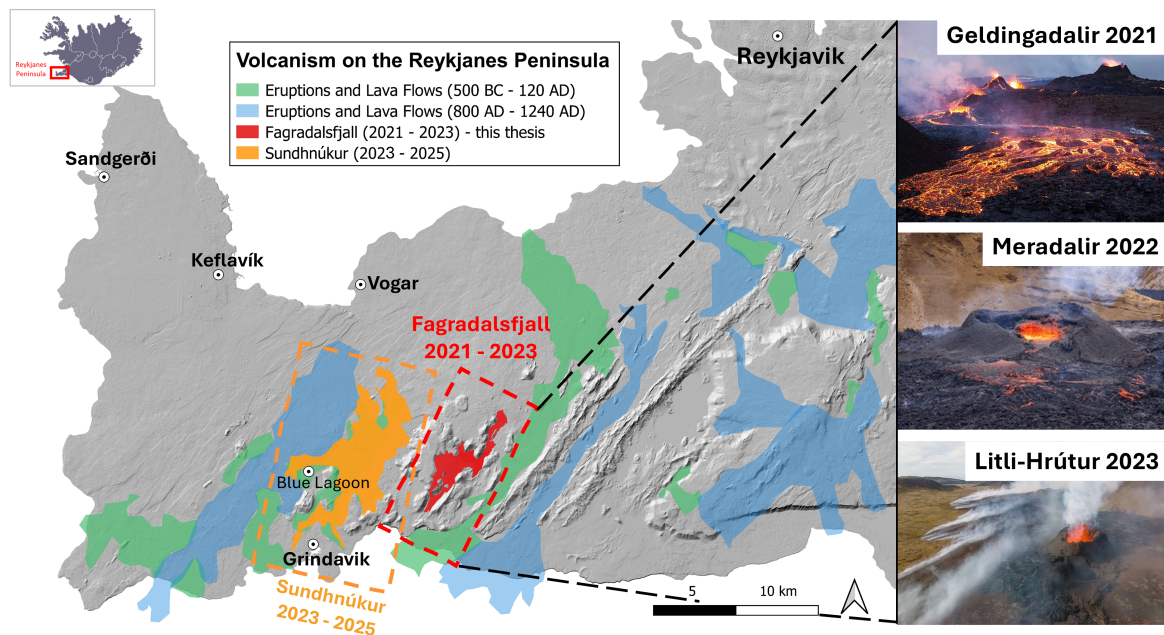


Figure 1.2: Overview Map of Recent Volcanism on the Reykjanes Peninsula. Green and Blue shading shows mapped lava extents during the previous two episodes of activity on the peninsula between ~ 500 BC – 120 AD and 800 AD and 1240 AD, respectively - from Sæmundsson et al. (2020). Red shading shows the lava extent from the Fagradalsfjall 2021-2023 eruptions, which form the central case studies and focus of this thesis. Orange shading shows the extent of the subsequent Sundhnúkur eruptions in 2023-2025 as of 17th July 2025. Photographs show the main vent(s) for each of the three Fagradalsfjall eruptions.

the 2022 and 2023 eruptions, activity was limited to one main active vent (with sporadic flank collapses of the crater walls during both eruptions) and lasted 3 weeks and 4 weeks, respectively. The Geldingadalir eruption in 2021 was, by contrast, far more prolonged, lasting almost 6 months from 19th March to 18th September and spanning four distinct eruption phases (as defined by Barsotti et al., 2023 and Pedersen et al., 2022) with 9 different vents being active, sometimes simultaneously, throughout the eruption. All three eruptions produced sizeable lava flows; the total volume of lava erupted was at least $150 \times 10^6 \text{ m}^3$ (2021), $1.6 \times 10^6 \text{ m}^3$ (2022), and $15.9 \times 10^6 \text{ m}^3$ (2023), for the different eruptions respectively.

All three of the Fagradalsfjall 2021-2023 eruptions also produced gas-rich plumes containing major gases as well as silicate and non-silicate PM (Halldórsson et al., 2022; Pfeffer et al., 2024; Wainman et al., 2024). The emission of major gas species (H_2O , SO_2 , CO_2 , H_2O , HCl , and HF) was routinely monitored throughout the eruptions by researchers at the Icelandic Meteorological Office and University of Iceland using FTIR and UV spectrometers (Halldórsson et al., 2022; Scott et al., 2023; Pfeffer et al., 2024). Some of this major gas data is presented in Chapter 3 of this thesis, as a supplement to multi-element direct sampling. Detailed investigation of SO_2 fluxes during the Fagradalsfjall 2021 eruption by Pfeffer et al. (2024) estimated relatively low SO_2 emission rates compared to Holuhraun 2014-2015 but demonstrated that stronger SO_2 fluxes were generally concurrent with a high amplitude of seismic tremor and intense fire-fountaining activity. Smekens et al. (2024) also used Open-Path Fourier-Transform Infrared (OP-FTIR) absorption spectroscopy measurements to observe rapid sulfate aerosol formation within a few seconds post-emission.

The impact of the volcanic plume on downwind air quality, including PM and SO_2 , during the Geldingadalir 2021 eruption was investigated by Whitty et al. (2026) using the permanent municipal regulatory AQ network supplemented with low-cost sensors near the eruption site. They found elevated PM and SO_2 concentrations at least 300 km from the vent, demonstrating the widespread dispersion and air quality impacts of even a relatively small fissure eruption. They also measured significant fine-scale temporal and spatial fluctuations in PM concentrations (PM_{10} , $PM_{2.5}$, and PM_1) in the capital area of Reykjavik (population $\sim 139,000$), highlighting disparities in population exposure that may not be captured by the current municipal AQ network or the resolution of the CALPUFF dispersion model that was used to provide ground level SO_2 forecasts throughout the Fagradalsfjall 2021-2023 eruptions (Barsotti et al., 2023;

Pfeffer et al., 2024; Whitty et al., 2026). The Litli-Hrútur eruption in 2023 also generated extensive moss wildfires (Schiffmann et al., 2025; Chapter 5 of this thesis). These were an additional source of air pollution across the Reykjanes Peninsula and form the focus of the work presented in Chapter 5 of this thesis.

The Fagradalsfjall 2021-2023 eruptions have generated intense scientific interest and provided an unprecedented opportunity to gain insights into a multitude of volcanic processes. This has included an improved understanding of precursor signals from ground deformation (Parks et al., 2023), seismicity (Greenfield et al., 2022; Fischer et al., 2022) and geothermal unrest (Flóvenz et al., 2022), and the use of geodetic inverse modelling to locate areas of sub-surface magma movement and forecast likely timescales and locations of eruption with a high degree of success (Parks et al., 2023). The use of lava flow modelling and near-real-time photogrammetric modelling to track lava transport (Pedersen et al., 2022; Pedersen et al., 2023) was also critical in managing one of the central hazards of these eruptions (Barsotti et al., 2023) and in the construction of deflective lava barriers (Sigtryggisdóttir et al., 2025). Studies focused on the eruptions' petrology and geochemistry have provided new constraints on underlying mantle compositions (Bindeman et al., 2022; Moussallam et al., 2024) and insights into crustal magma processing (Day et al., 2024), lateral magma transport (Caracciolo et al., 2025; Hobé et al., 2025) and the role of deeply generated mantle melts at mid ocean ridge spreading systems (Halldórsson et al., 2022; Kahl et al., 2023).

As discussed above, several studies have also focused on the emission of major gas species (Halldórsson et al., 2022; Pfeffer et al., 2024), aerosol formation in the volcanic plume (Smekens et al., 2024), and downwind air quality implications (Whitty et al., 2026). In addition to the work presented in this thesis, a few studies have also considered the behaviour of trace elements in the volcanic plumes at the Fagradalsfjall 2021-2023 volcanic eruptions. Edwards et al. (2024) investigated the behaviour of Hg and reported exceptionally low concentrations in the volcanic plumes at the Gedlingadalir 2021 and Meradalir 2022 eruptions. Hg is not included in this thesis due to the specific equipment needed to measure Hg in the volcanic plume, which would have precluded other multi-element sampling techniques. Levillayer et al. (2025) also consider the post-eruption emission of trace elements from lava flows and the cooling volcanic vent during the Fagradalsfjall 2021-2023 eruptions, producing a dataset which is highly complementary to the insights presented in Chapter 3 of this thesis. The synergies between the work presented here

(overall scope summarised in Figure 1.3) and additional work resulting from the Fagradalsfjall 2021-2023 eruptions are explored further in Chapter 6 of this thesis.

1.6 Thesis Aims and Organisation

The three studies presented in this thesis consider the behaviour of trace elements in volcanic environments using the Fagradalsfjall 2021-2023 eruptions as their central case studies. This research is driven by several underpinning research questions and aims, some of which were defined at outset of the project, whilst others formed through the natural progression of this work. These research questions are as follows:

- To what extent does lava flow outgassing contribute an additional flux of trace elements to the atmosphere during basaltic eruptions? How significant is this contribution compared to emissions released from the central vent(s)?
- How does the geochemical composition and trace element signature of lava flow outgassing vary compared to at-vent degassing? How do parameters such as lava temperature, fractional degassing, and flow dynamics affect the emission of trace elements?
- During downwind atmospheric transport in the aerosol plume, are elements deposited heterogeneously or homogeneously? How does this vary between wet and dry depositional processes, and could this be modulated by background meteorological conditions?
- During compound volcanic-wildfire events, how do emissions from volcanic sources (at-vent, lava flows) differ from those produced during wildfire burning?
- What mechanical interactions and/or chemical reactions occur upon mixing between volcanic and wildfire emissions? How might this alter the physicochemical properties and thus the transport and deposition mechanics of trace elements in compound volcanic-wildfire environments?

These research questions are addressed throughout this thesis, which is organised into the following sections:

- Chapter 2: I give an overview of the key sampling methods and analytical approaches used in this thesis. Methodology sections are included in Chapters 3, 4, and 5, with exact details relating to the specific study, and thus are not repeated in detail. Instead, I provide

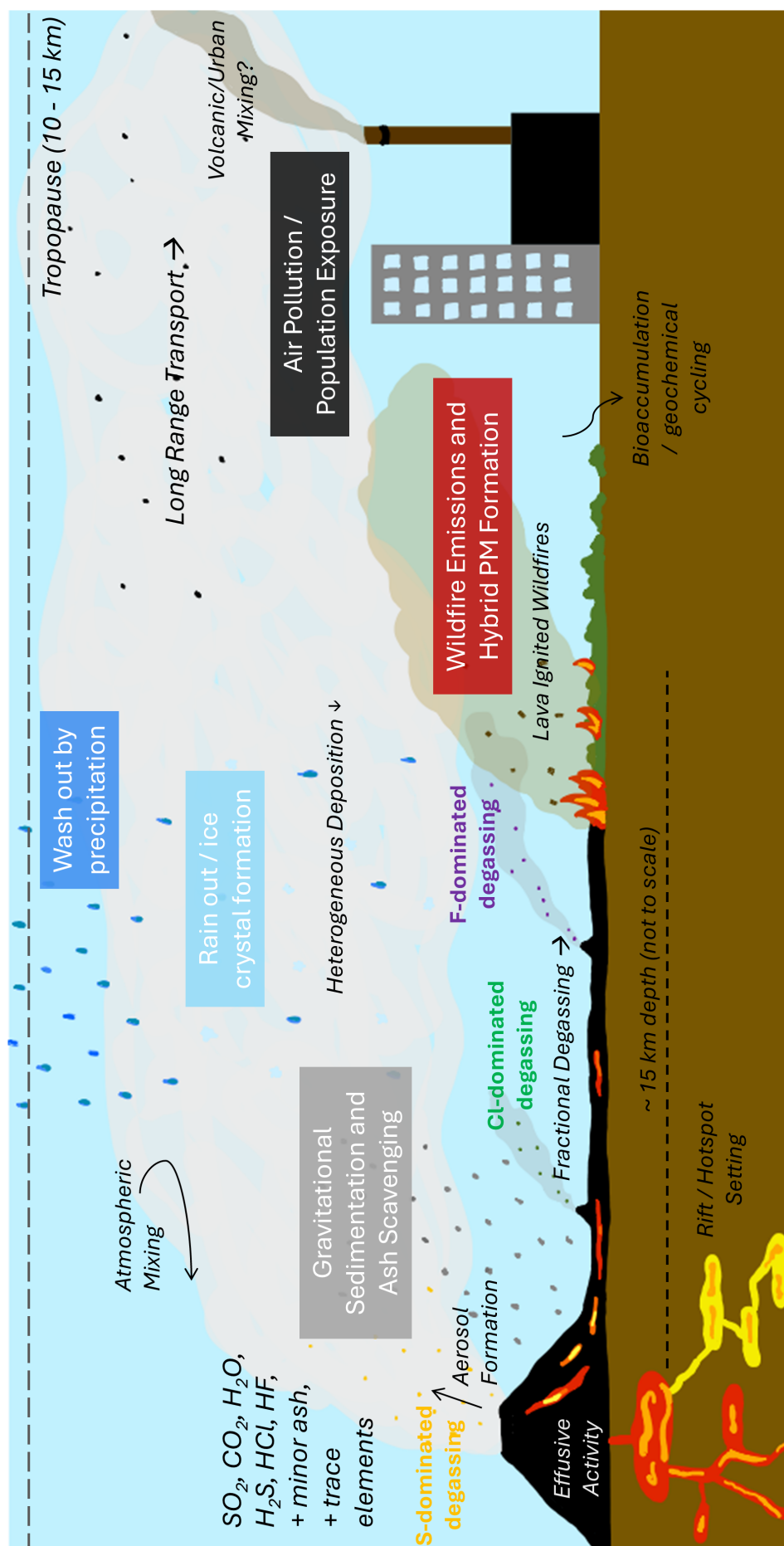


Figure 1.3: Overview of the emission sources, transport pathways, and depositional processes that are considered in this thesis. Chapter 2 considers the fractional degassing of trace elements from outgassing lava flows. Chapter 3 investigates the effect of background meteorological conditions on the heterogeneous deposition of trace elements from the effusive volcanic plume. Chapter 4 examines the mixing processes between volcanic and wildfire emissions and the consequences for the physicochemical characteristics of hybrid particulate matter. Chapter 5 places these studies in their broader context and considers important directions of future work, such as mixing between urban and volcanic emissions.

a more generalised overview of the key methodologies, outlining their recent development in the field of volcanic gas geochemistry, the limitations and challenges associated with each approach, and the reasoning behind their use in this thesis.

- Chapter 3: I investigate the emission of trace elements from outgassing lava flows at the Fagradalsfjall 2021-2023 eruptions and consider how the trace element signature of lava flow outgassing evolves downflow as the lava ages and cools. I demonstrate that element speciation and fractional degassing contribute to several geochemically distinct regions of outgassing based on lava temperature and flow dynamics. I highlight that lava flows contribute an additional and non-negligible source of trace elements and should be considered in overall hazard assessments. Supplementary Material for Chapter 3 is found in Supplementary Appendix A.
- Chapter 4: I compare trace element deposition behaviour from the volcanic plumes at the Fagradalsfjall 2021 and 2022 eruptions under different meteorological conditions. I demonstrate heterogeneous deposition of trace elements from the volcanic plume and suggest this is controlled by the interplay between element chemical speciation, water solubility of the resulting complexes, particle size distribution, and particle scavenging affinity. This has potential implications for seasonally dependent trace element deposition with consequences for the long-term surface delivery and human exposure to potentially toxic metals in volcanic environments. Supplementary Material for Chapter 4 is found in Supplementary Appendix B.
- Chapter 5: I investigate trace element dispersion behaviour in a compound volcanic-wildfire event at the 2023 Litli-Hrútur eruption and wildfires. I demonstrate that whilst volcanic eruptions and moss wildfires produce physiochemically distinct emissions, upon mixing, either at the lava-moss ignition interface, or during transport, they may undergo mechanical interactions. These interactions contribute to the formation of hybrid particulate matter with altered physicochemical properties, which I suggest may result in altered transport and deposition pathways for volcanic trace elements compared to standalone eruptions. Supplementary Material for Chapter 5 is found in Supplementary Appendix C.
- Chapter 6: I summarise the conclusions of this thesis in their broader context and recommend possible directions for future research.

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Chapter 2

Methods

This Chapter provides a general overview of the key sampling procedures and analytical approaches used in this thesis. Specific details of the samples collected and the extraction and analytical approaches used are provided in the methodology sections of Chapters 3, 4, and 5, and in the Supplementary Material.

2.1 Trace Element Sampling

2.1.1 Filter Packs

Filter packs have been a staple of in-situ volcanic plume sampling for several decades and have been used at a wide range of volcanoes globally (Crowe et al., 1987; Finnegan et al., 1990; Martin et al., 2008; Moune et al., 2010; Mather et al., 2012; Pfeffer et al., 2013; Zelenski et al., 2014; Mandon et al., 2019; Ilyinskaya et al., 2021). Filter packs vary in design but broadly consist of a series of stages over which air is drawn using an external pump and onto which bulk PM and gases are collected (See Figure 2.1). In this thesis, filter packs were used in two different setups: 1) containing only one PTFE filter on the first stage for PM collection or 2) with an additional 3 gas filters loaded behind the first PTFE filter. The gas collection filters are impregnated with a basic solution shortly prior to use to allow for the capture of acidic gases such as SO_2 , HCl and HF by reaction and conversion to their anions SO_4^{2-} , SO_3^{2-} , Cl^- , and F^- . Mioduszewski and Kress (2008) performed laboratory calibration of filter packs for volcanic gas sampling using an artificial fumerole and found that they were an effective sampling approach, although were prone to oversaturation on the filters, which could lead to erroneously low S/Cl and S/F ratios.

Measures taken to ensure undersaturation of the gas filters as part of the sampling approach employed in this thesis are described further in Section 2.2.1 below. Throughout this thesis, air flow through the filter was generated using an SKC Leland Legacy pump at a flow rate of around 10 L/min (exact flow rates given in Chapters 3, 4, and 5 methodologies and in the electronic supplementary material, +/- 5% flow rate accuracy as reported by the manufacturer). Prior to use in the field, filter packs were washed in a 10% solution of HNO_3 and rinsed in Milli-Q water ($> 18.2 M\Omega$, MQ) to minimise contamination between sampling campaigns. Filter packs were pre-loaded in an ISO 7 clean lab environment and sealed using parafilm to prevent contamination during transport to the field. A “field blank” sample was collected at the 2023 eruption by transporting a loaded and sealed filter pack to and from the field without opening it. This was used to constrain the possible contribution of transport and handling to overall trace element concentrations on the filter, although element concentrations on this field blank were comparable to concentrations in filter and water laboratory blanks (see Supplementary Material A), which were also negligible.

2.1.2 Cascade Impactors

Cascade impactors have also been used for in-situ plume sampling at a range of volcanoes globally and operate similarly to the filter packs outlined in Section 2.1.1 (Martin et al., 2008; Mather et al., 2012; Martin et al., 2012; Ilyinskaya et al., 2021). Cascade impactors consist of a series of stages, each containing a PTFE filter, between apertures of decreasing diameter (Hinds and Zhu, 2022). This offers the advantage of producing size-resolved PM and multi-element samples (compared to filter packs which collect bulk PM on a single stage). The largest PM ($> 2.5 \mu\text{m}$ diameter) is collected on the first stage, with decreasing particle diameters on the subsequent stages ($2.5 - 1.0 \mu\text{m}$, $1.0 - 0.5 \mu\text{m}$, $0.5 - 0.25 \mu\text{m}$) until the final after-stage, onto which the smallest particle size fraction ($< 0.25 \mu\text{m}$) collects. In Supplementary Material B, I compare the collection efficiencies of filter packs and cascade impactors in the volcanic plume and suggest that cascade impactors may be fractionally undersampling the most refractory elements, hosted in the coarsest PM size fraction. This effect has been observed previously in non-volcanic environments, due to increased wall deposition in the coarsest stages (Berlinger et al., 2021), and should be accounted for in future studies using cascade impactors to sample volcanic trace elements.

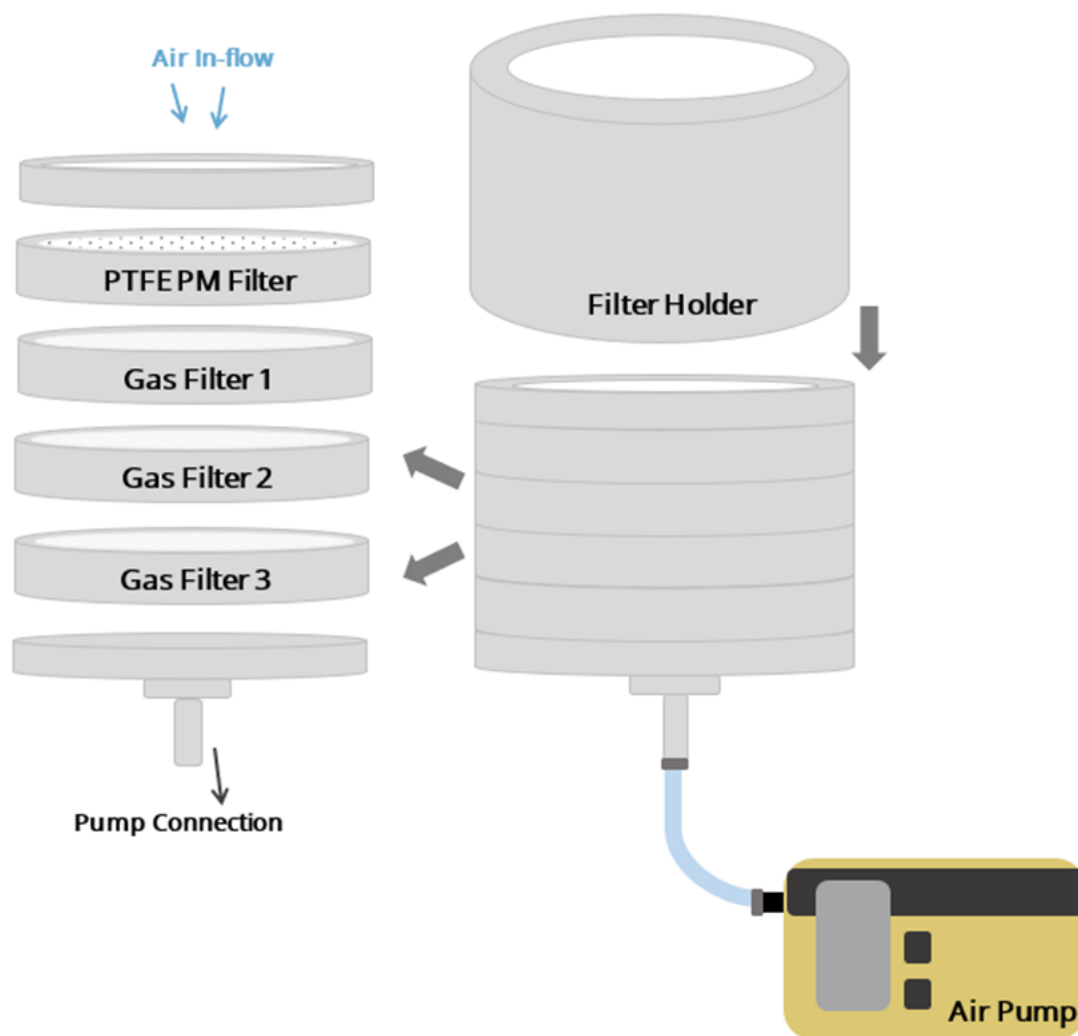


Figure 2.1: Schematic diagram of the filter pack sampling set up. Teflon filter stages and holders were bespoke 3D printed and can be configured to sample either just PM (only one PTFE filter on the first stage) or PM and gases simultaneously (PTFE filter + 3 acid gas filters on subsequent stages). Air flow through the filter is generated by connection to an external pump.

2.1.3 UAV Platforms

Elements of this section have also been published as Wainman (2024), Tools of the Trade: Using drones to sample volcanic plumes, Nature Reviews Earth and Environment.

Recent advances in UAV (uncrewed aerial vehicle; drones) technology have unlocked new opportunities for sampling volcanic trace elements and allowed access to previously unreachable and dangerous regions of the volcanic plume (i.e., very near vent, within ~ 50 m; Liu et al., 2020; Wainman, 2024; Thivet et al., 2024). UAV-mounted approaches do not require grounding of the buoyant volcanic plume, which depends strongly on weather conditions and local topography. They can also cover a much wider area of the plume from a single take-off location (e.g., up to ~ 1 km away from the take-off location for the UAVs used in this thesis) without requiring the continuous manual relocation of sampling equipment. For example, fixed-wing drones have been used to sample ash-rich volcanic plumes at high altitudes (up to 2 km vertical ascent, e.g., at Manam Volcano in Papua New Guinea; Liu et al. (2020)) whilst rotary style drones have been used to sample at lower altitudes during gas-rich eruptions (e.g., in this thesis; Wainman, 2024).

Increasing payload capacities (up to 2.7 kg on the DJI Matrice 300 RTK used for aerial sampling at the Fagradalsfjall 2022 and 2023 eruptions) mean that multiple sensors can be mounted and used simultaneously. In this thesis, the combination of a filter pack or cascade impactor (attached to the UAV leg), pump (mounted on the UAV body) and compact MultiGAS unit (attached on the opposite leg to maintain balanced weight distribution; see Figure 2.2) was the most common. This is because the SO_2 timeseries from the MultiGAS was critical for estimating the total time the UAV spent “in-plume” and thus performing post-processing corrections on the filter pack trace element concentrations (described in methodology sections in Chapters 3 and 4). In some instances, the filter pack/pump or multiGAS unit was exchanged for an Hg sampler (results presented in Edwards et al. (2024)) or an Optical Particle Spectrometer (OPS). The present UAV payload limitations and relative size and weight of the sampling instruments (which are not currently optimised for UAV platforms) meant that no more than 2 or 3 sampling instruments could be mounted on the UAV simultaneously without risking an unbalanced take-off and in-flight turbulence. Throughout this thesis UAV sampling was performed by hovering in place in a discrete location in the volcanic plume. Filter pack and cascade impactors produce bulk samples, rather than continuous time series data (e.g., as done by MultiGAS and OPS instruments), meaning that each filter pack can only be used to collect a single sample to avoid

overlapping signals. Due to UAV battery life limitations, this meant that in some instances multiple flights were conducted using the same filter pack/cascade impactor to the same region of the plume. Performing multiple flights helped to ensure element concentrations were above detection limits, but it introduces uncertainty and a potential source of contamination from dust that is remobilised during take-off and landing.

2.1.4 Ground-based Sampling

Filter pack and cascade impactor samples were also collected in this thesis using ground-based platforms. Ground-based sampling directly complemented UAV approaches as a way of measuring ground-level trace element concentrations, which are more representative of potentially inhalable compositions and thus the most relevant for assessing potential population exposure (as reported in Chapter 5). The set-up for ground-based sampling was similar to that on the UAV, although filter pack and cascade impactors were instead mounted on a portable backpack. This supported a “drop and go” approach, where the backpack could be quickly transferred to the location of interest before retreating to a safer location. Whilst in-situ sampling of volcanic aerosols and trace elements was the primary focus of this thesis, this was supplemented in Chapter 4 by the collection of ground-based snow samples that had been deposited following snowfall through the volcanic plume. Combined UAV and ground-based measurements were thus used to provide direct insights into depositional processes occurring in the volcanic plume. Possible future applications of combined UAV and ground-based approaches (e.g., biomonitoring as discussed in Section 1.4.2) are discussed in Chapter 6.

2.2 Analytical Approaches

2.2.1 Geochemical Analysis

Geochemical analysis of the major anions (SO_4^{2-} , Cl^- , and F^-) that collected on the PTFE and treated gas filters during plume sampling was conducted using Ion Chromatography (IC) at the University of Leeds (on a Thermo Dionex IC3000 ion chromatograph system) and at the University of Iceland (on a Thermo Dionex ICS2000). Ion chromatography measures the concentrations of ionic species by separating them according to interaction with a resin. IC analysis was also calibrated against stock standards and a certified reference material (e.g., ASSIN-02). F^- signals can be affected by the glycerol, which was used to pre-treat filters

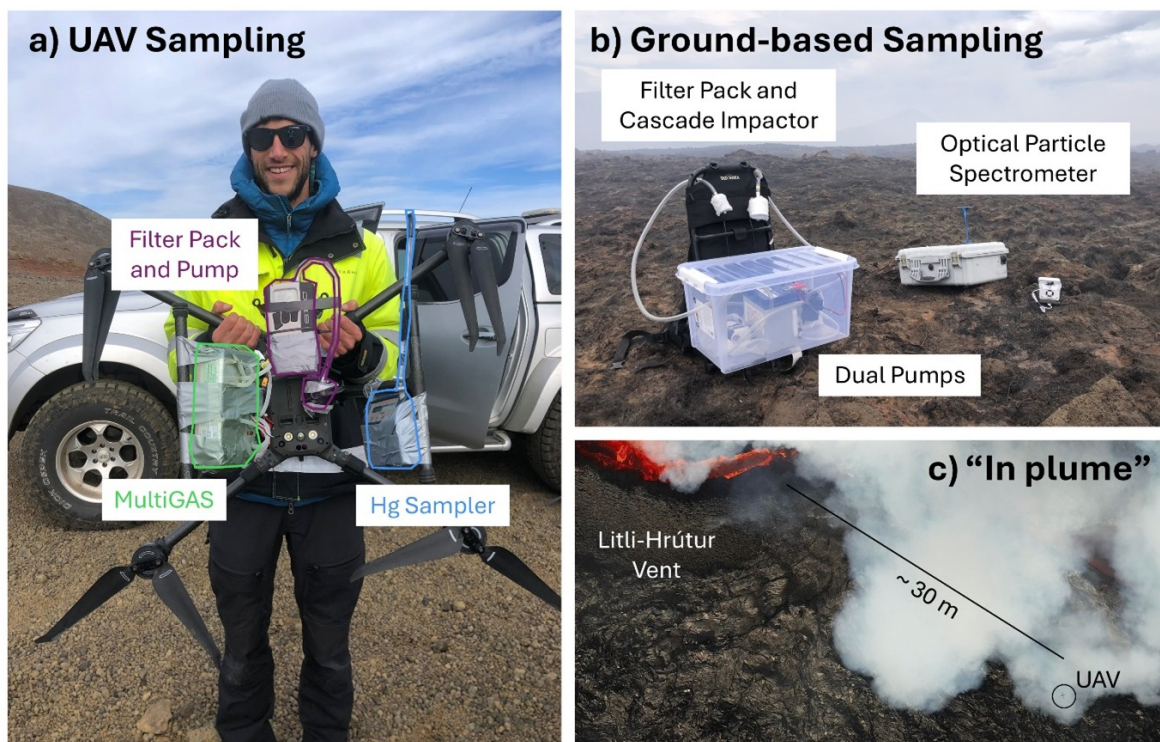


Figure 2.2: UAV and Ground-based sampling approaches. a) Instrumentation set up on the UAV in 2022. Instruments include a compact MultiGAS unit, a filter pack and pump set up, and an additional Hg sampler (pushing the payload limit of the drone but possible on this day due to exceptional flying conditions). b) Ground-based sampling set up at the Litli-Hrútur 2023 eruption and wildfires with simultaneous filter pack, cascade impactor, and optical particle spectrometer (OPS) measurements. c) Aerial photo of the UAV in the eruption plume at the Litli-Hrútur 2023 eruption.

before sampling, and by the H_2O_2 which was used to oxidise captured acidic gases during extraction (Wittmer et al., 2014). F^- data are therefore reported for completeness in the electronic supplement, but are not used to interpret in-plume concentrations. A major challenge with the use of base-treated gas filters is that at high concentrations or over long exposure periods (which are needed to ensure trace elements are above detection limits), saturation can occur (defined as when $> 10\%$ of total SO_4^{2-} is present on the final filter). If filters do saturate, this means SO_4^{2-} concentrations may be underestimated. All gas filters collected in 2021 were saturated, meaning we decided to use KOH rather than K_2CO_3 for the pre-treatment of the gas filters in 2022 and 2023 (and in 2023, thicker, more absorbent pads were used). Gas filters in 2022 saturated to a lesser extent than in 2021, and gas filters in 2023 did not saturate at all despite being exposed to comparable SO_2 concentrations across similar flight durations, suggesting this was an effective change in methodology.

The PTFE filters collected using filter packs and cascade impactors were extracted according to a two-stage sequential leaching process. This leaching process is reported in Mason et al. (2021) and Ilyinskaya et al. (2021) and detailed in the methodology sections of Chapters 3, 4, and 5 in this thesis, and so is not repeated here. Following extraction, (solution) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to analyse for an array of over 50 trace elements at the Open University (OU; on an Agilent 8800 ICP-MS/MS (“triple quad”) instrument). ICP-MS uses a plasma to ionise the elements in a sample and then measures trace element concentrations (down to ppt) by using a mass spectrometer to separate and detect ions based on their mass-to-charge ratios. Using a standard ICP-MS set up can, however, result in isobaric (e.g., $^{204}Hg^+$ on $^{204}Pb^+$) and polyatomic (E.g. $^{40}Ar^{16}O$ on ^{56}Fe) interferences for some elements (such as Bi, As, Pb, and Se, which are of particular interest in volcanic plumes). The triple quad set-up (used at the OU) minimises these interferences by using tandem quadrupoles and a collision-reaction cell set up (ICP-MS/MS; Figure 2.3; Balcaen et al., 2015). In this set up, the initial quadrupole (Q1) acts as a preliminary filter and rejects all ions without the desired mass-to-charge ratio which produces a “polished” ion stream, a collision gas is then fed in (He, O_2, NH_3) which removes interferences by colliding with and removing larger polyatomic ions, the much cleaner ion stream is then passed into the second quadrupole (Q2) to the detector with fewer interferences and improved detection limits. ICP-MS/MS analysis at the OU was run with multiple different collision gases per element. This allowed for post-run processing and optimisation based on internal calibration standards because the “best choice” of collision gas

can vary by element and by sample matrix (Balcaen et al., 2015). Note that at present, no certified reference material (CRM) exists which encompasses all of the characteristic elements and concentration ranges found in the secondary non-silicate volcanic aerosol fraction. For example, BHVO-2 (Hawaiian Basalt) has ppm levels of Zr but no Se, whereas volcanic aerosols have ppm levels of Se but bdl concentrations of Zr. Similarly, the NIST SRM 1648a CRM, which is urban dust from an industrial setting, is fundamentally different to primary volcanic aerosols in its relative concentrations of major and trace elements (e.g., lacks data for elements Te, Tl, and Sn, which are all in high concentrations in our volcanic samples). As such, instead of using an ill-fitting CRM, we ran internal synthetic calibration standards during our ICP-MS analysis. These were made up of certified stock solutions diluted to encompass the full range of element concentrations in our samples. These internal standards were run every 4- 6 unknown samples, allowing the optimal gas mode to be selected and to monitor for instrument drift. During post-processing, internal standard measurements were also compared back to the known diluted stock concentrations to assess the reproducibility and accuracy of our analyses (see the electronic supplement sheet B1 for element-by-element RSD and Average/Standard comparisons).

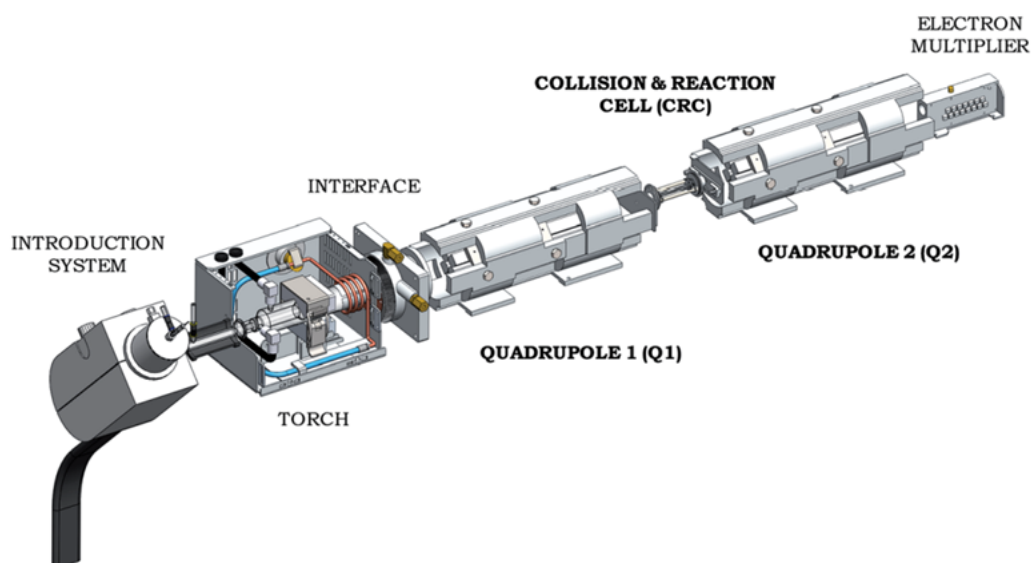


Figure 2.3: Schematic overview of triple quad ICP-MS/MS set up. From Bolea-Fernandez et al. (2017).

2.2.2 Microscopy

Scanning Electron Microscopy (SEM)

SEM analysis has been used routinely to analyse the geochemical and morphological characteristics of volcanic PM (Delmelle et al., 2007; Martin et al., 2009; Moune et al., 2010; Mandon et al., 2019; Zelenski et al., 2020; Trejos et al., 2021) and was used in Chapter 5 of this thesis, to conduct geochemical and morphological analysis of PM produced during a compound volcanic-wildfire event. An SEM produces images by scanning the surface of a sample with a beam of electrons that interacts with atoms in the sample. Secondary electrons may be emitted by atoms which have been excited by the electron beam, whereas backscattered electrons are those that originate in the electron beam and are reflected (“backscattered”) out of the specimen by elastic scattering interactions. The detection of these two different types of elements results in secondary (SE) and back-scattered (BSE) electron images. SE images generally reflect the surface topography of a sample, whereas BSE images are sensitive to mean atomic mass, so they can be used to show contrast between areas of different compositions. PM collection for SEM analysis was improvised during the Litli-Hrútur 2023 eruption using the PTFE filters that are typically used for bulk geochemical sampling (Section 2.1.1). These PTFE filters are comprised of C, O, H, and F and thus when imaging the organic PM (also C-rich) that was produced during the wildfire burning it was found that SE imaging provided the best contrast between PM and the filter (compared to BSE imaging which had low contrast due to the similar compositions of the PM and background PTFE filter). SEM imaging was performed at the Leeds Electron Microscopy and Spectroscopy Centre (LEMAS) on a W-filament Tescan VEGA3 XM. W-filament SEMs have an imaging resolution down to $\sim 0.02 \mu\text{m}$ and thus are sufficient to image most of the particle size spectrum found in volcanic plumes (e.g., Martin et al., 2009). The imaging of the smallest aerosol size fraction was, however, somewhat limited by the structure of the background PTFE filter, which contained holes and “blob-like” structures and made it difficult to differentiate between the background filter and the finest PM.

SEM imaging may also be coupled with electron dispersive spectroscopy (EDS) analysis, and in this thesis, it was performed at the University of Leeds using an X-max 150 SDD EDS detector. EDS provides qualitative data on PM compositions by detecting the characteristic X-rays that are emitted when the electron beam interacts with the sample. This approach was successful in differentiating between silicate PM (e.g., identifying an Augite crystal and basaltic

glass shard; Chapter 5) and wildfire PM, but was of limited use in determining even qualitative compositions for the finer PM size fraction. This was due to the interaction volumes associated with EDS analysis (see Supplementary Material C), which are generated by the electron beam. Interaction volumes in these samples were around 1-3 μm diameter which exceeded the diameters of the smallest particles ($< 1 \mu\text{m}$) and thus meant that any EDS data included the composition of the particle as well as the surrounding filter.

Transmission Electron Microscopy

Compared to SEM-EDS analysis, transmission electron microscopy (TEM) offers much higher resolution imaging (0.1 – 0.5 nm depending on the sample). This is because TEM uses much higher electron accelerating voltages, resulting in smaller de Broglie wavelengths, and passes electrons through a very thin (electron-transparent) sample, reducing potential interactions. When combined with Electron energy loss spectroscopy (EELS), which measures the energy lost by the electrons when they excite the atoms in the specimen to emit X-rays, this can provide compositional data on ultra-fine particles. The presence of ultra-fine S and Cl-rich aerosols on particle filters and as coatings on larger volcanic PM has been inferred previously through S and Cl peaks in EDS spectra (Martin et al., 2009; Mandon et al., 2019) but a method for routinely imaging and analysing the composition of this ultra-fine volcanic aerosol is still needed. The TEM analysis included in Chapter 5 of this thesis presents a preliminary approach to investigating the behaviour of ultra-fine S and Cl-rich volcanic aerosols. The exact methodology of this approach is detailed in Chapter 5, Section 5.2.5, including the use of a focused ion beam (FIB) to “cut out” the moss particle from the SEM stub for finer-scale TEM analysis. With considerable refinement, this method could be a valuable tool for investigating the finest scale volcanic PM (Pfeffer et al., 2006). Future development and possible applications of this approach (e.g., for investigating interactions between volcanic PM and urban pollutants) are outlined in Chapter 6.

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Chapter 3

Trace element emissions vary with lava flow age and thermal evolution during the Fagradalsfjall 2021–2023 eruptions, Iceland

L. Wainman, E. Ilyinskaya, M. Pfeffer, C. Mandon, E. Bali, B.A. Edwards, B.I. Kleine-Marshall, S.R. Gudjonsdottir, A. Cotterill, S.W. Scott, P. Wieser, A. Stefánsson, E.J. Nicholson, J. Sepulveda-Araya, S. J. Hammond, B. E. Kunz, F. Jenner, J.R. Gunnarsson, A. Aiuppa, M. Burton, T.A Mather.

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- Particulate matter (PM) and gases were measured in lava flow emissions at increasing distances from the crater (increasing lava ages) as well as above a stagnant lava pond at the Fagradalsfjall 2021-23 eruptions.
- Thermochemical modelling suggests that speciation is a key control on the down-flow fractionation in trace element outgassing from cooling lavas.
- Sulfur-complexing element (Se, Te, As) emissions decreased most rapidly down-flow whilst some chloride-complexed (Cu, Rb, Cs) elements become more abundant relative to at-crater emissions.

Abstract.

Basaltic fissure eruptions emit volatile and environmentally reactive gases and particulate matter (PM) into the lower troposphere (e.g., SO_2 , HCl, and HF in the gas phase; Se, As, Pb as complexes in the PM phase). Lava flows from fissure eruptions can be spatially extensive, but the composition and fluxes of their emissions are poorly characterized compared to those from main vent(s). Using UAS-mounted (drone) samplers and ground-based remote FTIR spectroscopy we investigate the down-flow compositional evolution of emissions from active lava flows during the Fagradalsfjall 2021-2023 eruptions. The calculated fluxes of volatile trace metals from lava flows are considerable relative to both main vent degassing and anthropogenic fluxes in Iceland. We demonstrate a fractionation in major gas emissions, with decreasing S/halogen ratio down-flow. This S-Cl fractionation is reflected in the trace element degassing profile, where the abundance of predominantly sulfur-complexing elements (e.g., Se, Te, As, Pb) decreases more rapidly in down-flow emissions relative to elements complexing as chlorides (e.g., Cu, Rb, Cs), oxides (e.g., La, Ce) and hydroxides (e.g., Fe, Mg, Al, Ti). Using thermochemical modeling, we explain this relationship through temperature and composition-dependent element speciation as the lava flow ages and cools. As a result, some chloride-complexing elements (such as Cu) become relatively more abundant in emissions further down-flow, compared to emissions from the main vent or more proximal lava flows. This variability in down-flow element fluxes suggests that the output of metals to the environment may change depending on lava flow age and thermal evolution.

Plain Language Summary

Lava flows, such as those formed during the recent eruptions in Iceland (2021-2023), emit gases, particles and droplets to the atmosphere. These include an array of different metals, some of which may be harmful to the environment and human health. In this study, we use drone-mounted equipment and a remote-sensing spectrometer to collect samples and the measure gases and particles above lava flows at increasing distances from the vent. Some elements that predominantly bond with sulfur, tend to diminish in abundance as the lava flow ages, while those elements that predominantly bond with chloride increase in abundance with increasing distance from the vent. By modelling how elements preferentially bond together at different temperatures, we can explain how different elements behave when emitted from increasingly colder lava flows. Overall, the quantity of metals emitted from lava flows during the Fagradalsfjall eruption is equal to or greater than emissions from human-related activity in Iceland during 2021.

3.1 Introduction

Volcanic emissions from effusive basaltic fissure eruptions consist of major gases (H_2O , SO_2 , H_2S , CO_2 , HCl , HF) and particulate matter (PM), including an array of metal and metalloid trace elements (Zoller et al., 1983; Symonds et al., 1987). Some of these elements, such as As, Cd, Cr, Pb, Se, Tl, and W, are classified as ‘metal pollutants’ (World Health Organisation, 2007) and thus, are both an environmental and air quality hazard for exposed communities (Stewart et al., 2021). During intense and prolonged activity, the eruptive outgassing of trace metal and metalloid elements can be comparable to anthropogenic emission fluxes from entire regions and countries (Ilyinskaya et al., 2021). Metal and metalloid elements are released during magma degassing directly into the atmosphere, either as free gases, or more commonly, complexed with major gas species to form oxides, halides (such as chlorides or fluorides), sulfides, sulfates, hydrides, or hydroxides (Symonds et al., 1992; Moune et al., 2010; Mandon et al., 2019; Zelenski et al., 2021). Upon outgassing at the air interface, metal and metalloid bearing gases are rapidly partitioned into a particulate phase (defined in this paper as particulate matter; PM) either via desublimation (gas-to-particle conversion), droplet condensation (Symonds et al., 1987), or scavenging of metal and metalloid elements by aerosols and ash (Moune et al., 2006). The composition and total emission flux of metal and metalloid elements is controlled by several factors, including melt composition, oxygen fugacity (fO_2), and the thermodynamic properties of metal/metalloid-containing compounds (Symonds et al., 1987; Symonds and Reed, 1993; Churakov et al., 2000; Williams-Jones and Heinrich, 2005). Melt composition is a primary control both on the concentrations of metals themselves, as well as on the availability of key ligand-forming elements (S, O, H, Cl, F), which are critical to metal speciation and emission (Symonds et al., 1992; Hinkley et al., 1994; Zelenski et al., 2021). Gas emissions from hotspot basaltic eruptions such as from Kīlauea, (Hawai’i) and Holuhraun 2014-2015 (Iceland) are generally lower in Cl relative to eruptions in arc settings, reflecting the more limited availability of the Cl ligand due to the absence of a recycled slab component (Mather et al., 2012; Gauthier et al., 2016; Allard et al., 2016; Edmonds et al., 2018; Mandon et al., 2019). Hotspot settings are generally associated with lower metal fluxes and a higher relative abundance of sulfur-complexing elements such as Se, Te, and Cd, although few studies have investigated this in the context of rift-dominated systems such as the Reykjanes Peninsula (Zelenski et al., 2013; Edmonds et al., 2018).

Degassing from the main volcanic vent(s) has been the primary focus of previous investigations (e.g., Mather et al., 2012; Ilyinskaya et al., 2017; Mandon et al., 2019; Mason et al., 2021), and yet basaltic eruptions also generate extensive lava flows which can be an additional source of gas and PM emissions (e.g., Thordarson and Self, 2003). Toutain et al. (1990) found that down-flow sublimate mineral assemblages at Piton de la Fournaise volcano were dominated by chlorides and fluorides but lacked sulfides, sulfates or oxides, which were most likely degassed closer to the vent. They did not link this to individual trace element behaviour, however, and instead suggested the distribution of elements depends on temperature and element volatility, with the more volatile elements such as Rb, Cs, Se, Pb and Tl being associated with deposits from lower-temperature flows. Previous approaches have defined metal volatility using either an emanation coefficient (ϵ_X) describing the extent to which an element is released in the gas phase (Pennisi et al., 1988; Edmonds et al., 2018), or an enrichment factor (EF), describing the degree to which an element is enriched in the volcanic gas and non-silicate aerosol phase relative to silicate material (Aiuppa et al., 2003; Moune et al., 2010; Mandon et al., 2019). Moderate to highly volatile elements are defined as having $\epsilon_X > 0.05$ % (Rubin, 1997) and include elements such as Te, Se, Cd, Pb, As, Ag, and Sn, whilst more refractory elements include those such as Fe, Ce, La, Ca, and Mg, which have $\epsilon_X < 0.001$ %. Recent advances in sampling and analytical approaches have prompted renewed study of down-flow degassing evolution, with analysis of individual trace element evolution, and simultaneous gas measurements at increasing distances down-flow. Quantification of the magnitude of metal and metalloid emissions from lava flows, relative to main vent degassing and anthropogenic emissions, is also important for understanding their relative contribution to potential tropospheric air quality and environmental hazards. This knowledge is particularly important if lava flows extend kilometers away from the main eruptive vent towards population centers, exacerbating the likelihood of ground-based exposure to volcanic pollutants such as SO_2 , PM less than $2.5 \mu m$ ($PM_{2.5}$), PM less than $10 \mu m$ (PM_{10}) and metals and metalloid elements (e.g., Pb, As, Cd) emitted from lava flows.

In this study, we use filter packs mounted on uncrewed aircraft systems (UAS) and Fourier Transform Infrared Spectroscopy (FTIR), to investigate the at-crater and down-flow emission of gases and trace elements during the 2021-2023 Fagradalsfjall eruptions on the Reykjanes Peninsula. Combined with equilibrium thermochemical modelling, we demonstrate that element speciation, which shows a dependence on lava temperature, is a key control on degassing behavior and down-flow fractionation in trace element emissions. Finally, we quantify the respective fluxes

of volatile trace elements from at-crater and lava flow sources, showing that they both equal or exceed Icelandic anthropogenic emissions in 2021 during periods of active eruptive activity.

3.2 Geological Context

3.2.1 The Fagradalsjall Eruptions 2021-2023

The three eruptions included in this study (2021 - Geldingadalir, 2022 - Meradalir and 2023 - Litli Hrútur) occurred within the Fagradalsfjall volcanic system, which is one of six volcanic systems in the Reykjanes Volcanic Zone on the Reykjanes Peninsula (See Figure 3.1 and Einarsson and Sigurgeirsson (2019)). Prior to the eruption in 2021, the Fagradalsfjall system had been dormant for 6000 years, while the wider peninsula had 800 years of quiescence. The 2022 and 2023 eruptions migrated progressively NE compared to the location of the 2021 eruption, although fissures all had a similar NE-SW strike and were located within ~ 5 km of each other.

Geldingadalir 2021 Eruption

Following a 14-month period of seismic unrest (Barsotti et al., 2023), the 2021 Fagradalsfjall eruption began on the 19th March (Sigmundsson et al., 2022; Halldórsson et al., 2022). The eruption continued for 6 months and progressed through four stages of activity (stages defined by Barsotti et al. (2023) and Pedersen et al. (2022)). The earliest stage (Phase I: 19th March – 5th April) was characterized by effusive activity from a single vent, followed by the opening of additional vents (including vents 2, 3, and 5 from which gas emissions were measured with FTIR, see section 3.3.4 below) during Phase II (5th April – 27th April). The composition of the lava changed significantly during the first 50 days of the eruption (between Phase I and Phase II) from a depleted low K_2O/TiO_2 composition to one that was more enriched, with a higher K_2O/TiO_2 ratio (Halldórsson et al., 2022). During Phase III (27th April – 28th June) activity was again concentrated to a single vent before the intensity of activity decreased during Phase IV (28 June – 18 September) and lava effusion from the main vent became cyclical. All phases of activity were associated with the emission of a plume of gas (Pfeffer et al., 2024) and PM from the main vent(s) as well as lava flows extending up several kilometers from the main crater(s). Mean lava thickness for the eruption exceeded 30 m, covering 4.8 km^2 with a bulk volume of $150 \pm 3 \times 10^6 \text{ m}^3$ (Pedersen et al., 2022). The mean bulk effusion rate varied between phases of the eruption, ranging from $1 - 8 \text{ m}^3/\text{s}$ in March–April and increasing to $9 - 13 \text{ m}^3/\text{s}$

in May–September (Pedersen et al., 2022). Volcanic plume samples presented in this work were collected on 23rd March 2021 (SFP3 and SFP4, Phase I) and 6th April 2021 (SFP8 and SFP12), Phase II). Figure 3.1 shows lava flow and sample location maps.

Meradalir 2022 Eruption

On 3rd August 2022 an eruption began at Meradalir, ~ 1 km to the NE of the previous eruption site on the Reykjanes Peninsula. After the initial fissure opening, activity became localized to a single vent, which was active until 21st August 2022. The effusion rate was initially $32 \text{ m}^3/\text{s}$ during the first hours of the eruption, then waned to an average of $11 \text{ m}^3/\text{s}$ between 4th and 13th August and decreased further to $3 - 4 \text{ m}^3/\text{s}$ between 13th and 15th August (Gunnarson et al., 2023). Lava flows between 5 - 15 m thick extended up to 2 km into the Meradalir valley, although were less laterally extensive than flows formed in the 2021 eruption, with a perched lava pond of 20 - 40 m thickness forming around the active crater. One lava flow sample was collected above a visibly degassing vent on the edge of the lava pond on 19th August 2022 (LW17) and two above vent samples were collected (LW1 and LW2) on 16th August 2022 – see Figure 3.1 and Table 3.1.

Litli-Hrútur 2023 Eruption

On 10th July 2023 an eruption started near Litli-Hrútur ~ 2 km to the NE of the 2022 Meradalir eruption and continued until 5th August 2023. Multiple eruption fissures stretched for over 1 km with an initial effusion rate of up to $50 \text{ m}^3/\text{s}$ during the first day of the eruption (Global Volcanism Program, 2023). The fissure quickly reduced to form a single active cone with an average effusion rate of $9 - 13 \text{ m}^3/\text{s}$ for the first several weeks of the eruption, before decreasing to $3 - 4 \text{ m}^3/\text{s}$ by early August (Global Volcanism Program, 2023). Lava flowed generally southwards, laterally extending towards the lava from the Meradalir 2022 eruption, although several crater rim collapses led to lava flowing towards the north and west of the crater. Extensive wildfires were also generated where lava flows ignited moss that covers much of the landscape in this region. Three samples were collected above laterally extending lava flows on 13th July 2023 (LHFP3 and LHFP4) and 19th July 2023 (LHFP9) and above the active vent on 19th July 2023 (LHFP8), see also Figure 3.1 and Table 3.1. Samples in 2023 were collected upwind of nearby wildfires to minimize contamination of the filters by wildfire pollution.

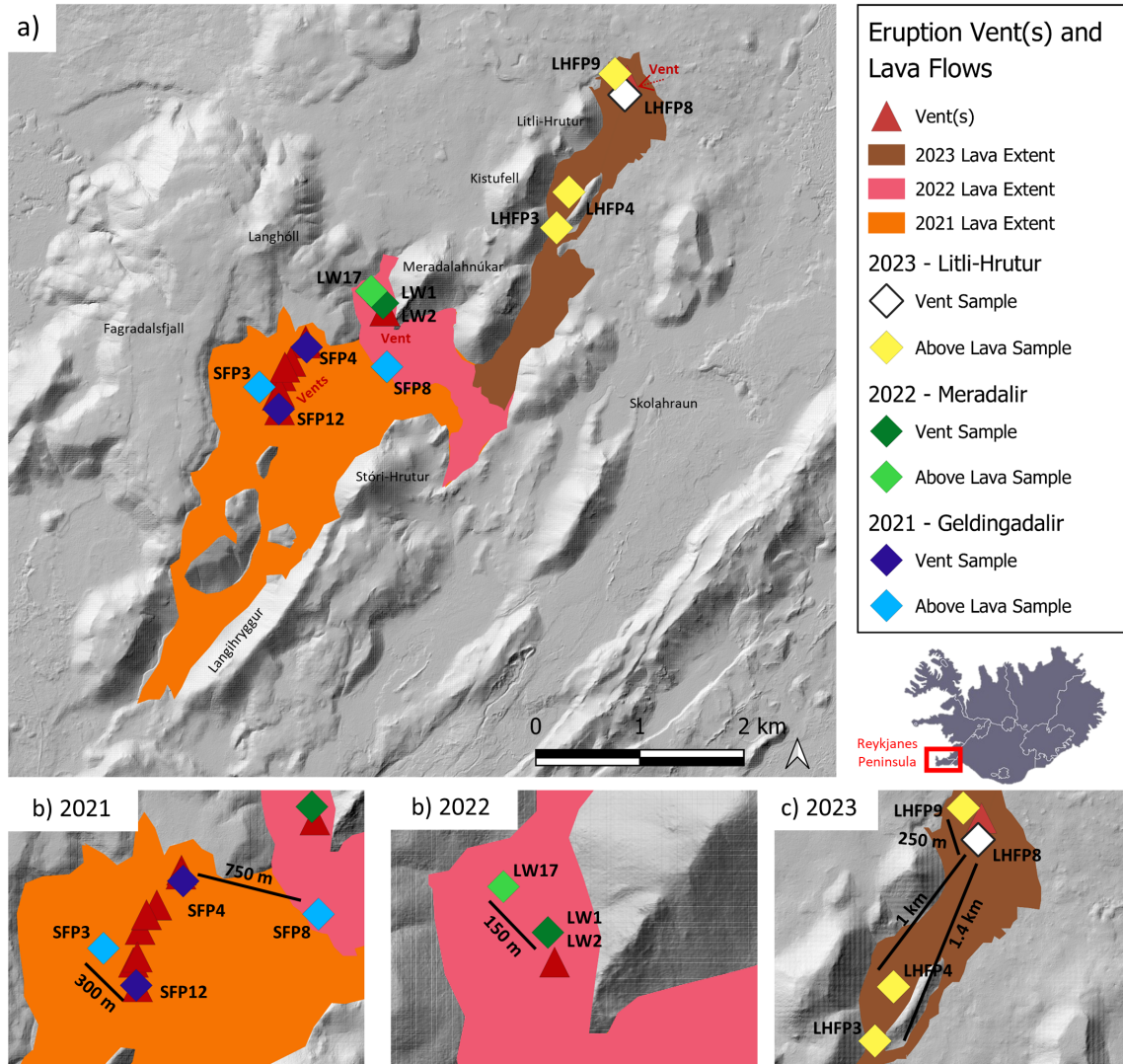


Figure 3.1: Map of sampling locations. a) Overview of lava flow extent for the three eruptions included in this study, red triangles show the locations of active vents. Diamonds show filter pack sampling locations, with darker colors showing at-vent samples and lighter colors showing samples collected above actively degassing lava flows. b) Fagradalsfjall 2021 - SFP3, SFP4, SFP8 and SFP12 were collected on separate days with lava samples (SFP3 and SFP8) at 300 m and 750 m from their concurrently active vents (SFP4 and SFP12, respectively). c) Meradalir 2022 – LW17 was collected 150 m from the vent above a perched lava pond. LW1 and LW2 were both collected above the main active vent. d) Litli-Hrútur 2023 – LHFP3 and LHFP4 were collected on the same day at 1.4 km and 1 km from the vent (LFP8), respectively, with LHFP9 collected subsequently at 250 m from the vent.

3.3 Methods

3.3.1 Filter Pack Sampling

Filter packs mounted on UAS (DJI Matrice 600 Pro in 2021, DJI Matrice 300 RTK in 2022 and 2023, see Supplementary A Figure A.2 for full drone set up) were used to collect in-situ samples of gases and aerosol PM above degassing lava flows. Total sampling duration ranged from 15 to 70 minutes, although due to UAS battery life limitations, most samples were the cumulation of multiple flights to the same location (see Table 3.1). The UAS hovered as close as vertically possible (~ 20 -60 m) above the lava surface where lava outgassing was visible, limited by the heat from the lava flows. There is some uncertainty associated with the unknown swirling of air masses as they rise and convect above the lava flows and vent, as well as the impact of the rotary drone propellers on the active pumping of gases and PM through the filter pack. Clear distinctions could, however, be made between vent and lava flow emissions, where filter packs above lava flows were collected well below the downwind lofting height and upwind of the central vent buoyant plume. Samples above lava flows were collected at a range of distances from the main vent, from 200 m to 1.4 km down-flow across the three sampling years. A Multi-GAS instrument from University of Palermo (Aiuppa, 2005, Liu et al., 2020, the same unit type used in Burton et al. (2023)) was co-located on the drone for simultaneous time-series measurements of SO_2 concentrations (time resolution 1 Hz). The Multi-GAS contains SO_2 and H_2S electrochemical sensors (T3ST/F-TD2G-1A and T3H-TC4E-1A; both City Technology) and is calibrated for 0 to 200 ppmv and 0 to 50 ppmv, respectively – see Liu et al. (2020).

Mounted filter packs consisting of 4 stages were used in two different configurations: either containing just one filter for PM collection (PM Filter specifications: Whatman™ WTP polytetrafluoroethylene (PTFE) 47-mm diameter, pore size 1.0 μ m) or with an additional 3 filters loaded behind the first PM filter for gas collection (Gas Filter Specifications: Whatman™ Quantitative Filter Papers, Ashless, Grade 41, 55-mm diameter (2021) and 47-mm diameter (2022), Millipore 47-mm diameter absorbent pads (2023)). The filters for gas collection were impregnated (5 % K_2CO_3 + 1 % glycerol in 2021, 5 % KOH + 1 % glycerol in 2022 and 2023) shortly prior to use (Ilyinskaya et al., 2017; Mason et al., 2021). Base treatment of gas filters allows for the capture of acidic gases such as SO_2 , HCl and HF by reaction and conversion to their anions SO_4^{2-} , SO_3^{2-} , Cl^- , and F^- . Gas filters were considered saturated if > 10 % of total SO_4^{2-} was present on the final gas filter stage (as defined by Mason et al. (2021)). All gas filters collected

in 2021 were saturated, and thus we decided to use KOH rather than K_2CO_3 impregnation for the gas filters in 2022 and 2023. Gas filters in 2022 and 2023 did not saturate despite being exposed to comparable SO_2 concentrations across similar flight durations. Airflow through the filter pack was generated using an SKC Leland Legacy pump, also mounted on the UAS (see Table 3.1 and Electronic Supplementary Sheet A1 for individual sample flow rates). The flow rate was set to the highest value that the pump was able to sustain (6 – 13 L/min). The highest sustained flow rate varied according to which filter set up was used (i.e., 1 or 4 filters loaded) and was also sensitive to the curvature of the connective tubing between pump and filter when mounting the equipment on the drone. Immediately after sampling, filter packs were sealed using Parafilm to prevent particle loss and contamination during transport.

Time-averaged in-plume SO_2 concentrations were calculated using the co-collected Multi-GAS SO_2 timeseries, excluding data < 0.5 ppmv (the baseline between in-plume peaks in SO_2) within the known flight-time window. Mason et al. (2021) and Edwards et al. (2024) use background thresholds of 1 ppmv and 1.3 ppmv, respectively. Using alternative baselines of 0 and 1 ppmv resulted in a difference of less than 1 % in our corrected in-plume flight times. The time averaged SO_2 concentrations should be viewed as minimum values as some in-plume measurements were made when SO_2 concentrations were above the maximum detection limit of the sensor (saturation occurred at ~ 220 ppmv, % of time above Multi-GAS saturation recorded in the Electronic Supplement Sheet A1). The total time filter packs spent inside the aerosol plume (defined as $SO_2 > 0.5$ ppmv) was used to correct for total plume volume sampled by the filter packs.

3.3.2 Extraction and Compositional Analysis

The samples were handled in a class-10000 (ISO 7) clean laboratory environment at the Institute of Earth Sciences, University of Iceland and the School of Earth and Environment, University of Leeds. Gas and PM filters were extracted following an established procedure (Ilyinskaya et al., 2021; Mason et al., 2021). All filters were cut into quarters and transferred to acid-cleaned 50 ml centrifuge tubes using acid-cleaned metal-free scissors and tweezers prior to the extraction process.

Gas filters were leached in 20 ml Milli-Q ($> 18.2 M\Omega$, MQ) water and 250 μ l H_2O_2 (to oxidize collected sulfur species to sulfate) and then shaken for 20 mins. 1.5 ml from these solutions was pipetted for anion concentration measurements by ion chromatography (IC) at the Department

of Geography, University of Leeds (on Thermo Dionex ICS5000) and Institute of Earth Sciences, University of Iceland (on Thermo Dionex ICS2000).

Material collected on PM filters was extracted using a two-stage sequential leaching method (Ilyinskaya et al., 2021; Mason et al., 2021). The water-soluble PM fraction was first extracted in 20 ml MQ water + 200 μ l propan-2-ol (to reduce the hydrophobicity of the PM filters), shaken and placed in a sonic bath (20 mins each), before being centrifuged at 3000 rpm for 20 mins. 10 ml of the solution was then pipetted to 15 ml acid-clean tubes for analysis by ICP-MS/MS (Agilent 8800), with another 1.5 ml pipetted for IC analysis (as described for the gas filters above). The remaining solution and filters were transferred to an acid-cleaned 22 ml PFA vial. 5 ml UPA grade concentrated HNO_3 was added to the PFA beaker and samples dried on a hot plate at 55 °C. 1 ml UPA grade concentrated HNO_3 and 1 ml UPA grade concentrated HF were pipetted to the solid residue and refluxed for 3 h at 110°C with lids on the PFA beakers. The lids were then removed, and samples dried at 55°C. 10 ml UPA grade concentrated HNO_3 was then pipetted to the solid residue and refluxed on a hot plate at 90-100°C for 3 hrs. Filters were then removed from the beakers using acid-cleaned metal-free tweezers and stored in original 50ml centrifuge tubes. The solution was then dried down at 55°C and 0.5 ml UPA grade concentrated HNO_3 was pipetted to the final solid residue and refluxed at 90-100 °C for 1 h to get the sample back into solution. 10ml MQ was pipetted into the PFA beakers and then transferred to an acid-cleaned sample tube for analysis by ICP-MS/MS.

PM filter samples and blanks were analyzed for major and trace elements by ICP-MS/MS in the School of Environment, Earth and Ecosystem Sciences at the Open University, UK. Field, lab, and filter blanks were used to quantify the level of contamination at all stages of the sampling and extraction process and were found to be negligible (see Supplementary A Figure A.3 for blank comparison). Synthetic calibration standards were doped with the same solution matrix as samples in order to eliminate ionisation effects (particularly with samples containing propan-2-ol). Ionisation effects were monitored by running an on-line internal standard throughout all measurement sessions. Elements were analyzed using a triple quad set up with different collision gas modes (no gas, O_2 , and NH_3) to minimize polyatomic and isobaric interferences. This allows for lower detection limits and improved accuracy across the range of elements analyzed.

Using ground mass major and trace element compositions from each of the three eruption years as representative silicate ash compositions (see Section 3.3.4 for details of groundmass analysis),

a weighted ash fraction (WAF) calculation (Aiuppa et al., 2003) was also performed for filter pack trace element concentrations in this study. The WAF calculation assumes that the concentration of volatile element A on the filter is derived from two volcanic components, silicate ash and non-silicate aerosol, and was performed as a check on the relative contribution of silicate ash and dust to overall element concentrations on the filters (see Supplementary A Note 1 for full details of the calculation). Across all samples the proportion of ash X_{ash} on the filter by weight was $< 1 \times 10^{-3}$ (Supplementary A Table A.1). Given the very small contribution of silicate ash, we use non-ash corrected element concentrations in the main body of this work to allow for inclusion of a greater array of trace elements. Supplementary A Figure A.7 shows a comparison of non-ash-corrected and ash-corrected data, with minimal differences in element concentrations across all samples.

3.3.3 Gas Composition retrieved from FTIR Spectra

Selected gas ratios (SO_2/HCl , SO_2/HF , HCl/HF , mol/mol) and gas composition data (SO_2 , HCl , HF , H_2O , CO_2 , mol %) were obtained using open-path Fourier Transform Infrared FTIR spectra throughout the 2021 Fagradalsfjall eruption. Data included in this study were collected on 23rd March (vent measurements previously reported in Halldórsson et al. (2022) and 14th April 2021 (which are the most closely aligned with our aerosol samples) from within 300 m of vents 2, 3 and 5 (overview of measurements performed in Table 3.1, major gas data reported in Table 3.2). The open-path spectra were collected with a MIDAC FTIR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and 3-inch Newtonian telescope with a 10 mrad field of view. Interferograms and single beam spectra were collected at 0.5 cm^{-1} resolution approximately every 2 s. Examples of collected spectra from the same eruption on a different day are shown in Scott et al. (2023). The column amount of gases contributing to the measured spectra was determined using the Reference Forward Model (Dudhia, 2017) to simulate absorptions of target volcanic and atmospheric gas molecules in a specified spectral range using line parameters taken from the HITRAN database (Rothman et al., 1998). The model uses a two-layer atmosphere species reflecting a short path through a warm plume containing volcanic gas species and cooler ambient air for the rest of the path between spectrometer and infrared source (Burton et al., 2007). The volcanic gas temperature was set between 450 and 400 K for the vent measurements and to between 320 and 350 K for the lava flow measurements, using the temperature-dependent $\nu_1 + \nu_3$ feature at $2450 - 2550\text{ cm}^{-1}$ to estimate gas tempera-

ture (La Spina et al., 2015; Smekens et al., 2024). This temperature range reflects rapid cooling of the volcanic gas as it mixed with the atmosphere. The calculations were conducted using the software FTIR FIT (Burton et al., 2007). The wavebands selected for obtaining retrievals were 2020–2150 (for CO_2 , H_2O), 2450–2650 (SO_2), 2600–3100 (HCl) and 4000–4100 cm^{-1} (HF). Gas ratios (SO_2/HCl , SO_2/HF , and HCl/HF) were obtained for each measurement by averaging retrieved column amounts for a given dataset (e.g., the mean and SD of SO_2 molecules cm^{-2} divided by HCl molecules cm^{-2}). To calculate gas composition (mol %), correction for ambient air, H_2O , and CO_2 column amounts were performed by linear regression and subtracting the y-intercept from retrieved column amounts. Gas ratios for at-vent and above flow measurements are reported in Table 3.2 and gas compositions, used for thermochemical modelling input, are reported in the Electronic Supplement Sheet A6.

3.3.4 Groundmass Major and Trace Element Composition

Matrix glass samples from all three eruption years were analyzed for major and trace elements via JEOL JXA-8230 SuperProbe electron probe micro-analyzer (EPMA) at the Institute of Earth Sciences, University of Iceland and LA-ICP-MS/MS (Agilent 8800) at the Open University using analytical techniques outlined in Jenner and O'Neill (2012) for trace elements. The Ag analysis were done by line scans on matrix glasses, with the same approach as described in Wieser et al. (2020) for Se analysis in melt inclusions. The ZrO interference correction was done as described in Reekie et al. (2019), with reference material analyses for Ag from Jenner et al. (2015). These analyses were undertaken to determine an ash composition for each eruption (see the electronic supplement sheets A8 and A9).

3.3.5 Liquid Only Thermometry

Liquid-only thermometry was performed using Thermobar (Wieser et al., 2022), using the major element concentrations from samples for all three eruption years. Calculations were performed using equations (15) and (22) from Putirka (2008), equation (6a) from Sugawara (2000), and Helz and Thornber (1987). For the 2021 eruption, the calculated temperatures ranged from 1164°C to 1193°C, 1164°C to 1185°C in 2022 and 1162°C to 1187°C in 2023 ($\pm 30^\circ C$, See supplementary A Table A.2). No liquid only thermometry has been calibrated specifically for Iceland and thus multiple globally calibrated thermometers were used to assess the sensitivity of calculated temperatures to the chosen thermometer. Temperatures were consistent within error of one

Table 3.1: Overview of sampling measurements collected in this study. *Simultaneous Multi-GAS data was not collected on two flights in 2023, hence no in-plume correction has been applied. Plume volume and plume sample duration therefore refer to total volume and total sample duration. PM Only = single PTFE filter loading in filter pack. 3G + PM = PTFE filter on first stage with three gass filters on subsequent stages.

Filter Packs							
Sample ID	Sampling Date	Lava Flow Style	Distance from Vent (m)	Plume Volume Pumped (L)	Filter Pack Set Up	Number of Flights	On-board MultiGAS
SFP3	23/03/2021	Lava (Linear)	300	149	3G + PM	2	Yes
SFP4	23/03/2021	At-crater	<100	117	3G + PM	1	Yes
SFP8	06/04/2021	Lava (Linear)	800	171	PM Only	3	Yes
SFP12	13/04/2021	At-crater	<100	493	PM Only	4	Yes
LW1	16/08/2022	At-crater	<100	830	3G + PM	3	Yes
LW2	16/08/2022	At-crater	<100	176	3G + PM	1	Yes
LW17	21/08/2022	Lava (Ponded)	150	248	PM Only	1	Yes
LHFP3	13/07/2023	Lava (Linear)	1400	527*	3G + PM	3	No
LHFP4	13/07/2023	Lava (Linear)	1000	548*	PM Only	3	No
LHFP8	19/07/2023	At-crater	<100	514	PM Only	2	Yes
LHFP9	19/07/2023	Lava (Linear)	250	52.3	3G + PM	2	Yes
FTIR							
Source name	Date	Measurement Type	Description		Range from source (m)		
5A	4/14/2021	At-crater	5A center top vent		154 +/- 3		
5A	4/14/2021	At-crater	5A right top vent		152 +/- 3		
5B	4/14/2021	At-crater	5B left wall vent		155 +/- 2		
5B-L	4/14/2021	Lava (Linear)	5B bottom where lava running out		143 +/- 3		
5A-L	4/14/2021	Lava (Linear)	5A main outflow		129 +/- 3		
5AB-M	4/14/2021	Lava (Linear)	5A and 5B merging lava rivers		103 +/- 3		
3-L	4/14/2021	Lava (Linear)	top of new lava river left side of 3		161 +/- 4		
B	3/23/2021	At-crater	main vent intermittent lava spatters		187 +/- 11		
A	3/23/2021	At-crater	2nd vent		175 +/- 4		
D	3/23/2021	Lava (Linear)	fast flowing lava channel end margin		280 +/- 12		
E	3/23/2021	Lava (Linear)	high speed lava channel		195 +/- 2		
C	3/23/2021	Lava (Linear)	lava flow right side of cone		277 +/- 8		

another across all samples and equations (See Table A.2 in Supplementary A). The samples used were either airfall tephra or quenched lava samples collected close to the active fissure or vent and thus constrain a minimum eruptive temperature of $1180^{\circ}\text{C} \pm 30^{\circ}\text{C}$ (used as the input for HSC thermochemical modelling below).

3.3.6 Thermochemical Modelling

The Gibbs free energy minimisation (GEM) module of HSC chemistry (version 9.9.2, Outotec Research Oy, Finland) was used to model equilibrium gas phase element speciation in the lava flow emissions. Model inputs are major and trace species gas concentrations (kmol), pressure, temperature and the phases expected in the aerosol plume (see Symonds and Reed (1993); Gerlach (2004); Martin et al. (2006) for detailed description of the model and Mason et al. (2021); Mandon et al. (2019) for more recent applications). Trace element speciation in the aerosol emissions of a degassing lava flow was modelled under the following conditions: major gas concentrations (e.g., SO_2 , CO_2 , H_2O , H_2S , HCl , HF) were derived from FTIR measurements collected on 14th April 2021 (sample 5A for at-crater and sample 5AB-M for lava conditions in Figure 4), trace element concentrations from FP sample SFP3 (collected above lava flow) and SFP4 (collected at-crater), 1 bar pressure, and temperature range of 400 to 1200 $^{\circ}\text{C}$ to investigate the temperature dependence of element speciation. See the electronic supplement sheet A6 for all input conditions and sheet A7 for the full modelled output list of species expected in the plume.

Species modelled in this study are limited to the gas phase to investigate element speciation at the point of emission at the lava-air interface, and therefore the role of speciation behaviour in the relative volatilisation of different trace metals from lava flows as they cool and age down-flow. Gas phase-only modelling was also performed by Mason et al. (2021), and Mandon et al. (2019). As such, similarly limiting our modelling to the gas phase allows for comparison of metal and metalloid speciation between rift-dominated (Fagradalsfjall, this study), hotspot (Mason et al. (2021)) and arc (Yasur, Mandon et al. (2019)) settings, respectively. Mason et al. (2021) previously investigated the effects of mixing with the atmosphere on element speciation behaviour by increasing the amount of oxygen input into their model over a series of steps to account for an increasingly dilute plume. They found that once a “compositional discontinuity” (around 14 mol % air) was reached, the speciation behaviour of certain elements may be altered (i.e. from a sulfide to a chloride). We choose not to include post-emission mixing with air in

our modelling approach as the focus of this study is to investigate the relationship between the emission behaviour of different elements in thermally and compositionally evolving flows and the speciation of those elements at the point at which they are emitted. The concentration of a given element measured on the filter is not affected by the speciation of that element when it is collected (i.e., Zn is measured as Zn irrespective of being ZnS or ZnCl). This means that post-emission changes in speciation (due to mixing with external air) do not affect our comparison between element speciation at emission (from modelling results) and relative behaviour in down-flow emissions (collected via filter pack sampling). We do account for increased oxidation of the lava down-flow, however, by increasing the SO_2/H_2S ratio between vent and lava in our model inputs.

In Section 3.5.1, modelling is performed over the 400 – 1200°C temperature range, where the decrease in temperature reflects cooling of the lava (i.e., a lower emission source temperature) rather than the cooling of a single packet of gaseous plume due to mixing with ambient air. Modelling was performed down to 400 °C to account for the widest range of cooling of the lava flows. Nonetheless, crystallization of basaltic glass occurs in air at ~ 840 °C (Burkhard, 2005) with the glass transition occurring at ~ 730 °C (Ryan and Sammis, 1981). Below 700°C the flows will therefore be almost completely solidified. Fractures in the lava flow may facilitate continued outgassing, although the magnitude of emissions from nearly solidified lava flows is likely to be considerably lower than from fully molten, moving flows. The effect of this degree of cooling on the emission of trace elements remains uncertain, for example, the extent to which trace elements can diffuse through the remaining melt and be outgassed from nearly-solidified lava flows.

3.4 Results

3.4.1 At-vent and Down-flow Degassing of Major Gas Species

As shown in Figure 3.2, FTIR measurements, from both crater and lava flow emissions, reveal a decrease in SO_2 /halogen gas ratios with increasing distance from the crater during the 2021 eruption. These measurements were performed at two active craters and several down-flow locations close to the active craters, as detailed in annotations on Figure 3.2 and the Electronic Supplement Sheet A5). In Figure 3.2, measurements from degassing lava flows are ordered by increasing distance from their respective vents, although there was some potential mixing

between lava flows from the multiple craters that were active in close proximity during sampling. For both data sets, SO_2/HCl and SO_2/HF molar ratios are higher at-vent compared to lava flow measurements (see Table 3.2). On 23rd March 2021, the average at-vent SO_2/HCl ratio was 93 ± 18 mol/mol, whilst the average SO_2/HF ratio was 216 ± 50 mol/mol. On 14th April, these ratios were significantly lower, with an average SO_2/HCl of 20 ± 4 mol/mol and SO_2/HF of 55 ± 18 mol/mol. Both datasets show a decrease in SO_2 /halogen ratios along flow, with the most distal SO_2/HCl and SO_2/HF ratios decreasing to ~ 10 mol/mol and ~ 20 mol/mol, respectively. Figure 2 shows that HCl/HF also decreases with increasing distance from the vent (grey squares), suggesting a relative increase in HF outgassing in the more distal lava flows. Since all FTIR measurements were collected above relatively young lava flows, within 300 m of an active vent, it remains unclear to what extent SO_2 /halogen ratios would continue to decrease (if at all) in older and more evolved flows.

3.4.2 Trace Element Emissions

During ICP-MS analysis 57 elements were measured above detection limits on PM filter samples. At-crater concentrations ranged from $> 1 \times 10^{-5} g/m^3$ for elements such as Mg, Ca, K, Al, Na, Fe, and Se, between 1×10^{-5} and $1 \times 10^{-7} g/m^3$ for Ba, Ti, Mn, Ni, Cu, Zn, As, Sn, Pb, Cd, Te, and Ge, and $< 1 \times 10^{-7} g/m^3$ for Li, Cr, Co, Sb, Cs, Tl, Ag, and the REE (Supplementary Sheet A3). Element concentrations in samples collected above outgassing lavas $[X]_{lava}$ were normalized to element concentrations in at-crater samples $[X]_{at-crater}$ to compare relative down-flow depletion in trace element emissions between samples and eruption years. Trace elements showed a range of relative depletion rates and behaviors (as discussed further in Section 3.5.2 below). Te, Se, As, Pb, and Sn consistently showed the highest relative depletions in lava outgassing compared to at-crater emissions, with concentrations in the most distal lava FP samples being up to three orders of magnitude lower than in at-vent emissions. More moderate rates of down-flow depletion are shown by other elements, including Mn, Cu, Rb, Cs, as well as Ag, Zn, and Cd which are up to one order of magnitude less abundant in down-flow emissions compared to at-vent element concentrations. La, Ce, Mg, Fe, Ti, and Al show the lowest relative rates of depletion down-flow, with comparable element concentrations between at-vent and lava flow emissions.

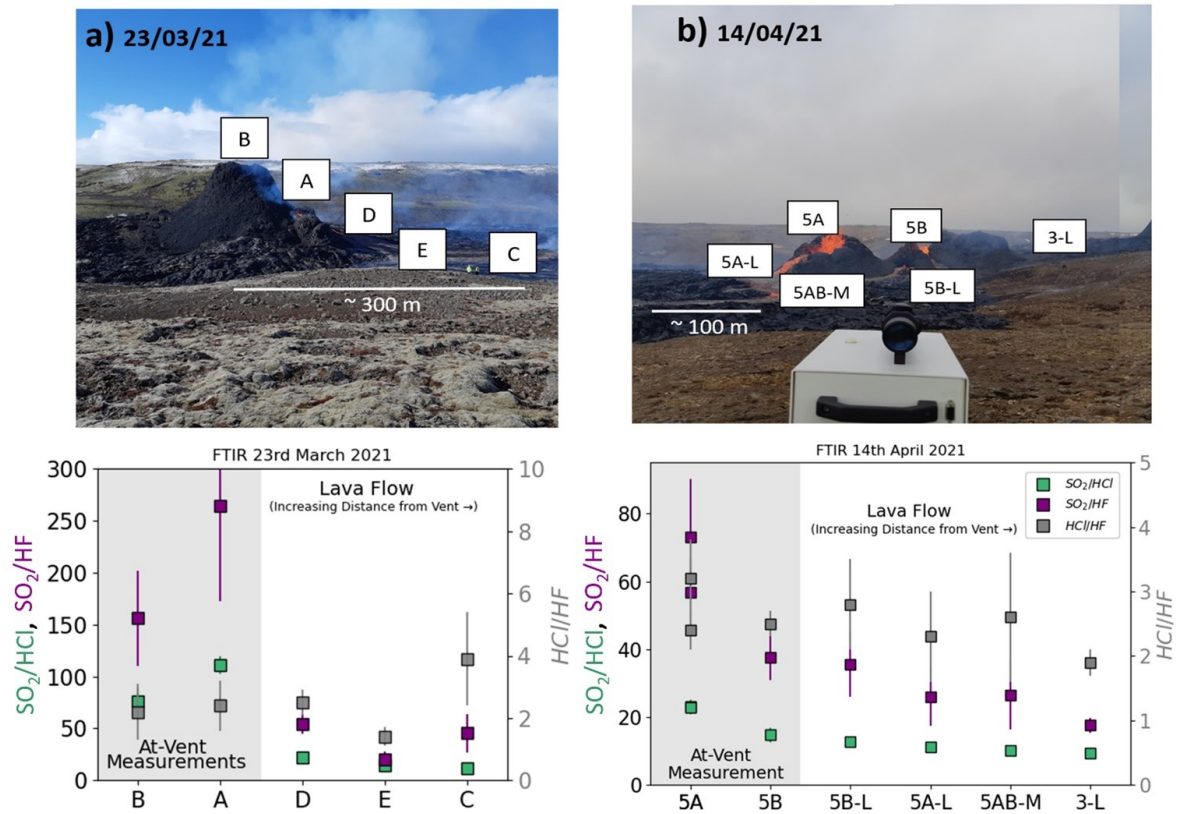


Figure 3.2: FTIR measurements collected within 300 m of source at-vent and adjacent lava flow locations during the 2021 eruption. Panel 2a shows annotated photograph of vent 2 (23/03/21). Panel 2b shows annotated photographs of vent 5 (14/04/21). Panels 2c and 2d show SO_2 /halogen gas ratios in mol/mol, with lava flow measurements ordered on the x-axis by increasing distance from vent. Green squares show SO_2 /HCl ratios and purple squares show SO_2 /HF, both of which are lower in lava flow measurements compared to main vent degassing and decrease as lava flow distance from the active vent increases.

Table 3.2: Overview of gas ratios measured using FTIR and MultiGAS at-vent and above lava flows. Changes in SO_2 /Halogen ratios down-flow are shown in Figure 2. Data from Halldórsson et al. (2022) is included for comparison between at-vent FTIR measurements. For both datasets SO_2 /Halogen ratios fall within the same order of magnitude and show similar ranges between measurements. SO_2 /HCl on the 14th April is notably lower than previous measurements (both in this study and in Halldórsson et al. (2022)), reflecting the changing lava composition between Phase I and Phase II of the 2021 eruption. FTIR measurements reported in this study are split by sampling date and ordered by increasing distance from the vent (all within ~ 300 m).

Date of measurement	Measurement Type	Figure 2 ID	SO_2 /HCl	SO_2 /HF	H_2S/SO_2
			mol/mol	mol/mol	mol/mol
FTIR - this study					
4/14/2021	Crater	5A	23.3	52.5	-
4/14/2021	Crater	5A	23.0	76.7	-
4/14/2021	Crater	5B	14.8	37.0	-
4/14/2021	Above flow	5B-L	12.6	32.2	-
4/14/2021	Above flow	5A-L	11.3	24.3	-
4/14/2021	Above flow	5AB-M	10.0	23.3	-
4/14/2021	Above flow	3-L	10.0	20.0	-
3/23/2021	Crater	B	75.0	125.0	-
3/23/2021	Crater	A	114.0	228.0	-
3/23/2021	Above flow	D	22.4	55.3	-
3/23/2021	Above flow	E	14.4	18.7	-
3/23/2021	Above flow	C	11.6	29.5	-
FTIR - Halldórsson et al., 2022					
23/3/2021	Crater	-	65.3	261.0	-
25/3/2021	Crater	-	59.2	98.7	-
25/3/2021	Crater	-	67.8	169.5	-
25/3/2021	Crater	-	75.4	125.7	-
31/3/2021	Crater	-	30.9	72.0	-
31/3/2021	Crater	-	33.2	39.8	-
31/3/2021	Crater	-	31.9	55.8	-
5/4/2021	Crater	-	49.7	139.2	-
5/4/2021	Crater	-	45.4	63.6	-
5/4/2021	Crater	-	48.8	113.9	-
5/4/2021	Crater	-	51.6	137.7	-
MultiGAS - this study					
23/03/2021	Above flow	300 m from vent	-	-	0.15
13/04/2021	Crater	-	-	-	0.29
23/03/2021	Crater	-	-	-	0.00
16/08/2022	Crater	-	-	-	0.23
16/08/2022	Crater	-	-	-	0.19
19/07/2023	Above flow	250 m from vent	-	-	0.21

3.5 Discussion

We now explore further the behaviour of selected elements, considered representative of the range of element volatilities and speciation behaviors, through thermochemical modelling and discuss our observations in the context of the degassing behaviour of major gases (SO_2 , HCl, HF). We propose a mechanism where element speciation plays a dominant role in controlling the down-flow fractionation in trace element emissions from outgassing lava flows, where the speciation behaviour of some elements is dependent on the age and thermal evolution of the lava.

3.5.1 Trace Element Speciation under Lava Flow Conditions

As lava flows are exposed to ambient surface temperatures, they undergo cooling and temperature-dependent crystallisation. Using at-crater major gas and trace element input conditions (outlined in Section 3.3.7 and the Electronic Supplement Sheet A6), element equilibrium speciation was modelled across the 1200 °C – 400 °C temperature range to simulate post-eruptive cooling of the lava (Cashman et al., 1999) and investigate subsequent changes in element speciation due to decreasing lava temperature (Figure 3.3). Liquid thermometry constraints from quenched lava and tephra samples provide a minimum eruptive temperature of 1180 °C $\pm$ 30°C. As shown in Figure 3.3, at this temperature, with at-vent major gas and trace element input conditions, the resultant groups of gaseous complexes are: sulfides (Se, Te, As, Pb, Sn), chlorides (Cs, Rb, Cu, Ce), hydroxides (Mn, Fe, Al, Ti, Mg), oxides (La), and elemental forms (Ag, Zn, Cd). Nonetheless, uncertainties in trace element and major gas input conditions are reflected in the thermochemical modelling output, particularly the temperatures at which speciation transitions occur. The sensitivities of modelled speciation behaviour to major gas and trace element input conditions are investigated below; however, the temperature dependent speciation transitions modelled here should be considered as approximate constraints on transition temperatures.

As shown in Figure 3.3, refractory elements Ti and Al complex predominantly as hydroxides across the whole temperature range. By contrast, Fe and Mg complex as hydroxides at higher temperatures but transition to predominantly chloride species under lower temperature conditions. La and Ce transition from oxide to chloride complexing behaviour with decreasing temperature, with a further transition at lower temperatures to include an additional fluoride component. A similar chloride-to-fluoride transition is also seen for elements Cs, Al, Mg, and Rb

with decreasing temperatures. Cu remains complexed as a chloride across the whole modelled temperature range. Only three elements, Ag, Cd, and Zn, show elemental speciation behaviour, although all have a greater chloride component at lower temperatures. The remaining elements, Pb, Sn, As, Se, and Te predominantly complex as sulfides across the modelled temperature range, although Pb and Sn show a transition to chloride-complexing behaviour at lower temperatures. By contrast, As shows a higher temperature transition, with an increasing oxide component under higher temperature conditions.

In addition to cooling, lava flows also undergo compositional changes as they age, due to crystallisation and associated enrichment of incompatible elements in the residual melts. This includes decreasing SO_2 /halogen ratios in lava flow emissions with increasing distance from the crater (shown with FTIR measurements in Figure 3.2) as well as becoming increasingly oxidised as the lava reacts with air down-flow (Lerner et al., 2021). Multi-GAS measurements were used to constrain approximate SO_2/H_2S ratios (where SO_2/H_2S reflects the ratio between the oxidised species SO_2 and the more reduced species H_2S) for at-vent and lava flow emissions. At-vent emissions had a lower SO_2/H_2S ratio of ~ 6.6 , whilst emissions sampled above the lava had a higher SO_2/H_2S ratio of ~ 12.1 , reflecting increased oxidation down flow (see Supplementary Sheet A5). To account for variations in gas composition, thermochemical speciation modelling was repeated at 1180 °C under both at-crater (higher SO_2/HCl , lower SO_2/H_2S) and lava flow (lower SO_2/HCl , higher SO_2/H_2S) gas input conditions. Trace element inputs from at-crater (SFP4) and lava (SFP3) filter pack samples were also used to account for down-flow changes in element chemistry. The minimum temperature input was set to 1180 °C $\pm$ 30°C based on liquid thermometry constraints and held constant across both crater and lava inputs to deconvolve the effects of decreasing lava temperature (modelled above) from the effects of changing composition.

As shown in Figure 3.4, speciation groupings (by mol %) are modelled to be broadly similar under both at-crater and lava flow conditions at 1180°C. Only elements As and Te show a difference in their modelled speciation behaviours; complexing dominantly sulfides under at-vent conditions to predominantly complexing as to oxides (As) and elementally (Te), respectively, under lava flow conditions. Minor changes in modelled speciation behaviour are also suggested for Mg, Fe, Ce, Rb, Ag, and Pb, in the form of a small increase (< 10 %) in the proportion of chloride-complexed species under lava flow trace element and major gas input conditions. This shift from sulfide to chloride speciation most likely reflects the decreasing availability of the S^{2-} ligand

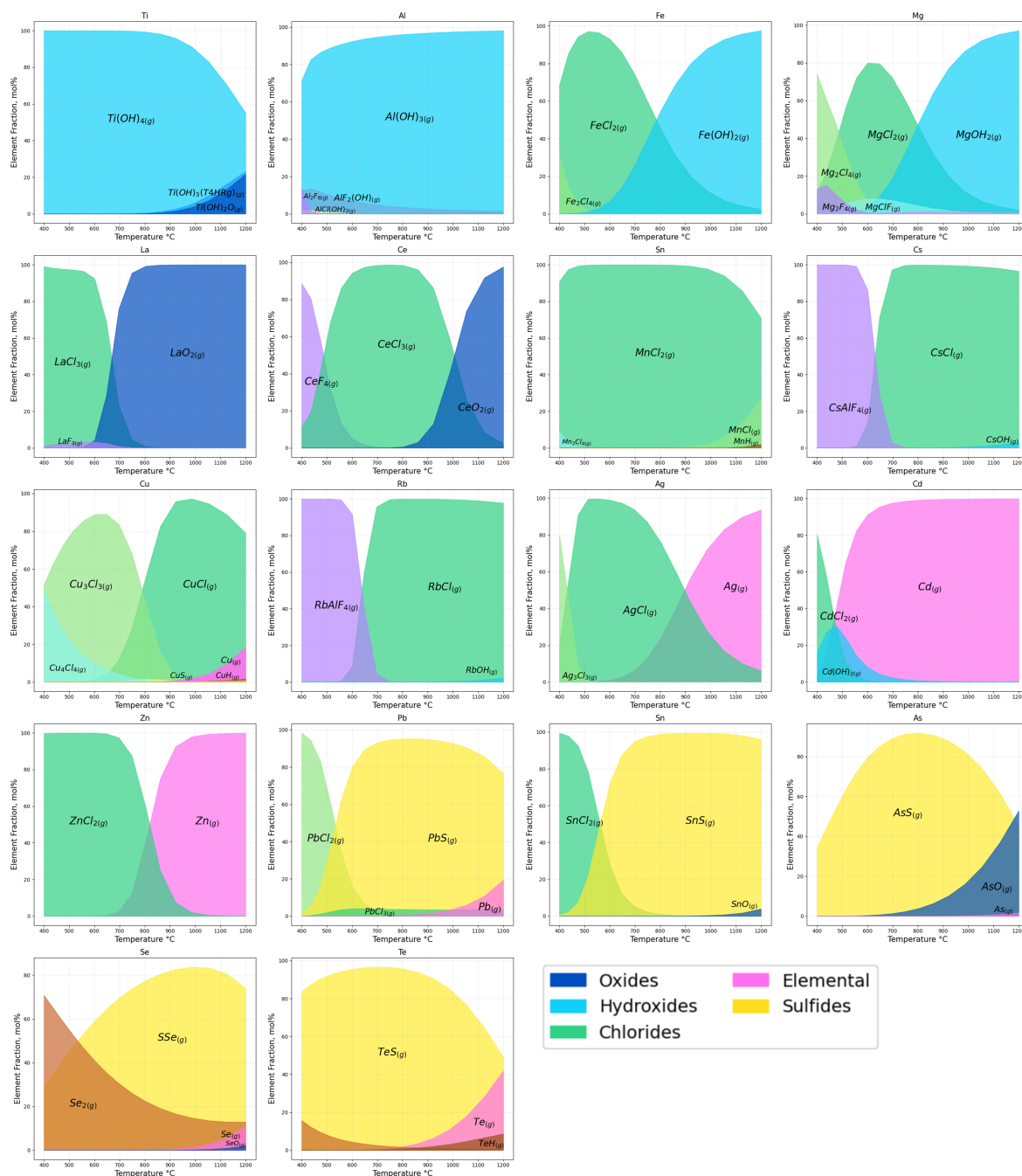


Figure 3.3: Equilibrium element speciation modelling between 400°C and 1200°C. Input trace element and major gas compositions are from the 2021 at-crater FP sample (SFP4) and FTIR vent measurements; input conditions are outlined in full in Supplementary Sheet A7.

(lost to degassing) and relative increase in the availability of the Cl^- ligand as the lava evolves compositionally down-flow, which is reflected in the decreasing SO_2/HCl ratio with distance from vent (Figure 3.2). Several elements, such as Mg, Al, and Ce also have a slightly greater fluoride component when modelled using lava flow compositional inputs (trace elements and gases), although overall the proportion of fluoride-complexed species for these elements remains minor relative to the chloride and oxide-complexed component. The increased prevalence of a fluoride complexed component also likely reflects a relative increase in the availability of the F^- ligand with increasing distance down-flow, shown by decreasing HCl/HF with increasing distance from vent (Figure 3.2). Further compositional changes in older, more evolved lava flows than captured by our measurements and modelling, may drive continued progression towards increasing chloride and fluoride speciation.

Overall, the speciation behaviors identified here in the Fagradalsfjall emissions (both under lava and at-crater conditions) are consistent with previous modelling work for the Fissure 8 plume during the Kīlauea 2018 eruption (Hawai'i), with nearly identical complexing behaviour across the array of trace elements common to both studies (Mason et al., 2021). Given the similarities in plume chemistry between the Fagradalsfjall 2021 and Kīlauea 2018 eruptions, it is expected that these similar input chemistries would result in similar model output speciation results. Nonetheless, differences in element speciation behaviour are seen when compared to modelling performed with inputs from arc-setting volcanoes. For example, Zn and Pb, show elemental and sulfide speciation, respectively, in both the Fagradalsfjall and Kīlauea plumes, however, show predominantly chloride speciation in similar modelling work for the Yasur volcanic plume (Mandon et al., 2019). We propose that this difference can be explained based on the relative availability of S^{2-} and Cl^- ligands. High SO_2/HCl mass ratios were measured in gas emissions from Fagradalsfjall in 2021 (25 - 40; this study) and Kīlauea 2018 (32 - 35; Mason et al., 2021), reflecting the absence of a Cl-rich recycled slab component seen at subduction zone volcanoes such as Yasur (SO_2/HCl mass ratio = 5.6 - 12.8; Mandon et al., 2019) where the Cl- ligand is more abundant. Together, this difference in speciation and gas composition highlights the importance of the S^{2-} ligand for metal transport in rift-dominated settings, as has already been identified at hotspot basaltic volcanoes such as Kīlauea (Mason et al., 2021).

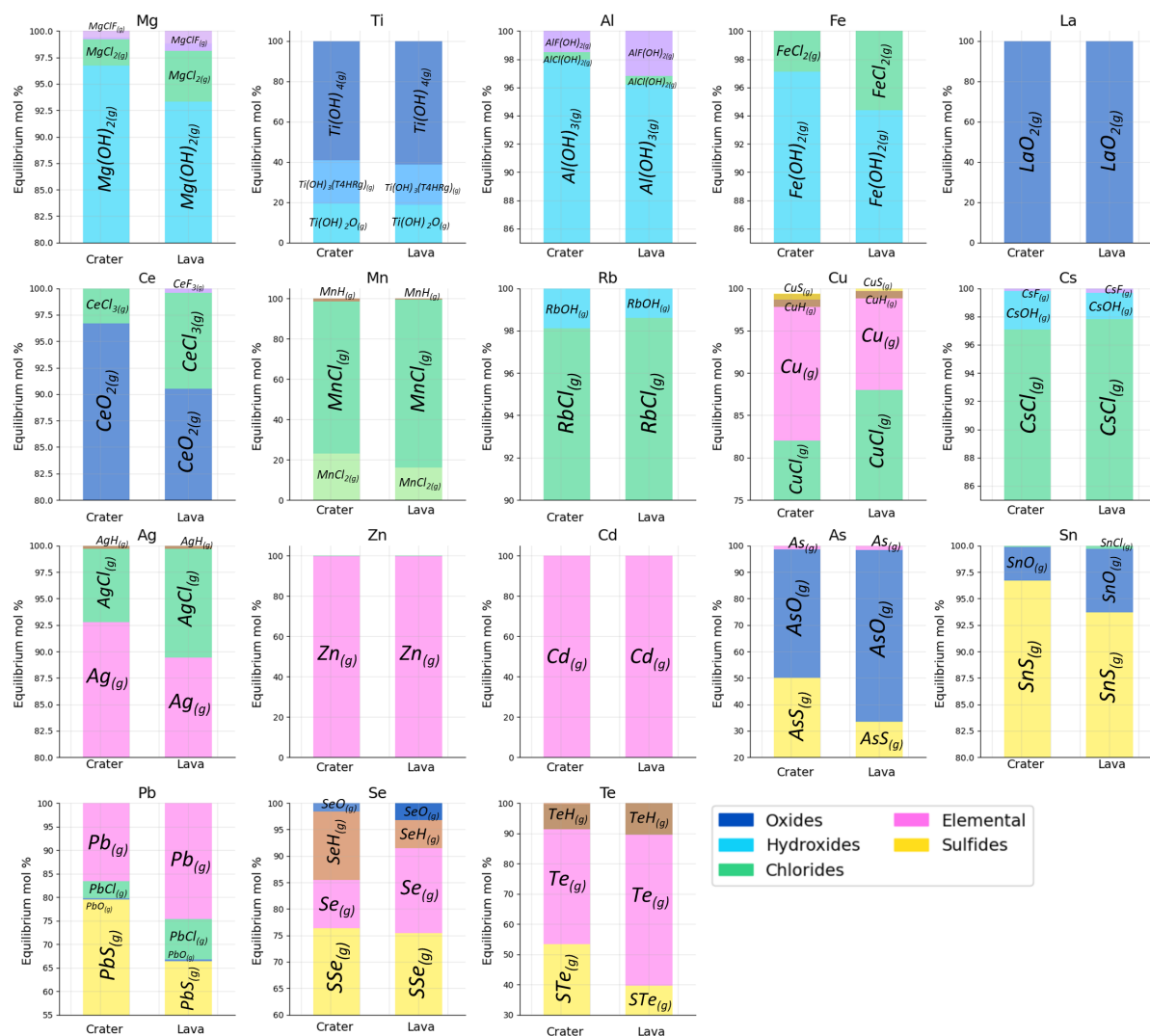


Figure 3.4: Element Speciation at 1180°C (based on liquid thermometry temperature constraints) under at-crater and lava flow conditions. Input SO_2/HCl ratios were constrained from FTIR ($SO_2/HCl_{crater} = 23$ mol/mol, $SO_2/HCl_{lava} = 11.3$ mol/mol), and input SO_2/H_2S from MultiGAS data ($H_2S/SO_{2crater} = 0.29$ mol/mol, $H_2S/SO_{2lava} = 0.15$ mol/mol). Modelling was performed using Gibbs free energy minimisation module of HSC Chemistry. Trace element and concentration inputs from lava flow filter pack (SFP3) and at-crater filter pack (SFP4) from the 2021 eruption.

3.5.2 Down-flow Evolution of Trace Element Emissions

Figure 3.5 shows element concentrations in FP samples collected above outgassing lava flows at different distances from the crater, normalised to at-crater element concentrations. Datasets have been grouped by those collected above laterally extending, visibly flowing, red-hot lava (Panel a - all samples in 2021 and 2023) and those collected above a single vent in a ponded, stagnant lava field (Panel b; 2022). See Supplementary A Figure A.3 for pictures of example lava flow conditions.

Across all three eruptions, the sulfur-complexing elements (as defined by modelling in Section 3.5.1) Se, Te, As, Pb, and Sn (shown in yellow) deplete more rapidly relative to chloride (green), elemental (pink) and oxide/hydroxide (blue) complexing elements with increasing distance from the source crater. For emissions above red-hot lava flows, sulfur-complexing elements are up 3 orders of magnitude lower in concentration than in at-vent emissions within 1 km down-flow, whilst the concentrations of chloride complexing elements are only one order of magnitude less than in crater emissions at the same distance. For samples collected above the ponded lava field in 2022, the sulfur-complexing elements show a similar degree of depletion to those samples at ~ 1 km distance in 2023, despite being much more proximal to the vent. The relative behaviour of chloride, oxide, and hydroxide-complexing elements, however, shows a greater dependence on lava flow style. For example, chloride-complexing elements Mn, Cu, Rb, and Cs show a relative depletion compared to refractory elements in 2021 and 2023 emissions (above red-hot lava flows), but a relative enrichment compared to the same refractory elements in 2022, when the lava field was ponded. The refractory elements (e.g., La, Ce, Mg, Fe, Ti, Al, shown in blue, Figure 3.5) show minimal down-flow depletion above the red-hot lava flows in 2021 and 2023, but are depleted by up to an order of magnitude in emissions sampled above the ponded lava vent in 2022.

An overall down-flow fractionation between S and Cl can be seen both in the behaviour of sulfur and chloride-complexing elements in filter pack samples (Figure 3.5) and in the decreasing SO_2 /halogen ratios with increasing distance down-flow (Figure 3.2) observed in FTIR measurements. Filter pack samples collected during the Holuhraun 2014-2015 eruption showed a reduction in S/Cl and S/F ratios from the syn-eruptive gas plume (analogous to our at-vent samples) to the post-eruptive gas phase (lava flow), which was explained by Rayleigh distillation and decreasing availability of S in the crystallising magma (Sigmarsson et al., 2020). Aiuppa

(2009) similarly conclude lower SO_2/HCl and SO_2/HF ratios are characteristic of the late stages of volcanic degassing, where the higher melt solubilities of the halogens mean they are less likely to enter the gas phase relative to S. Observations of SO_2 and HCl gas fluxes during the 2008-2009 eruption of Mt Etna and adjacent periods of quiescence suggest that halogen degassing is driven by prolonged shallow crystallization, whilst S is lost more rapidly from the melt (La Spina et al., 2023).

Toutain et al. (1990) observe a similar fractionation in S - Cl and S - F in degassing lava flows on Piton de la Fournaise, with an absence of sulfides or sulfates further down-flow, leaving sublimates instead dominated by chloride and fluoride species. This can be seen in Figure 3.5 (denoted by bolder dashed lines), where S(PM) decreases much more rapidly in down-flow emissions relative to Cl(PM) and F(PM) in both 2021 and 2023 samples. The more rapid depletion of sulfur-complexing elements down-flow compared to other complexes most likely reflects earlier upstream sulfur degassing where the rapid volatilization and emission of sulfur-complexing elements close to the vent leaves them in low abundances in the silicate melt with little then left to degas down-flow. Both FTIR and trace element concentrations show the highest rate of depletion in S and sulfur-complexing elements within a few hundred meters of the vent with the rate of depletion then plateauing in the more distal lava flow samples. However, the higher solubilities of Cl and F in the silicate melt mean that their degassing is delayed they remain in greater abundance in the down-flow region (following the accepted sequence of volatile solubility $S < Cl < F$ in basaltic melt; Carroll and Webster, 1994). Consequently, chloride- and fluoride-complexing elements continue to degas even in the most distal regions of lava flows. Sigmarsson et al. (2020) and Toutain et al. (1990), also report a decrease in HCl/HF with increasing distance down flow which is similarly seen in our FTIR data (in Figure 3.2). Nonetheless, there is no indication of a coincident increase in the volatilisation and emission of fluoride-complexing elements (such as Al, Cs, Ce, Rb) in the most distal regions down-flow. This can be explained by speciation modelling under a more evolved lava flow composition (Figure 3.4), which shows that although the relative importance of fluoride complexes does increase compared to main vent emissions, fluorides still remain a minor component compared to chlorides and hydroxides in overall element complexing behavior. Even with an increase in F degassing down-flow the impact on trace element emissions would therefore still be limited. The limited role of F degassing may reflect the young ages of the lava flows that were sampled, and so under more evolved lava flow conditions (older and more degassed) it is possible that relatively greater emission of fluoride complexing elements such as

Ce, Al, Rb, and Cs could be observed with increasing distance down-flow.

Toutain et al., 1990 previously identified a down-flow fractionation in trace elements based on element relative volatility, rather than speciation, where volatile elements such as Rb, Cs, Se, Pb and Tl were detected in low-temperature deposits, but refractory elements (such as Fe, Mg, Ti, Ce) were not detected. This result was attributed to refractory elements not being volatilized down-flow at lower temperatures. Supplementary A Figure A.6 shows Figure 3.5 with elements colored by emanation coefficient rather than speciation behaviour (description of emanation coefficient calculation in Supplementary A Note 2, and coefficients included in the Electronic Supplement Sheet A12). Element emission behaviour down-flow shows a strong correlation with element emanation coefficients, although this is unsurprising given the strong link between speciation and volatility (i.e. sulfides and chlorides are relatively more volatile than oxides and hydroxides). The effects of the volatility fractionation can also be seen in the filter pack sample from 2022 (ponded lava field), where the relative depletion in down-flow emissions between chloride and oxide/hydroxide elements is reversed relative to samples in 2021 and 2023 (see Figure 3.5), with the chloride group of elements showing relative enrichment compared to oxide/hydroxide elements in 2022. Sample collection in 2021 and 2023 occurred above red-hot lava flowing laterally away from the vent, whereas the 2022 sample was collected above an isolated degassing vent, that had been present within the ponded lava field for at least 3 days, with no incandescent lava visible. The 2022 sample, therefore, likely represents degassing from the oldest and most evolved lava flow across the 3 eruptions that we sampled. As the lava flow cools, the extent to which the most refractory elements (e.g., Fe, Mg, Ti, La) are volatilized decreases, whilst the more volatile halogen gases (and F- and Cl-complexed elements with them) continue to be volatilized to a greater extent at lower temperatures (volatility fractionation; identified in Toutain et al. (1990)). Nonetheless, volatility alone cannot explain element behaviour in 2022. Elements Ce, Ag, Cu, Rb, and Cs all show similar rates of depletion in downflow emissions, however, they have a wide range of emanation coefficients (Ce being the most refractory; $\epsilon = 3.2 \times 10^{-5}$, and Ag being the most volatile; $\epsilon = 0.5$). Instead, the commonality across that group of elements is their speciation behaviour and predominantly complexing as chloride species (as shown by modelling in Figures 3.3 and 3.4 above).

As shown in Figure 3.5, Ce and Ag also show notably variable behaviour across the different eruption years which have varied lava flow styles. In 2021 and 2023 (red-hot lava flows), Ce

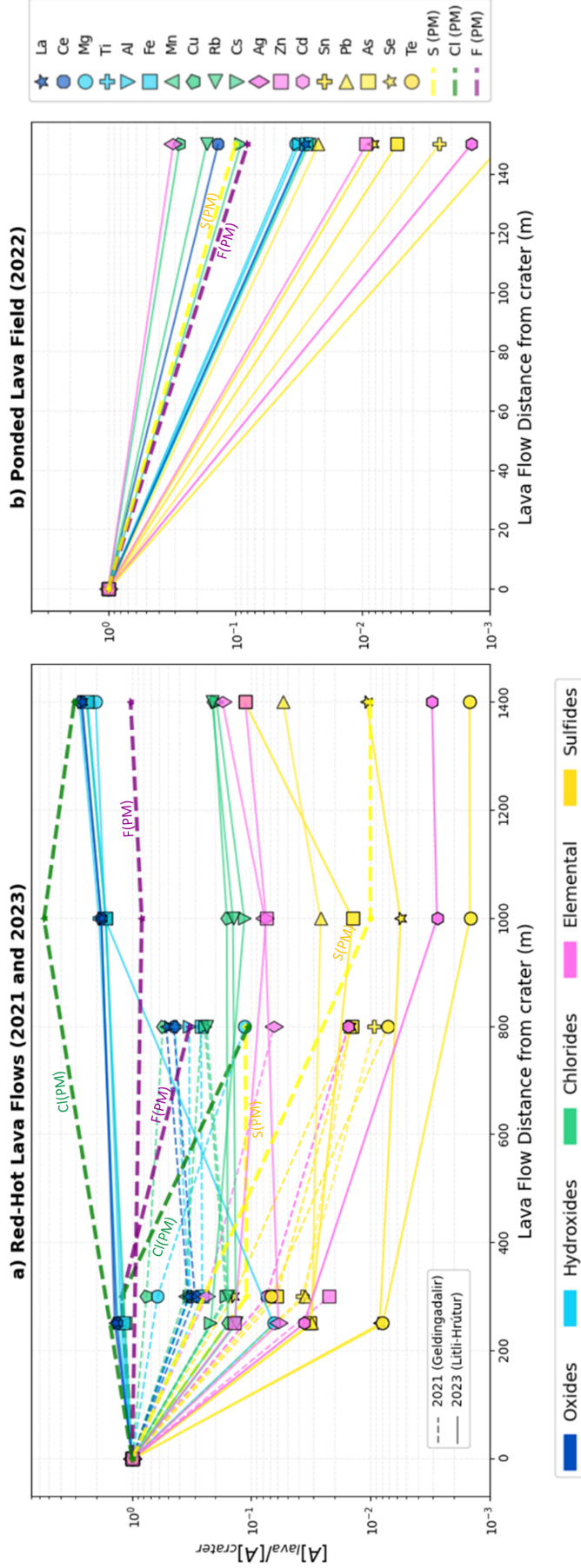


Figure 3.5: Trace element emission evolution along degassing lava flows at the 2021, 2022, and 2023 Fagradalsfjall eruptions. Panel a: Geldingadalir 2021 eruption and Litli-Hrútur 2023 eruption. Panel b: Meradalir 2022 eruption. Y-axis shows the lava flow $[A]_{lava}$ concentration (μ/m^3 air pumped) normalized to the source concentration $[A]_{crater}$ at discrete distances sampled along the lava flow ranging from 200 m to 1.4 km (3 samples in 2021, 2 in 2022, and 4 in 2023). The concentrations shown in Figure 3.5 are non-ash corrected in order to include the more refractory elements such as Fe, Mg, and Ti, although the ash corrected version is shown in Supplementary A Figure A.5. The proportion of ash on the filters X_{ash} is $< 1 \times 10^{-3}$ across all samples used in this study and thus, as shown in Supplementary A Figure A.5 the ash correction has negligible impact on element concentrations. Lava flows in 2021 and 2023 were extending laterally, the and thus relative distance from the vent also reflects relative flow age within each sampling year. The down-flow sample in 2022 was collected above a degassing vent within a ponded lava field, and thus the close distance to the vent is not necessarily representative of a younger sample age. Element colouring in Figure 3.5 reflects major speciation behaviour modelled for lava flow conditions at 1180°C , where yellow are the S-complexing elements, pink the elemental, green Cl-complexing, and blue the hydroxide and oxide complexing elements (see Figure 3.4).

behaves similarly to the other oxide and hydroxide-complexed elements, whilst in 2022, ponded lava flow emissions, Ce tracks more closely with chloride complexing elements such Rb and Cs. Considering the temperature dependence shown by Ce speciation behaviour (Figure 3.3) this potentially reflects a transition from Ce complexing as an oxide to chloride being the dominant species as the lava flow cools. When modelled under lava flow rather than crater conditions (Figure 3.4), the relative importance of chloride/fluoride speciation also increases for Ce, and thus the later volatilisation of Cl and F may further contribute to increased emission of Ce in an older and compositionally more evolved flow. Ag also shows variable depletion depending on lava flow style, behaving similarly to the elementally complexed Zn in 2021 and 2023, but then tracking much more closely with the chloride complexing elements Cu and Rb above the ponded lava field in 2022. As with Ce, Ag also undergoes a speciation transition towards a more dominant chloride component at lower temperatures (see equilibrium speciation modelling in Figure 3.3). Given the vent within the ponded lava field had been present for several days and did not show visibly incandescent lava, it is reasonable that this sample represents emissions from a colder and more degassed lava. Lava flow age can therefore be linked to the thermal evolution and composition of gas emissions which, as suggested by thermochemical modelling, are both key controls on trace element speciation and emission behaviour in outgassing lava flows.

Overall, several transitions in lava outgassing composition are observed within our Fagradalsfjall dataset. These are outlined schematically in Figure 3.6 and include: 1) predominant degassing of SO_2 and sulfur-complexing elements at-vent; 2) a rapid drop off in S emissions as lava flows age and cool, leaving more distal emissions governed by chloride and oxide/hydroxide degassing; 3) continued cooling means the volatilization of refractory elements also decreases, leaving the most evolved lava flow outgassing dominated by Cl-gases and volatile chloride-complexed elements; 4) increasing F/Cl ratios down-flow (also observed by Toutain et al. (1990), Sigmarsson et al. (2020)) suggest there is the potential that even colder and more evolved lava flow emissions may be dominated by the outgassing of fluoride-complexed elements (such as Rb, Mg, Al Cs, and Ce at lower temperatures).

The compositional evolution of lava flow emissions from S-dominated degassing near-vent to an increasingly Cl and F-dominated regime down-flow has implications for different trace metal exposure hazards, which we suggest may vary depending on lava flow age and thermal evolution.

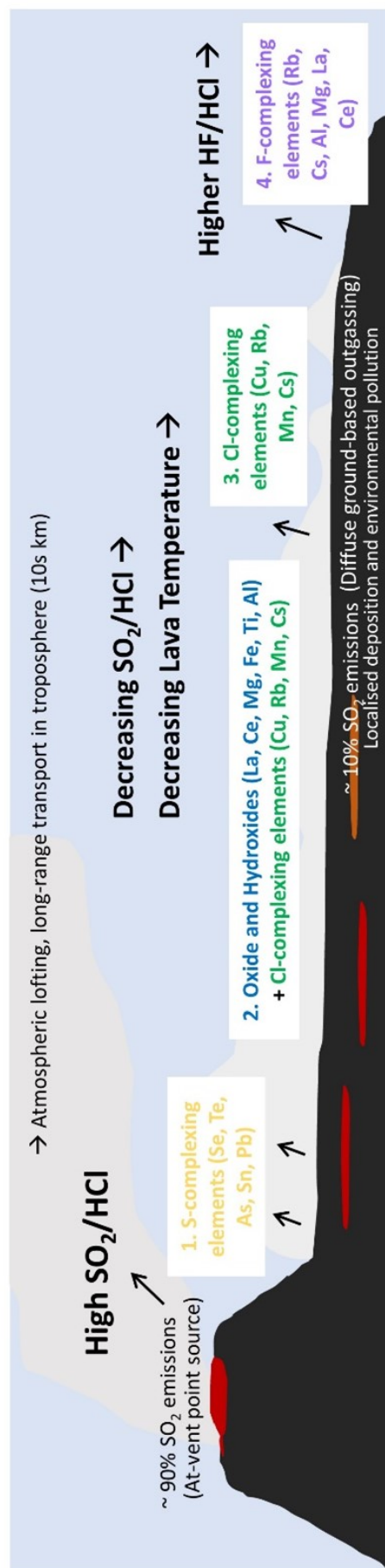


Figure 3.6: Schematic diagram of the observed and modelled transitions in the gas and trace element composition of lava flow outgassing emissions. Phases 1, 2, and 3 were observed in trace element and major gas behaviour in this study. At-vent emissions are also dominated by Phase 1. Phase 4 inferred from speciation modelling and increasing HF/HCl ratios down-flow (supported by similar observations in Toutain et al. (1990) and Sigmarsson et al. (2020)). 90 % of total volcanic SO_2 emitted at vent as calculated below based on lava degassing data from Pfeffer et al. (2024). Atmospheric lofting and long-range transport of elements (up to 50 km) in the main vent plume reported by Ilyinskaya et al. (2021) for the 2018 Kīlauea eruption (Hawai‘i).

Emissions from the youngest lava flows are likely dominated by trace metals such as Se, Sn, Te, Pb, As, whilst further down-flow the emission trace metal profile is dominated by elements such as Cs, Rb, Cu, Zn, Ce.

3.5.3 Trace element fluxes

The relative fluxes of trace elements from lava flows is more poorly constrained compared to at-vent emissions, and yet could have important implications for understanding the potential contribution of lava flow outgassing to overall volcanic emissions, environmental loading, and air quality impacts. Trace element fluxes cannot be measured directly but can be estimated by combining element X/SO_2 ratios with independent measurements of SO_2 flux:

$$X_{Flux} = SO_{2Flux} * X/SO_2 \quad (3.1)$$

where X_{flux} and SO_{2Flux} are the flux of element X and SO_2 respectively, and X/SO_2 is the concentration ratio of element X and SO_2 derived from filter pack and Multi-GAS measurements. SO_2 fluxes were taken from DOAS traverse measurements during the 2021 eruption (Pfeffer et al., 2024), across the two periods most closely aligned with our sampling dates (i.e., the 21/03 and 24/03 span the time window in which our sampling on the 23/03 took place). The minimum and maximum SO_2 fluxes were used to calculate upper and lower bound estimates for trace element emission fluxes and were between 11 – 99 kg/s SO_2 flux between 21st and 24th March 2021, and between 21 – 97 kg/s SO_2 flux between 13th and 17th April 2021 (from Pfeffer et al. (2024)).

Groundmass glass (GG) and melt inclusion (MI) data reported in Pfeffer et al. (2024) were used to estimate the relative proportions of at-vent and lava flow degassing in 2021, assuming total volcanic SO_2 flux is derived predominantly from at-vent degassing, but with an additional lava outgassing component. MI and GG data are from quenched lava and airfall tephra samples collected during the 2021 eruption (see Pfeffer et al. (2024) for full methodology). To calculate the relative proportion of at-vent outgassing, we use a bulk approach which subtracts the average S content of tephra groundmass glass (120 ppm) from the average S content of the undegassed melt inclusions (960 ppm), divided by the average S content of the undegassed melt inclusions (960 ppm) to get an at-vent degassing proportion of 88 % (± 2 % - 1SD). The relative proportion of lava flow degassing was then calculated by subtracting the minimum S content of lava sample

groundmass glass (40 ppm) from the average S content of the tephra groundmass glass (120 ppm) and dividing by the average S content of the undegassed melt inclusions (960 ppm). This constrains a relative lava degassing proportion of $\sim 8\%$ ($\pm 4\%$ - 1SD), although it does not account for the effects of fractional crystallization down-flow. The proportion of total degassing comprised from vent and lava sources was therefore taken forward as 90 % vent degassing and 10 % lava outgassing when calculating the relative emissions of trace elements from vent and lava below.

The calculated emission rates of selected volatile and potentially toxic trace metals (Cr, Ni, Cu, As, Se, Pb, Cd) from volcanic sources during the 2021 Fagradalsfjall eruption are comparable to or greater than equivalent annual average anthropogenic emissions in Iceland during 2021 (Figure 3.7; black bars). The elements shown in Figure 3.7 were chosen as they are identified as metal pollutants in Iceland (Environmental Agency of Iceland, 2023). Across all seven elements, main vent volcanic emission fluxes (grey bars) were estimated using both upper (90 kg/s SO_2) and lower (10 kg/s SO_2) SO_2 fluxes. During the period of active eruptive activity, the emission rates (in kg/s) of several elements, such as Cr, Ni, Cu, and Pb, main vent volcanic are comparable in magnitude to anthropogenic emissions, whilst for elements (As, Se, and Cd) volcanic emissions are 2-3 orders of magnitude greater than those from anthropogenic sources during the 2021 eruption.

Trace element fluxes from lava flows were also calculated using 10 % of the total volcanic SO_2 flux (from DOAS) at both an upper (10 kg/s) and lower estimate (1 kg/s). These lava flow SO_2 fluxes were then combined with element $[X]/[SO_2]$ ratios from one proximal vent (SFP3 – 300m) and one more distal (SFP8 – 800m) FP sample to estimate element emission rates. Lava flow emissions of Cr, Ni, and Pb are up to an order of magnitude lower than main vent and anthropogenic emissions for the lower bound SO_2 flux but remain comparable in magnitude under higher SO_2 fluxes. For elements such as As, Se, and Cd, lava flow emissions remain up to 2 orders of magnitude greater than anthropogenic fluxes, even with the lower SO_2 flux estimate. However, fluxes remain lower than emissions from the main volcanic vent.

The exception to these observations is Cu, where the estimated flux from the most distal lava flow sample exceeds that from both the main vent and the more proximal lava flow sample. The higher $[Cu]/[SO_2]$ ratio most likely reflects the more prolonged degassing of chlorides (as Cu predominantly complexes with Cl) relative to sulfide degassing down-flow. The effects of

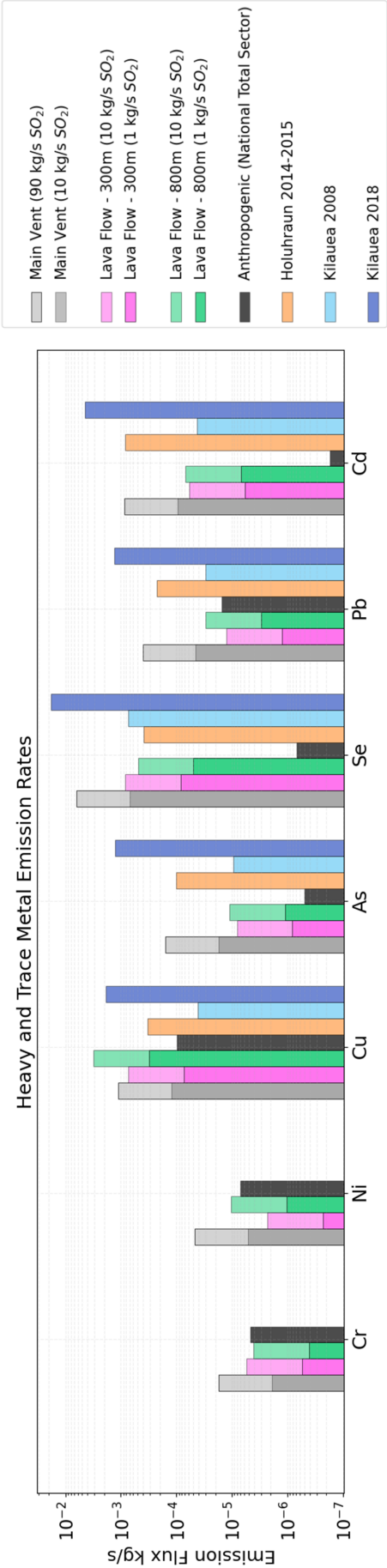


Figure 3.7: Emission flux estimates from volcanic sources at the Fagradalsfjall 2021 eruption and anthropogenic emissions in Iceland 2021 (Environmental Agency of Iceland, 2023). Volcanic emissions are divided into main vent and lava flow estimates, where, based on petrological estimates, lava flow emissions account for $\sim 10\%$ of total SO_2 flux. Trace element fluxes were calculated by combining independent DOAS SO_2 flux estimates and $[X]/[SO_2]$ ratios from filter pack samples SFP3 (300 m) and SFP8 (800 m). $[X]/[SO_2]$ data is reported in Supplementary sheet A11. Also shown is a comparison of Icelandic volcanic emission fluxes with fluxes from other global basaltic eruptions. Holuhraun 2014-2015 data from Gauthier et al. (2016) Kilauea 2008 and 2018 data from Ilyinskaya et al. (2021). X/SO_2 and emission flux data for a wider selection of elements and gases are included in Supplementary Sheet A11.

element speciation behavior and the transition towards a more chloride-dominated degassing profile in more evolved lavas can similarly be seen in Ni, Pb, and Cd, where the more distal lava flow has a higher estimated emission flux of these elements for a given SO_2 flux. Nonetheless, SO_2 degassing rapidly drops off as the lava flows become more evolved further from the vent. Therefore, whilst lava flow emission fluxes have been calculated using the same upper and lower SO_2 bounds, the more distal lava flow likely sits at the lower end of estimated SO_2 fluxes, whereas the more proximal sample is closer to the upper bound SO_2 flux. As such, although greater for a given SO_2 flux, the actual down-flow trace element emission of Cl-complexing elements in more distal lava flows may not exceed that of the more proximal lava flow emissions. By contrast, the sulfur-complexing elements (Se, Cd, As) show either greater trace element emission fluxes in the more proximal lava flow sample, or a much smaller difference between proximal and distal samples. The percentage decrease in element emissions was calculated between the more proximal (300 m from vent, upper bound of 10 kg/s SO_2) and more distal (800 m from vent, lower bound of 1 kg/s SO_2) lava flows for 2021 (Supplementary Sheet A12). Between 300 m and 800 m from the vent, element fluxes decreased to a highly variable extent, between 5 % (Nd) and almost 100 % (Zn, Ca, Mo). The sulfur-complexing elements such as Se, Te, Cd, and As showed some of the greatest decrease in emissions (between 94 and 86 % decrease), whilst chloride complexing elements such as Cu, Rb, and Cs decreased to a lesser extent (between 13 – 58 %). Fractionation in element emissions is therefore occurring proximally to the vent, with the rapid reduction in sulfur-complexing elements (approx. 90 % reduction) occurring between 300 and 800 m, whilst the reduction in chloride complexing element fluxes occurs more gradually, with emissions of these elements persisting further down-flow.

Compared to anthropogenic activity, which generally leads to continuous emission output, emissions from volcanic activity cease or are greatly reduced during periods of quiescence. Assessing the significance of volcanic emissions within Iceland compared to anthropogenic emissions, therefore, requires consideration of the timeframe over which emissions are being released. Volcanic sources are most significant over timescales of eruptive activity which are typically weeks or months depending on the eruption. Volcanic activity on the Reykjanes Peninsula has become more frequent over the past 4 years, with 8 eruptions occurring between March 2021 and March 2024. The relative importance of volcanic emissions to the atmosphere, on both a regional and national scale, has therefore increased. Compared to global anthropogenic emissions of trace metals, Icelandic national sector emissions are however, relatively low, with global fluxes being

dominated by China, India, Russia, and the U.S. (Zhu et al., 2020). Emission fluxes from the Fagradalsfjall 2021 eruption were comparable to those from the Kīlauea 2008 (Ilyinskaya et al., 2021) and Holuhraun 2014-2015 eruptions (Gauthier et al., 2016), although much lower than emission fluxes calculated for the Kīlauea 2018 eruption (Ilyinskaya et al., 2021).

During the 2018 Kīlauea eruption (Hawai'i) and 2021 Tajogaite eruption (Cumbre Vieja, La Palma), lava flows progressed towards, and reached, populated areas. Emissions from outgassing lava flows therefore, potentially increased population exposure to volcanic pollutants even when the main plume from the volcanic vent was not grounding in that area (National Park Service, 2021, BBC News, 2021). Compared to emissions from the main volcanic vent, which are generally concentrated from a single point source, emissions from degassing lava flows occur dispersed over a much greater area and so are more dilute as well as less thermally buoyant than the main vent plume. Trace elements emitted from degassing lava flows are therefore more likely to be concentrated at ground-level and dispersed more locally (10s m) than those emitted in the main vent plume (10s km – see Ilyinskaya et al. (2021)). Whilst this study focused on relatively young lava flows which degassed during ongoing periods of eruptive activity, lava flows may continue to degas for weeks and months following an eruption and thus present a prolonged risk to air quality and environmental exposure to heavy metals (Simmons et al., 2017). The most recent Sundhnúkur 2023-2024 eruptions on the Reykjanes peninsula have also occurred with much higher initial effusion rates (over $1200 \text{ m}^3/\text{s}$ in the first few hours) and in closer proximity to people working (including the workers building the lava barriers, which has even included scraping cooled lava to be used as fill material in the barriers) compared to the Fagradalsfjall 2021-2023 eruptions. The ongoing frequency at which eruptions are now occurring on the peninsula (weeks-months), leading to repeated emission of fresh lava flows, means there is greater potential for localised environmental metal pollution (for example, in hydrological reservoirs).

3.6 Conclusions

Using UAS-mounted samplers, we collected particulate matter (PM) and gas samples above outgassing lava flows at increasing distances from the source during the Fagradalsfjall 2021-2023 eruptions. We find that the composition of emissions from degassing lava flows evolves as the flow ages and cools:

- Near-vent emissions have high SO_2 /halogen ratios and are dominated by the outgassing of S-complexing trace elements such as Se, Te, Pb, As, and Sn, where speciation groupings were defined from thermochemical modelling.
- S degassing rapidly decreases as lava flows age and cool, accompanied by progressively reducing SO_2 /halogen ratios. Outgassing becomes dominated by chloride (Cs, Cu, Mn, Rb), oxide (Ce, La), and hydroxide (Mg, Ti, Fe, Al) complexed elements.
- Decreasing lava temperatures result in reduced volatilisation of the most refractory elements as well as resulting in a transition in speciation behaviour in some elements, such as Ag and Ce. The most distal lava flow emissions are therefore dominated by Cl degassing and Cl-complexed elements.
- According to our modelling and previous measurements, the most evolved (oldest, coolest) lava flows transition further to being dominated by fluoride degassing, with increasing F/Cl ratios down-flow and increased emission of fluoride-complexed elements (Rb, Cs, Al) as inferred from speciation modelling. This remains a hypothesis to be tested for these recent Icelandic eruptions.

Overall, these results evidence that the hazard posed by trace metal emissions, particularly in terms of potential public exposure, is not constant and instead depends strongly on lava age and thermal evolution. Estimated fluxes of volatile trace metals from degassing lava flows were shown to be only an order of magnitude less than those from main vent degassing and for a selection of environmentally polluting elements, greater than or equal to anthropogenic fluxes in Iceland. This finding highlights the importance of considering lava flow outgassing in total volcanic emissions budgets for basaltic eruptions, where their contribution may have previously been disregarded. The Sundhnúkur 2023-2024 eruptions, which remain ongoing at the time of writing, continue to impact the environment. Protracted degassing from the regular and voluminous lava flows leads to localised contamination by metal pollutants which is particularly hazardous given the proximity of flow emplacement to substantial population centres on the Reykjanes peninsula.

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Chapter 4

Heterogeneous trace element deposition from an effusive volcanic plume

Laura Wainman, Evgenia Ilyinskaya, Melissa Anne Pfeffer, Celine Mandon, Enikő Bali, Penny Wieser, Brock Edwards, Martin Voigt, Barbara I. Kleine-Marshall, Sýlvía Guðjónsdóttir, Abigail Symons, Adam S. Cotterill, Samantha J. Hammond, Barbara Kunz, Frances Jenner, Anja Schmidt, Andri Stefánsson, Emma Nicholson, Sæmundur Halldórsson, Jóhann Gunnarsson Robin, Alessandro Aiuppa, Mike Burton, Tamsin A. Mather.

Abstract

Effusive basaltic eruptions are an important source of volatile trace elements to the troposphere. Utilizing advances in uncrewed aerial vehicle (UAV) technology we perform in-situ multi-element sampling of effusive volcanic plumes from the Fagradalsfjall (Iceland) 2021-2022 eruptions to compare trace element deposition behavior under varied meteorological conditions. We demonstrate fractionation between refractory and more volatile elements, driven by gravitational sedimentation, and enhanced by scavenging during snowfall through the plume. We find that the depositional behaviour of volatile elements also has meteorological control, with alkali metals deposited more efficiently via wet deposition than elements such as Se, As, and Cd, which are preferentially deposited via diffusional processes. We propose that heterogeneous element deposition behaviour reflects the complex interplay between gas-phase speciation, water solubility of the resulting complexes, particulate size distributions, and affinity for scavenging by larger ash particles. Constraining the effects of meteorological conditions on the depositional pathways

of trace elements from volcanic plumes is critical, both for using trace elements as proxies in the cryogenic record, and for assessing and mitigating exposure in nearby communities, where for volcanoes in regions with pronounced wet and dry seasons, the delivery and bioaccumulation of potentially toxic elements may vary seasonally.

4.1 Main Text

Emissions of gas and particulate matter (PM) from effusive basaltic eruptions are an important natural source of volatile elements to the troposphere (Nriagu, 1989; Ilyinskaya et al., 2021). Elements may be released both as silicate material (e.g., ash) or in the gas phase, either elementally or more commonly, complexed as oxides, halides, sulfides, or hydroxides (Mandon et al., 2019; Moune et al., 2010; Symonds et al., 1992; Zelenski et al., 2021). Upon emission, these magmatic gases cool through mixing with the atmosphere and may undergo rapid droplet condensation and gas-to-particle conversion (Symonds et al., 1987; Smekens et al., 2024). The resulting aerosol PM is transported downwind in the volcanic plume and may be dispersed 10s to 100s km (Hong et al., 1996; Calabrese et al., 2011; Mather et al., 2012; Ilyinskaya et al., 2017). During transport, wet and dry depositional processes remove PM (as well as gas phase species) from the plume and thus deliver a range of elements to the surface (Delmelle, 2003; Moune et al., 2006; Calabrese et al., 2011; Mather et al., 2012; Ilyinskaya et al., 2021). The additional input of these elements may act as essential nutrients for land and ocean ecosystems (González-Santana et al., 2024) or can accumulate to harmful levels in biological and hydrological reservoirs (Mather et al., 2003; World Health Organisation, 2007; Jones and Gislason, 2008; Martin, Mather, Pyle, et al., 2010; Calabrese et al., 2011; Mather et al., 2012; Calabrese et al., 2015; Liotta et al., 2017; Department for Environment (DEFRA), 2025). Over 10% of the world's population lives within 100 km of an active volcano (Loughlin et al., 2015) and thus may be exposed to elevated levels of trace metals via volcanic emissions, concentrated in water or soil (Stewart et al., 2021). Understanding the processes that facilitate element deposition to the environment is therefore critical to constraining their atmospheric lifetimes and dispersion patterns. This has implications both for mitigating human exposure during volcanic unrest, for the use of trace elements as proxies in the cryogenic record (Hong et al., 1996; Mason et al., 2022; Vallelonga et al., 2003; Rakociński et al., 2021; Kellerhals et al., 2010), and may provide a natural analogue to anthropogenic point source emissions of trace elements.

The deposition of trace elements from the atmosphere may be facilitated by both wet and dry processes (Kawaratani and Fujita, 1990; Wesely and Hicks, 2000; Cheng et al., 2021; Li et al., 2023). Dry deposition is a continuous process that is highly dependent on the physical characteristics of the receiving surface (Wesely and Hicks, 2000). It can occur via turbulent eddies, which drive the particles and gas molecules toward the surface layer, where for the smallest particles and molecules ($< 0.1 - 1 \mu m$) Brownian diffusion then causes them to diffuse across the laminar boundary layer to the surface where they are collected. For the larger particles, impaction is also a key process, where particles collide with and adhere to surfaces, as well as gravitational sedimentation, where the largest particles fall out under their own weight, and thus generally have shorter residence times in the atmosphere (Wesely and Hicks, 2000; Mather et al., 2003). Wet deposition can occur via rainout (in-cloud scavenging), where particles and gases are incorporated into cloud droplets and ice crystals, or act as cloud condensation nuclei and ice nucleating particles, which subsequently fall out as precipitation. Wet deposition can also occur via washout (below cloud scavenging), where falling precipitation (rain or, in this study, snow) captures the particulates as it passes through the plume via impact scavenging (Kawaratani and Fujita, 1990; Moune et al., 2006; Calabrese et al., 2011; Zhang et al., 2013; Cheng et al., 2021).

Recent investigation of the chemical evolution of Kīlauea’s plume during the 2018 eruption has advanced upon previous work, which has more commonly assumed that trace elements are removed from the plume homogeneously via depositional processes during plume transport downwind (Ilyinskaya et al., 2021). The observed fractionation in trace element composition of Kīlauea plume suggests that the more volatile elements (e.g., Cd, Te, Se), which form the most soluble complexes, may be lost preferentially in high-humidity conditions due to plume wash-out (Ilyinskaya et al., 2021). Inherent element characteristics (such as size-resolved mass distribution, magmatic volatility, and water solubility) as well as external factors, such as localized topography and background meteorological conditions, are hypothesised to play a role in governing element dispersion patterns and relative rates of deposition (Delmelle, 2003; Mather et al., 2003; Ilyinskaya et al., 2021; Edmonds, Mason, and Hogg, 2022). The ground-based sampling campaign at Kīlauea, however, was not able to directly track element fractionation occurring within the volcanic plume, because the nearest downwind sample was collected on the ground, 40 km from the vent. Equally, that study did not directly compare trace element behaviour under varied meteorological conditions during the same eruption (Ilyinskaya et al., 2021). Thus, the temporal and spatial scales over which heterogeneous deposition may occur

in the volcanic plume, as well as the impact of differing meteorological conditions on element deposition behaviour, remain uncertain.

The Fagradalsfjall 2021 – 2022 eruptions (Halldórsson et al., 2022), examined in this study, provided an exceptional opportunity to directly compare trace element deposition behaviour under different meteorological conditions within the same volcanic system. Effusive plumes of gas (H_2O , SO_2 , CO_2 , H_2S , HCl , HF) and aerosol PM were produced during both 2021 and 2022 eruptions (Halldórsson et al., 2022; Pfeffer et al., 2024; Caracciolo et al., 2025) and were dispersed in the lower troposphere, reaching Grindavik (12 km downwind) and the capital city, Reykjavik (45 km) on several occasions (Ilyinskaya et al., 2024; Whitty et al., 2026). Our samples at the 2022 eruption were collected within 2 km of the active vent(s), allowing us to constrain heterogeneous deposition and plume fractionation within the near-vent effusive plume. Advances in uncrewed aerial vehicle (UAV) sampling allowed for unprecedented access to the airborne volcanic plume to conduct in-situ sampling at-vent and in the surrounding atmosphere that would have been impossible with only ground-based sampling techniques (Liu et al., 2020; Wainman, 2024; see Fig 4.1). Fresh snowfall, which interacted with the volcanic plume during deposition, was also collected in the early phases of the 2021 eruption, allowing for a direct comparison of element deposition under varied conditions that favour wet and dry depositional processes.

4.2 Results

4.2.1 Magmatic Volatility, Water Solubility, and Particulate Size Distribution

Our at-vent Filter Pack (FP) measurements (Methods M1) constrain the trace element plume signature of the Fagradalsfjall 2021–2022 eruptions. An element’s magmatic volatility can be described by its emanation coefficient (ϵ_X – Methods M6) which quantifies the proportion of the element that is released from the magma into the gas phase (Lambert et al., 1985; Pennisi et al., 1988; Edmonds et al., 2018). Figure 4.2a compares element emanation coefficients for the Fagradalsfjall 2021-2022 eruptions with those reported for other global volcanoes. Emanation coefficients were calculated using an average of two at-vent filter pack (FP) measurements for both 2021 and 2022 eruptions and represent the mass % of each element degassed from the erupting lava. The least volatile elements are those with coefficients $\epsilon_X < 0.001\%$ and include

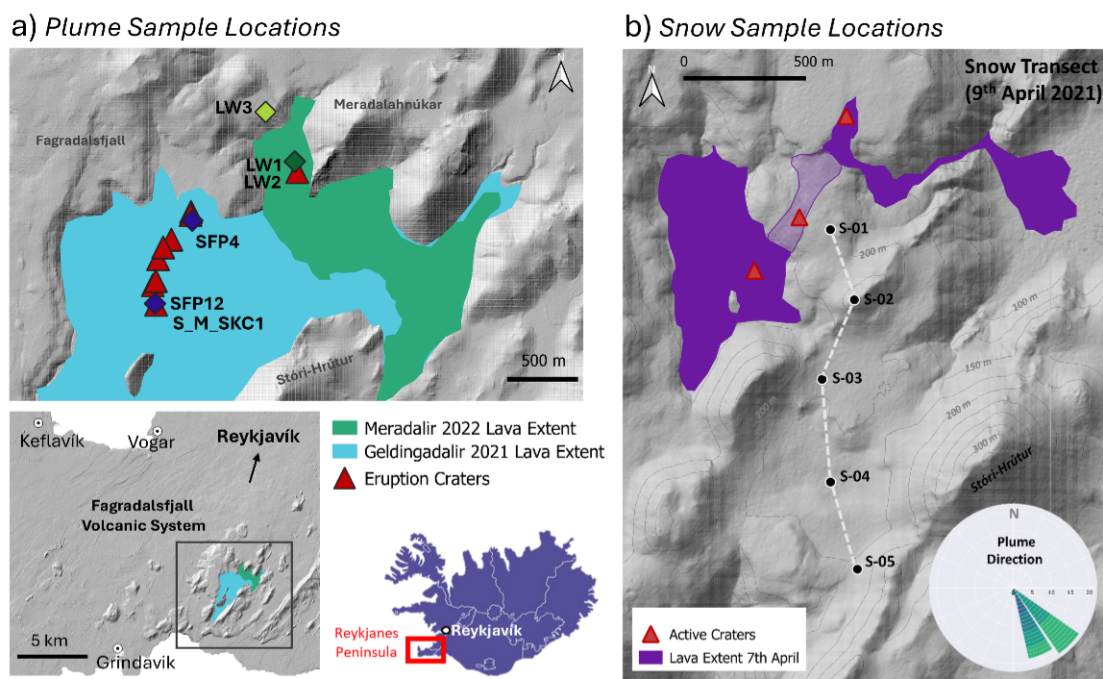


Figure 4.1: Plume and snow sampling locations. a) shows filter pack (FP) and cascade impactor plume sampling locations for the 2021 and 2022 eruptions, with the lava extent and active crater locations for each eruption also shown. See Supplementary B Table 1 for sampling dates and metadata overview. The broader geographic context of the eruptions within the Fagradalsfjall volcanic system on the Reykjanes peninsula is shown below, including proximities to nearby towns. b) shows snow sampling set up during the 2021 eruption using a transect beneath the plume. The Rose diagram shows the plume direction, which is 180 degrees from the conventional meteorological wind direction. The snow transect is approximately parallel to the prevailing wind direction. Solid purple fill shows the mapped lava extent on 7th April 2021, lighter purple fill shows additional approximate extent at the time of sampling on 9th April 2021. Composite DEM from Náttúrufræðistofnun Íslands (2020), Gunnarson et al. (2022), and Pedersen et al., 2022. The collection of samples following fresh snowfall is vital to avoid contamination between different snow-plume interactions and has previously been used to investigate the composition of volcanic plumes (Moune et al., 2006) and the global dispersal of trace metals to ice cores (Vallelonga et al., 2003; Kellerhals et al., 2010; Rakociński et al., 2021; Mason et al., 2022)

major elements such as Fe, as well as rare earth elements (REE) Nd, Sm, La, and Ce. Most other elements fall within the moderately to highly volatile range with emanation coefficients between 0.001% and 10%. The lower end of this range is made up of the alkali metals Li, Na, Rb, and Cs, whilst the more volatile elements include metals and metalloids Zn, Sn, Pb, and As. The most volatile elements are those with emanation coefficients $\epsilon_X > 10\%$ and include Cd, Se, and Te.

Previous investigations have shown that the more volatile elements ($\epsilon_X > 1\%$), such as Se, Te, Cd, Pb, and As, are predominantly hosted in the smallest size fraction of the aerosol PM and have the highest water solubilities (Ilyinskaya et al., 2021; Mather et al., 2012; Martin et al., 2008; Martin et al., 2009). In contrast, the most refractory elements, including Fe, Ce, La, Nd, Sm ($\epsilon_X < 0.001\%$) are generally found in the coarsest, ash-rich size fraction and are less water soluble (Ilyinskaya et al., 2021; Mather et al., 2012; Martin et al., 2008; Martin et al., 2009). Our size-resolved PM determinations (Methods M2) are illustrated in Figure 4.2b, which shows the mass % size distribution along with the water solubility, and the weighted ash fraction (WAF; the proportion of the element on the filter attributed to silicate ash) for a subset of trace elements. The REE (Ce, La, Nd, Sm), which are some of the most refractory elements, show the highest concentrations in the coarsest size fraction and are present in the plume as PM $> 0.25 \mu m$, with most being $> 1 \mu m$ in diameter. Other refractory elements, found predominantly in the coarsest fraction, are V and Fe, although these elements do have a ($\sim 50\%$) sub- $0.25 \mu m$ component. Across all refractory elements, the weighted ash fraction is $\sim 100\%$, indicative of being hosted in the silicate ash component of the plume (Ilyinskaya et al., 2021; Mather et al., 2012; Martin et al., 2008).

A general decrease in the contribution of silicate ash is seen with increasing element volatility, reflecting a greater contribution from condensed magmatic gases to the overall element concentration (Mather et al., 2003; Edmonds, Mason, and Hogg, 2022). For example, the most volatile elements (Se, Te, Cd, As) have WAF $< 1\%$, consistent with being hosted predominantly in the smaller (mostly $< 0.25 \mu m$) non-silicate aerosol fraction formed through gas-to-particle conversion (Whitby, 1978). The most refractory elements also show consistently lower water solubilities ($< 50\%$) than the more volatile elements ($> 60\%$). However, within the volatile fraction, the elements that have the lowest WAF and highest magmatic volatilities (e.g., Te, Se, Cd), are not consistently the most soluble (for example, Ag, Cs, Cu, Tl, and Pb all have higher

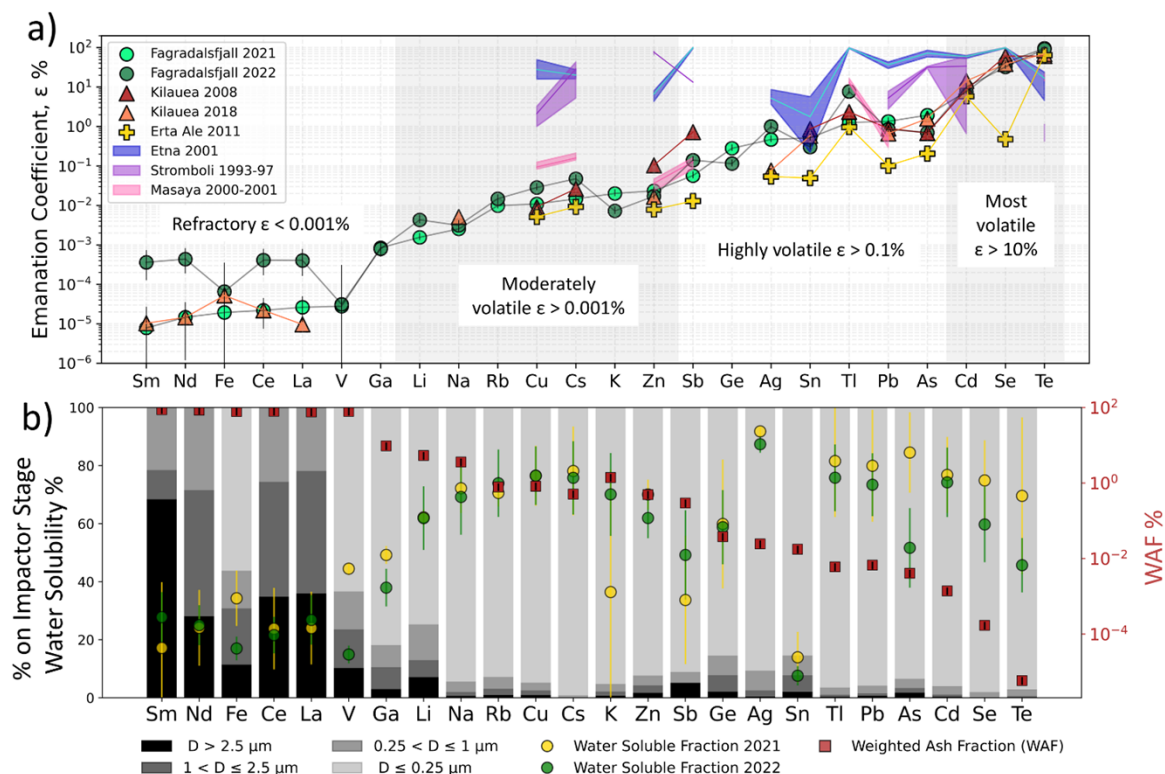


Figure 4.2: Element emanation coefficient, size distribution, water solubility, and ash fraction. a) Emanation coefficients calculated using the average of two at-source FP samples for each Fagradalsfjall eruption (2021: SFP4 (23/03/2021), SFP12 (13/04/2021). 2022: LW1 (16/08/2022), LW2 (16/08/2022)) with a weighted ash fraction (WAF) correction applied using matrix glasses from lava samples collected during the same eruption (see Methods, M6). Red triangles show coefficients calculated for the 2018 Kilauea eruption (Mason et al., 2021) and 2008 eruption (Mather et al., 2012). Yellow pluses for the Erta Ale 2011 eruption (Zelenski et al., 2013) and shaded lines show coefficients for arc volcanoes: Etna 2001 (Aiuppa et al., 2003; Aiuppa et al., 2002), Stromboli 1993-97 (Allard et al., 2000), and Masaya 2000-2001 (Moune et al., 2010) b) Size distribution data from cascade impactor sample (SMSKC1, collected on 06/04/2021) where grey bars show the % mass of each element found within a given size bin. The concentration of refractory elements collected in the coarsest size fraction is likely to be undersampled by the cascade impactor due to increased wall deposition in the coarsest impactor stage (Berlinger et al., 2021; Supplementary B Figure B.1). Elements are ordered by increasing emanation coefficient. Red squares show WAF, the proportion of the element concentration on the filter pack that is attributed to the silicate ash and dust component of the plume, calculated as an average of two filter pack samples (SFP4 and SFP12). Water solubility is calculated as the percentage of that element found in the water-soluble component of the total extraction (where the total extraction is the water and acid soluble components combined) and is shown by white circles (2021 – average of SFP4 and SFP12) and blue circles (2022 – LW1 and LW2), with the error bars showing the range between the two filter pack samples (See Methods, M4).

water solubilities than Te but Te is more volatile ($\epsilon_X > 10\%$). Sn and Sb also deviate from the overall trend of increased volatility, higher water solubility, and lower WAF, showing much lower solubilities and larger size fractions compared to similarly volatile elements.

4.2.2 Near-vent Trace Element Deposition

Trace element deposition is characterised by the UAV sampling in the downwind airborne 2022 eruption plume (Fig. 4.3a). Figure 4.3b shows the estimated percentage of the mass each element lost from the plume at 500 m downwind, where the symbol size denotes the average particle diameter (based on at-vent cascade impactor sample SMSKC1, Fig. 4.2b). The relative dilution of the plume due to mixing with air is calculated as $20 \pm 5\%$ between the vent (LW1) and 500 meters (LW3) based on the multi-GAS SO_2 concentration measurements (Methods M2). Assuming homogeneous dilution of the plume as it mixes downwind without any loss of elements through deposition, theoretical diluted downwind element concentrations may therefore be calculated as $20 \pm 5\%$ of those measured at-vent. Measured element concentrations in the downwind airborne plume were then subtracted from these theoretical diluted concentrations, with the difference between them being an estimate of the percentage of the mass of that element lost from the plume due to deposition. Over the first 500 m in the downwind plume, the most refractory elements, Ti, Fe, Mn, and REEs show the greatest percentage loss from the volcanic plume (13-17%) compared to the more volatile elements (e.g., Ag, As, Zn, Se) which range from 0-13% (Fig. 4.3b). Even within the volatile aerosol fraction, however, this varies between elements. For example, Sn, Se, and Te are the most depleted of the volatile fraction in the plume with 11-13% lost within 500 m, whilst other volatile elements Ag, Cu, and Cs show $< 5\%$ loss under the same atmospheric conditions. These estimates of element loss from the airborne plume within the first 500 m downwind range between 0 and 17%, suggesting that ~ 83 -99 % of the initial mass of volcanogenic trace elements released, may be subject to longer-range dispersion in the troposphere.

4.2.3 Deposition During a Snowfall Event

During the 2021 eruption, ground-based snow samples were collected within 2 km of the vent along a transect following the prevailing wind direction (Fig. 4.1b, Fig. 4.4a). Figure 4.4b shows element enrichments in the snow (at site S-02) relative to the basaltic lava on the y-axis and element enrichment in the aerosol plume relative to basalt on the x-axis, with both

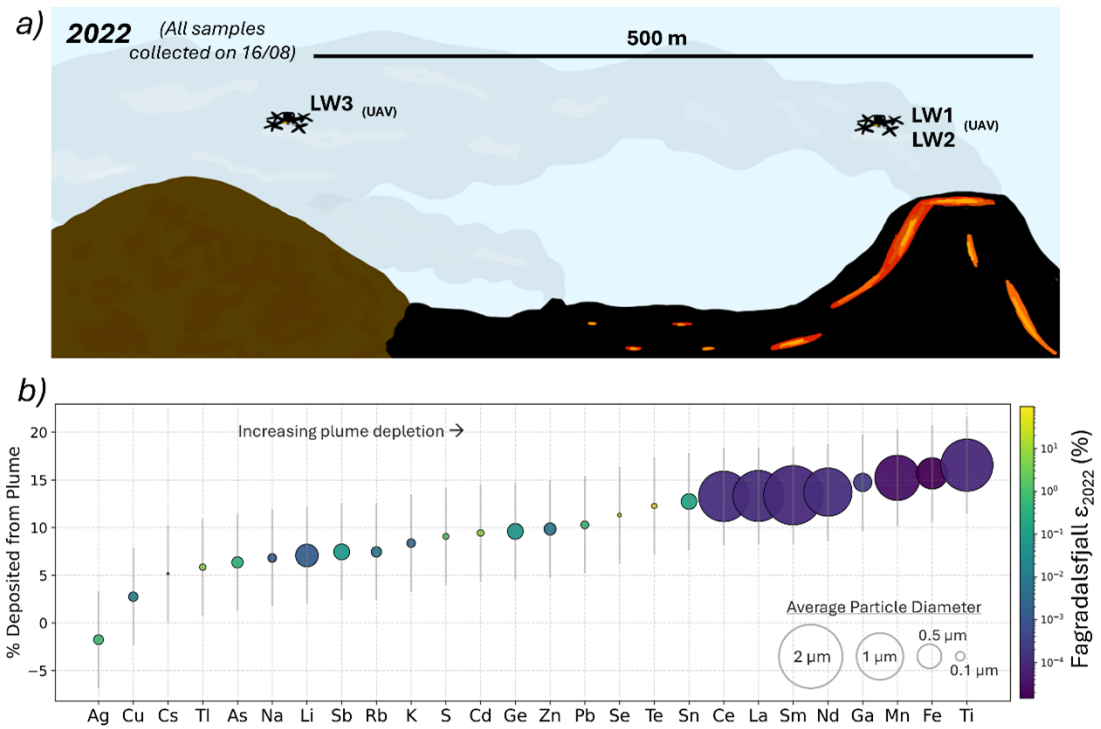


Figure 4.3: Element Deposition from the downwind airborne plume at the 2022 eruption. a) Dry sampling set up during the 2022 eruption with FP samples being collected at-vent as well as in the downwind plume. b) Percentage deposited of each element from the airborne plume at 500 m downwind (increasing loss from the plume towards the right). Circle size denotes the average particle size, as calculated using the distribution of elements across stages in the cascade impactor sample SMSKC1. Circles are colored according to the mean emanation coefficient for the 2022 eruption (ϵ_{2022}) as calculated in Methods, M7 and shown in Fig. 4.2a. Error bars show % deposited from the plume assuming dilution to 20 ± 5 % of original at-vent concentrations.

enrichment factors normalised to Mg as the refractory reference element (see Methods, M7 for EF_{Mg} calculation). If elements in the snow were homogenously deposited from the plume, they should lie on a straight line with a gradient of 1 (i.e. parallel to the 1:1 line), with the offset dictated by the overall efficiency of snow scavenging from the plume. For example, if the fallen snow contains 1% scavenged plume material with no relative fractionation between elements, they would all plot on the 1:100 line. In Figure 4b, however, the refractory elements (Fe, Ti, Mn, REE) plot between the 10:1 and the 1:1 line, indicating that these elements are more enriched in the snow relative to their concentrations in the volcanic plume. $EF_{plume/basalt}$ was calculated without ash correcting the plume sample, so the presented enrichment factors include the contribution of silicate ash. By contrast, the more volatile elements cluster around the 1:100 line, indicating significantly lower concentrations in the snow compared to their concentrations in the plume. There is also an overall offset from a 1:1 gradient, where elements such as Se, Cd, and Pb plot below the 1:100 line, whilst other elements such as Zn, Cu, Rb, and Na plot above the 1:100 line.

Figure 4.4c shows element concentrations in ground-based snow samples along the downwind transect, normalised to element concentrations in the at-vent plume sample. The lower panel of Figure 4.4c also shows the elevation profile of the snow transect collected on the 9th April 2021, with snow pH also plotted as an indicator of decreasing plume interaction. Trace element concentrations follow a similar profile, generally decreasing with increasing distance from the vent, although the rate of decrease varies significantly between elements. For example, at 800 m downwind, deposited concentrations of elements relative to the at-vent plume sample show: four orders of magnitude decrease for Se and Te; three orders of magnitude decrease for Cu, Cs, and Rb; and only one order of magnitude decrease for the refractory elements Fe, Mn and REE. This disparity between elements continues downwind, but the rate of decrease for most elements evens out beyond 800 m downwind. The exception to this is in the sample collected at 1200 m from the vent, where elements such as Ce, Mn, and La, and to a lesser extent K, Na, Rb, and Cs show an increase in deposited concentrations that are not observed for any of the more volatile elements such as Te or Se.

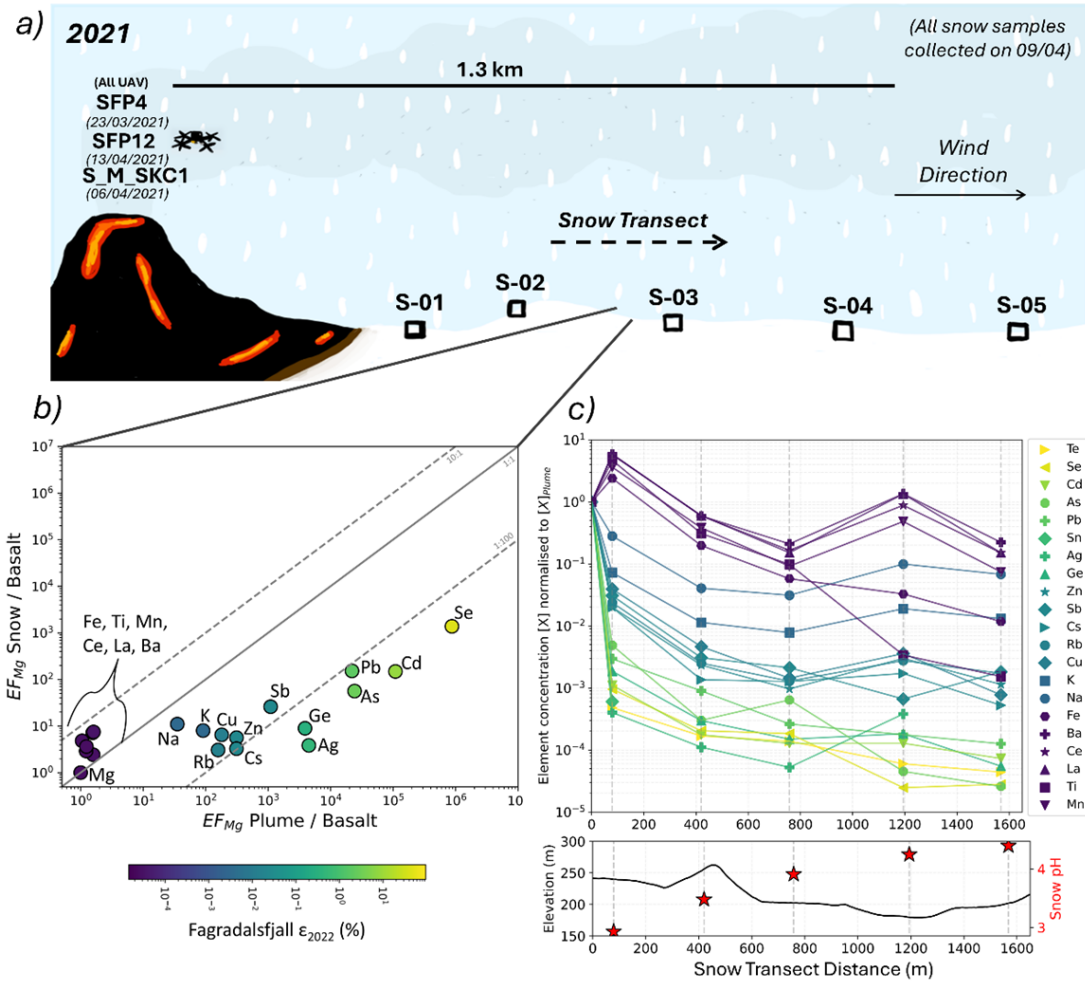


Figure 4.4: Element Deposition due to snow-plume interaction. a) sampling of wet deposition set up during the 2021 eruption, collecting a transect of snow samples from beneath the plume. At-vent FP and cascade impactor samples were also collected using UAV platforms, although these were not collected during a snowfall event. b) Heterogeneous scavenging of elements from the plume by falling snow. Enrichment Factors, EF, were calculated as outlined in Methods M7, relative to Mg as a refractory reference element. The y-axis shows EF for the snow sample S-02, and the x-axis shows EF for the plume sample SFP12, relative to element concentrations in the basaltic lava. Elements are colored by their emanation coefficients calculated in Methods, M7 and shown in Fig. 4.2a. Due to filtering of the samples (removing $PM > 0.45 \mu m$) prior to ICP-MS analysis the concentrations of the most refractory elements may be an underestimation, representing the contribution from partially dissolved ash, but not the larger ash particles which were removed via filtering. c) Concentrations of elements deposited via snow scavenging with increasing distance from the vent. The y-axis shows element concentration $[X]$ in the snow sample normalised to element concentration in the at-vent plume sample. The X-axis is the distance from the vent. Elements are colored by the emanation coefficient calculated in Methods, M7 and shown in Fig. 4.2a for the 2021 eruption. All snow samples were collected on the 9th April 2021 between 12 and 2 pm following fresh snowfall. The lower panel shows elevation change along the transect route shown in Fig. 4.1b for snow sample collection and red stars show pH measurements of the snow samples.

4.3 Discussion

4.3.1 Near-vent Ash-dominated Deposition

Under both sets of meteorological conditions sampled in this study, at the 2022 and 2021 Fagradalsfjall eruptions, respectively, trace element deposition from the near-vent plume was dominated by the preferential loss of refractory elements. Under dry conditions, as sampled in 2022, within 500 m of the vent, over 13% of the refractory elements (Fe, Mn, REE) had been lost from the volcanic plume, compared to $< 10\%$ loss for the more volatile trace elements. The preferential deposition of these refractory elements is consistent with them being hosted predominantly in the larger silicate ash component of the plume, which will thus settle out more quickly via gravitational sedimentation (Whitby, 1978; Wesely and Hicks, 2000; Mather et al., 2003). The resulting fractionation between refractory elements, hosted in the larger silicate ash particles, and the more volatile elements, hosted in the smaller non-silicate PM, is illustrated by Stokes' Law (see Supplementary B Table 2). For example, considering only sedimentation of spherical particles, for an ash particle of $100\ \mu\text{m}$ diameter it takes 1-2 minutes to settle 30 m in air, whilst a particle within the secondary aerosol fraction, with a diameter of $0.1\ \mu\text{m}$, would take ~ 10 days settling out over the same vertical distance. This underscores the strong size-dependent control on deposition via gravitational sedimentation, with particulate settling velocities spanning several orders of magnitude.

Under snowfall conditions through the volcanic plume, sampled at the 2021 eruption, the most refractory elements were also preferentially deposited from the effusive plume relative to the more volatile elements. The continued fractionation between volatile and refractory elements under snowfall conditions can be explained by three possible depositional processes: 1) gravitational sedimentation of the larger ash particles, which continues irrespective of snow fall through the plume, 2) snowfall through the plume enhances the preferential deposition of the silicate ash component via impaction scavenging, where particles with higher diameters are collected more efficiently by falling snow crystals (Cheng et al., 2021), 3) ash PM acts as ice nucleating particles in the volcanic plume, which has high concentrations of magmatic H_2O , and thus further enhances rainout (Maters et al., 2020). These processes are not mutually exclusive, and given the high concentrations of the refractory elements in the deposited snow compared to their in-plume concentrations (Figure 4.4b), it is probable that all three processes are happening in combination, resulting in efficient removal of the silicate ash component from the near vent plume. The

relative contributions of these different depositional processes remain unresolved, however, and are an important direction for future investigation.

It is also possible that sources external to the volcanic plume may have partially contributed to the high concentrations of refractory elements observed in the snow samples. This includes the remobilisation of geogenic dust, which contains lithogenic elements Fe, Mg, Al, and Ti (Baldo et al., 2020), as well as a contribution from sea spray aerosol, which contains elements such as Ca, Na, K, and Cl (Bertram et al., 2018). Both geogenic dust particles and sea spray aerosols are known to act as ice nucleating particles (Sanchez-Marroquin et al., 2020) and thus, if present in the background atmosphere alongside the volcanic plume, may have contributed to the additional deposition of some refractory trace elements, as well as Na and K, through in-cloud scavenging processes (Bertram et al., 2018; Sanchez-Marroquin et al., 2020). The slight increase in refractory element concentrations in the snow sampled at 1200 m downwind occurred in a relative topographic low adjacent to the topographic high of the hill Stóri-Hrútur (Fig 4.1b). The increased concentrations of refractory elements such as Ti, Fe, Na, and K at this distance may therefore be the result of enhanced precipitation formation (including dust and sea spray contributions as ice nucleating particles) and deposition due to mesoscale orographic effects as well as possible remobilisation and redeposition of ash particles (Mott et al., 2014).

The Fagradalsfjall 2021 and 2022 eruptions were dominated by effusive behaviour, with occasional lava fountaining, and are thus characterised as having mostly gas-rich and ash-poor plumes (Halldórsson et al., 2022; Pfeffer et al., 2024). Nonetheless, the observed fractionation between refractory and volatile elements through near-vent heterogeneous deposition (< 500 m of the vent) suggests that, even during effusive activity, the transfer of volcanic elements to the surface in the very near-vent environment may still be dominated by refractory elements under a range of meteorological conditions. Heterogeneous volatile-refractory deposition behaviour is consistent with previous studies at other volcanoes globally (Ilyinskaya et al., 2021; Calabrese et al., 2011; Mather et al., 2012; Mather et al., 2003). The observed heterogeneous deposition of refractory and volatile trace elements within only 500 m downwind of the volcanic plume also highlights the challenges of collecting true “at-vent” samples. The advances in UAV sampling approaches used in this study allow for in-situ airborne collection within < 50 m of the vent and thus minimise the potential effects of heterogeneous deposition (Liu et al., 2020; Wainman, 2024). However, prior to the use of UAVs for volcanic plume sampling, campaigns relying

on ground sampling approaches only likely collected “at-vent” samples > 100-200 m from the vent for safety and access reasons. This may have led to an underreporting of some elements, particularly the most refractory ones, which are lost most rapidly from the plume due to ash sedimentation. Thus, post-sampling adjustments may be necessary (based on 13-17% greater deposition of refractory elements reported above) when comparing to modern datasets.

4.3.2 Heterogeneous Deposition within the Non-silicate Fraction

In addition to the fractionation observed between refractory and volatile elements, hosted in the silicate and non-silicate aerosol components, respectively, there is evidence to suggest a further meteorologically dependent fractionation within the volatile element component. Under conditions that favour dry depositional processes, airborne sampling showed that elements such as Sn, Se, Te, and Pb were preferentially lost from the plume (Fig 4.3b), whilst under conditions that favour enhanced wet deposition, the alkali metals (Na, K, Rb, Cs) were more efficiently deposited (Fig 4.4b). At first glance, these two groups may be separated by their equilibrium element speciation behaviour. For example, thermodynamic modelling (Symonds and Reed, 1993; Gerlach, 2004; Martin et al., 2006; Mandon et al., 2025) of the gas-phase chemistry of the Fagradalsfjall volcanic plume (Wainman et al., 2024) showed that Cs, Cu, and Rb have an affinity for complexing as chloride species ($M-Cl$), whilst Se, Te, Sn, and Pb show more variable speciation behavior, forming sulfide ($M-S^{(-II)}$), sulfate ($M-S^{(+VI)}$) and oxide (M-O) complexes (M = element).

Considering the fractionation between volatile elements under dry conditions, it is those that predominantly form chloride species (Cs, Cu, Rb, Ag) which show the lowest rate of deposition in the near-vent plume (all < 10% within 500 m). By contrast, those elements which preferentially bond to form sulfates and sulfides (Se, Te, Sn, Pb) undergo more efficient removal and deposition from the plume (11-13% loss). Across these two groups of elements there is no significant difference in particle size distribution (Figure 4.3) and thus, in isolation, the different rates of deposition between these groups cannot be explained by gravity-driven sedimentation of larger particles (as hypothesised to explain the difference between volatile non-silicate and refractory silicate-hosted elements).

Nonetheless, differences in element PM size distribution and aerosol growth rates may still offer an explanation for the varied deposition behaviours observed between S and Cl complexing

elements. Comparison between an impactor sample collected at vent and an impactor sample collected ~ 500 m downwind at the 2021 eruption (See Supplementary Figure B.7) shows distinct differences in the size distribution and growth of Cl and S-complexed elements. Within the 500 m closest to the vent the S-complexed elements remain hosted in the very finest size fraction ($< 0.25 \mu\text{m}$) whereas the Cl-complexed elements show more consistent growth and, by 500 m downwind, are hosted to a greater extent in the $0.5 - 1 \mu\text{m}$ size fraction. It is well established that the accumulation mode size fraction ($0.1 - 1 \mu\text{m}$) has the longest residence time in the atmosphere due to inefficient depositional mechanisms (Wesely and Hicks, 2000; Mather et al., 2003). By 500 m downwind the Cl-complexed elements have undergone sufficient growth to enter into the accumulation mode size fraction, whereas the S-complexed elements remain on the very lower limit of the accumulation mode. The true size distribution of S-complexed elements in this mode remains uncertain as only the upper limit of $< 0.25 \mu\text{m}$ is known (i.e., many elements may be hosted in $\text{PM}_{10} \ll 0.25 \mu\text{m}$). As such, the S-complexed elements, lying outside of the accumulation mode may undergo more rapid deposition via efficient diffusional processes (Wesely and Hicks, 2000), whilst the Cl-complexed elements undergo relatively greater hygroscopic growth, possibly due to their higher solubilities, and thus are deposited from the near-vent plume less efficiently. Under conditions where snowfall interacts with the volcanic plume, as sampled at the 2021 Fagradalsfjall eruption, the fractionation between volatile elements during deposition is reversed, with the elements that commonly form chlorides being more efficiently deposited from the plume than those with an affinity to form S-complexes. The difference in deposition behaviour between these two groups could be explained by enhanced impact scavenging efficiency via below-cloud washout. Washout efficiency depends predominantly on aerosol diameter, where as discussed above, the Cl-complexing elements may undergo greater hygroscopic growth in the near-vent plume relative to the less soluble S-complexed elements (Cheng et al., 2021).

An alternative explanation is that the alkali metals (Na, K, Rb, Cs), which predominantly complex with Cl in the gas phase, are known to form soluble salts upon decompression and cooling (Higashi et al., 2005; Shimoyama et al., 2009; Desboeufs et al., 2005), whereas elements, such as Se, Sn, Cd, As, and Pb, which show more variable gas phase speciation behavior as sulfides, sulfates, oxides, and hydroxides, generally form less soluble or insoluble salts (Mather et al., 2012; Desboeufs et al., 2005). Impaction scavenging shows only a weak relationship with aerosol solubility, being more strongly affected by particle diameter (Li et al., 2023; Cheng et al., 2021),

so any solubility-dependent deposition is more likely to occur via in-cloud rainout processes. The high concentrations of magmatic water vapour in the volcanic plume may encourage snow crystal formation. Simulations using the ATHAM plume model suggested that scavenging by ice particles could increase the total scavenging efficiency for HCl from about 50% to about 90%, but for sulfur-containing gases SO_2 and H_2S , which are only slightly soluble in liquid water, scavenging efficiencies were lower at around 10 to 30% (Textor et al., 2003). We therefore hypothesise that the more soluble Cl-complexed elements are more likely to be incorporated during snow crystal formation in the plume, and thus that preferential deposition via rainout may explain their relative enrichment in deposited snow samples compared to the less soluble S-complexed elements.

The relationship between element speciation and deposition behavior during the snowfall event is supported by cluster analysis of elements in the snow samples, which results in four distinct groups of elements based on relative similarity in multivariate space (See Supplementary B Material for Cluster Analysis Methods and Supplementary B Figure B.5): 1) refractory elements associated with silicate ash and sea spray aerosol, 2) elements with a strong affinity for complexing with S, 3) elements with a strong affinity for complexing with Cl, and 4) elements with mixed speciation and complexing behaviors. The water solubilities presented in Figure 4.2 show some limited variations between elements that commonly complex with S and Cl, which may support this further (e.g., Cs, Cu, Rb > Se and Te). However, these water solubilities were determined under laboratory conditions during our two-stage extraction process (Methods M4) and so may not be fully representative of element solubilities under plume conditions (i.e., at higher temperatures and lower pH). There also remains uncertainty over the thermodynamic data for gas-phase species, particularly sulfur compounds, which are often lacking and commonly rely on extrapolations from lower temperatures (Symonds and Reed, 1993; Gerlach, 2004; Mandon et al., 2025). Speciation is also commonly modelled only in the gas phase (as in this study and others; Mason et al. (2021); Mandon et al., 2019), potentially overlooking important speciation changes during gas-to-particle conversion that could influence element water solubilities as they are transported in the downwind plume (Mason et al., 2021). Expanding thermodynamic datasets and modelling these transitions is therefore essential for more accurately constraining element speciation in aerosol PM and remains a key factor for advancing our understanding of speciation-solubility dependent element deposition processes.

4.3.3 Implications for Environmental Distribution

The mechanisms outlined in this study, to explain heterogeneous trace element deposition under varied meteorological conditions at the Fagradalsfjall eruptions, are well constrained and considered fundamental processes across the fields of atmospheric chemistry and physics (Wesely and Hicks, 2000; Cheng et al., 2021; Li et al., 2023). It is therefore highly probable that the same mechanisms that we invoke here may play a role in modulating heterogeneous deposition at other volcanoes globally, particularly where they have similar effusive degassing dynamics to the Fagradalsfjall eruptions. With many volcanoes situated in regions with pronounced wet and dry seasons, one possible implication could be for seasonal variations in trace element deposition to the surface in volcanic environments. Seasonal controls on precipitation have already been shown to be a key determinant of the bulk amount of trace elements deposited (e.g., less rainfall leads to atmospheric accumulation and lower rates of deposition; Li et al., 2023). If seasonally dependent deposition effects do occur, the environmental impact is likely to be particularly pronounced for continuously outgassing open vent volcanoes (Edmonds, Liu, and Cashman, 2022), such as Etna (Italy; Calabrese et al., 2011; Calabrese et al., 2015), Masaya (Nicaragua; Moune et al., 2010; Martin, Mather, Pyle, et al., 2010; Martin, Sawyer, et al., 2010; van Manen, 2014; Delmelle et al., 2002) or Yasur (Mandon et al., 2019; Cronin and Sharp, 2002) where continuous long-term emission and fractionated deposition may result in measureable differences in trace element delivery to terrestrial and aquatic reservoirs. Nonetheless, the long-term effect this may have on the bioaccumulation of trace elements is unclear and likely to be complex (i.e., due to heterogeneous processing of elements in soils and in uptake by plants). The absolute element concentrations measured in this study (ppb) represent an instantaneous snapshot of deposition and thus remain well below health hazard thresholds. However, the implications of potentially heterogeneous meteorologically dependent deposition on the long-term concentrations of elements in the surface environments surrounding active volcanoes remain unconstrained. The varied affinity of different elements for wet and dry deposition processes also highlights the potential for certain exposure pathways (e.g., aqueous or airborne) to be more important for certain elements. Calkins and Delmelle (2021) showed that exposure pathways can vary by demographics (i.e., between children and adults). Accounting for heterogeneous deposition of potentially toxic metals under different atmospheric conditions and via different pathways is therefore an important step towards understanding exposure to volcanic heavy metal pollution to advancing monitoring and hazard mitigation efforts.

The model that we present here, to explain the preferential wet deposition of soluble, chloride-forming elements within the volatile aerosol fraction, also offers a direct explanation for several geochemical signatures recently observed in polar ice cores. For example, Edmonds, Mason, and Hogg (2022) hypothesised that the decoupled chloride and sulfate signals in an ice core record from Antarctica, which has been linked to the 17.7-ka eruption sequence of Mount Takahe (McConnell et al., 2017), could be due to the early localised deposition of volcanic chloride aerosols through preferential wet deposition during downwind transport. Using a series of ice cores from Greenland, Hutchison et al. (2024) observed a similar decoupling in the deposition of S and Cl between inland and coastal ice core sites following the Icelandic Eldgjá eruption in 939 CE. They found that nssCl (non-sea-salt Cl) dominated volcanic fallout at the coastal ice core site (which was closest to Iceland) whilst at inland ice cores, nssS (non-sea-salt S) and nssCl were roughly equivalent. They suggest that this could be explained by the more rapid deposition of the Cl aerosols along the coast due to the wetter local atmospheric conditions (Hutchison et al., 2024). The observations we present here, directly from the Fagradalsfjall 2021-2022 eruption plumes, demonstrate the first direct measurements of preferential metal-chloride deposition via wet processes in an effusive volcanic plume as it is dispersed downwind. Coupled with recent ice core observations, this clearly highlights the importance of atmospheric processing in modulating the delivery of volatile metals to far-field environments and the need for further studies of trace element ice core signatures.

Future studies, at more volcanoes globally, under a greater range of environmental and meteorological conditions, and in ice core records, are essential to resolving the complex array of depositional and transport processes that control trace element dispersion in volcanic plumes. Continued advances in sampling approaches, especially UAV platforms, are likely to unlock even greater possibilities for in-situ, high-resolution sampling of airborne volcanic plumes. These UAV sampling technologies may also be relevant across a broad range of fields concerned with trace element emission and transport behavior in the atmosphere, with volcanic eruptions, such as the Fagradalsfjall 2021-2022 eruptions, potentially providing a natural analogue for anthropogenic point source emissions of similar trace elements (e.g., industrial smelters, shipping plumes, etc) which may be subject to similar underlying processes during transport and deposition in the atmosphere.

4.4 Methods

4.4.1 Filter Packs

Filter packs (FP) mounted on UAS (DJI Matrice 600 Pro in 2021, DJI Matrice 300 RTK in 2022 and 2023) were used to collect in-situ samples of gases and aerosol PM in the near-vent volcanic plumes at the 2021 and 2022 Fagradalsfjall eruptions. The UAS was used to hover within the volcanic plume (assessed visually during flying using the on-board camera) both directly above the main active vent and to up to 1 km away in the downwind plume. Sampling altitude ranged between 50 and 200 m above the flight take-off point. Total sampling duration ranged from 14 to 62 minutes for UAV-mounted FP samples, although due to UAS battery life limitations, most samples were the cumulation of multiple flights to the same location (see Supplementary B Table 1). The sampling set up consisted of a 4-stage Teflon filter pack holder secured to the UAV “leg”, connected via plastic tubing to a SKC Leland Legacy pump mounted on the body of the UAV (See Supplementary B Figure B.4). The combined weight of the filter pack and pump (and on-board Multi-GAS) was just lower than the payload capacities of the UAVs (2.7 kg). Thus, care had to be taken to ensure a balanced weight distribution on the UAV to avoid issues upon take-off and landing.

The 4-stage filter packs were used in two different configurations: either containing just one filter for PM collection (PM Filter specifications: Whatman™ WTP polytetrafluoroethylene (PTFE) 47-mm diameter, pore size 1.0 μm) or with an additional 3 filters loaded behind the first PM filter for gas collection (Gas Filter Specifications: Whatman™ Quantitative Filter Papers, Ashless, Grade 41, 55-mm diameter (2021) and 47-mm diameter (2022), Millipore 47-mm diameter absorbent pads (2023)). The filters for gas collection were impregnated (5% K_2CO_3 + 1% glycerol in 2021, 5% KOH + 1% glycerol in 2022 and 2023) shortly prior to use (as used in Ilyinskaya et al. (2021) and Mason et al. (2021)). Base treatment of gas filters allows for the capture of acidic gases such as SO_2 , HCl and HF by reaction and conversion to their anions SO_4^{2-} , SO_3^{2-} , Cl^- , and F^- . Gas filters were considered saturated if $> 10\%$ of total SO_4^{2-} was present on the final gas filter stage (as defined by Mason et al. (2021)). All gas filters collected in 2021 were saturated, and thus we decided to use KOH rather than K_2CO_3 impregnation for the gas filters in 2022. Gas filters in 2022 did not saturate despite being exposed to comparable SO_2 concentrations across similar flight durations. Airflow through the filter pack was generated using an SKC Leland Legacy pump, also mounted on the UAS. The flow rate was set to the

highest value that the pump was able to sustain (6 – 13.5 L/min). The highest sustained flow rate varied according to which filter set-up was used (i.e., 1 or 4 filters loaded) and was also sensitive to the curvature of the connective tubing between the pump and filter when mounting the equipment on the drone. Immediately after sampling, filter packs were sealed using Parafilm to prevent particle loss and contamination during transport.

4.4.2 MultiGAS

A multi-GAS instrument from the University of Palermo (Aiuppa, 2005; Liu et al., 2020; the same unit type used in Burton et al., 2007) was co-located on the drone for time-series measurements of major gas concentrations. The multi-GAS contains SO_2 and H_2S electrochemical sensors (T3ST/F-TD2G-1A and T3H-TC4E-1A; both City Technology, calibrated for 0 to 200 ppmv and 0 to 50 ppmv respectively, see Liu et al. (2020)), and an infrared spectrometer for CO_2 (Microsensorik Smartgas Modul Premium2, range 0–5000 ppmv). Data are collected at 1 Hz; however, the effective temporal resolution is limited by sensor response effects (< 20 seconds).

Time-averaged in-plume SO_2 concentrations for each FP and SKC sample were calculated using the co-collected multi-GAS SO_2 time series, excluding data < 0.5 ppmv (the baseline between in-plume peaks in SO_2) within the known flight-time window. Mason et al. (2021) and Edwards et al. (2024) use background thresholds of 1 ppmv and 1.3 ppmv, respectively. Using alternative baselines of 0 and 1 ppmv resulted in a difference of less than 1% in our corrected in-plume flight times. The time-averaged SO_2 concentrations should be viewed as minimum values as some in-plume measurements were made when SO_2 concentrations were above the maximum detection limit of the sensor (saturation occurred at ~ 220 ppmv). The total time FP and cascade impactor samples spent inside the aerosol plume (defined as $SO_2 > 0.5$ ppmv) was used to correct the total volume pumped for the in-plume volume sampled.

4.4.3 Cascade Impactors

The use of cascade impactors is similar to that of filter packs, where the impactor is connected to an air pump which draws the volcanic plume through a series of stages containing PTFE filters. Cascade (Sioutas SKC) impactors consist of 4 stages and an after stage and can thus resolve particles into a series of five size bins of decreasing particle diameter ranges - cut off diameters at $2.5 \mu m$, $1.0 \mu m$, $0.5 \mu m$, and $0.25 \mu m$ (with all PM smaller than $0.25 \mu m$ collected on the final after-stage). Cascade impactors were used during the 2021 eruption campaign to

collect a size-resolved sample (SMSKC1) above the main volcanic vent for comparison with a similar FP sample (SFP12). Although the samples were collected on different days, they were collected within the same phase of the eruption and thus we would expect a similar at-vent composition based on consistent relative element volatilities (Figure 4.2). Comparison between the two samples is shown in Supplementary B Figure B.1. The finest fraction containing the more volatile elements follows a 1:1 relationship in element concentration between FP and the cascade impactors, whereas the coarsest fraction, which predominantly consists of the more refractory elements is potentially being under sampled (by up to 5 times) in the cascade impactor relative to their collection on the FP. This may be due to increased wall deposition in the coarsest stages of the impactor (Berlinger et al., 2021).

4.4.4 Extraction and Compositional Analysis

The samples were handled in an ISO 7 clean lab environment at the Institute of Earth Sciences, University of Iceland and the School of Earth and Environment, University of Leeds. Gas and PM filters were extracted following an established procedure (Ilyinskaya et al., 2021; Mason et al., 2021). All filters were cut into quarters and transferred to acid-cleaned 50 ml centrifuge tubes using acid-cleaned metal-free scissors and tweezers prior to the extraction process. Gas filters were leached in 20 ml Milli-Q ($> 18.2 \text{ M}\Omega$, MQ) water and $250 \mu\text{l}$ H_2O_2 (to oxidise collected sulfur species to sulfate) and then shaken for 20 mins. 1.5 ml from these solutions was pipetted for anion concentration measurements by ion chromatography (IC) at the Department of Geography, University of Leeds (on Thermo Dionex ICS5000) and Institute of Earth Sciences, University of Iceland (on Thermo Dionex ICS2000).

Material collected on PM filters was extracted using a two-stage sequential leaching method (Ilyinskaya et al., 2021; Mason et al., 2021). The water-soluble PM fraction was first extracted in 20 ml MQ water + $200 \mu\text{l}$ propan-2-ol (to reduce the hydrophobicity of the PM filters), shaken and placed in a sonic bath (20 mins each), before being centrifuged at 3000 rpm for 20 mins. 10 ml of the solution was then pipetted to 15 ml acid-clean tubes for analysis by ICP-QQQ MS (Agilent 8800), with another 1.5 ml pipetted for IC analysis (as described for the gas filters above). Water solubility of each element was calculated as the percentage of that element found in the water-soluble fraction, compared to the bulk PM extracted from the filter pack. The remaining solution and filters were transferred to an acid-cleaned 22 ml PFA vial. 5 ml UPA grade concentrated HNO_3 was added to the PFA beaker and samples dried on a hot

plate at 55°C. 1 ml UPA grade concentrated HNO_3 and 1 ml UPA grade concentrated HF were pipetted to the solid residue and refluxed for 3 h at 110°C with lids on the PFA beakers. The lids were then removed, and samples dried at 55°C. 10 ml UPA grade concentrated HNO_3 was then pipetted to the solid residue and refluxed on a hot plate at 90-100°C for sample back into solution. 10 ml MQ was pipetted into the PFA beakers and then transferred to an acid-cleaned sample tube for analysis by ICP-MS/MS.

PM filter samples and blanks were analysed for major and trace elements by ICP-QQQ MS in the School of Environment, Earth and Ecosystem Sciences at the Open University, UK. Field, lab, and filter blanks were used to quantify the level of contamination at all stages of the sampling and extraction process and were found to be negligible. Matrix-matched synthetic calibration standards were prepared using certified stock solutions diluted to encompass the full range of element concentrations in our samples. Internal standards were doped with the same solution matrix as samples to eliminate ionisation effects (particularly with samples containing propan-2-ol). Ionisation effects were monitored by running an on-line internal standard throughout all measurement sessions. Internal standards were run every 4-6 actual samples to monitor performance and instrument drift, as well as to select the optimal gas mode per element. Internal standard measurements were then compared to known diluted stock concentrations to assess the reproducibility and accuracy of our analyses (see the Electronic Supplement sheet B1 for element-by-element RSD and Average/Standard comparisons). Elements were analysed using a triple quad set-up with different collision gas modes (no gas, O_2 , and NH_3) to minimise polyatomic and isobaric interferences (Balcaen et al., 2015; Cox et al., 2019). This allows for lower detection limits and improved accuracy across the range of elements analysed.

4.4.5 Snow Sampling

During the 2021 eruption, fresh snow samples were collected surrounding the active vent (within 2 km). The snow samples were collected in acid-washed (1M HCl, followed by rinsing in MQ water) plastic bags. Samples were collected along a transect at increasing distance from the main vent and parallel to wind direction on the 9th April 2021 between 12 pm and 2 pm local time. Collection following fresh snowfall through the plume is important for minimising contamination and overlap between different plume events. Previous studies have employed a similar approach, using samples of snow which had freshly fallen through the plume to investigate the gaseous and trace element composition of the volcanic plume (Hekla, 2000 eruption; Moune et al., 2006).

Sample bags were stored frozen until processing (< 1 week). Snow samples were unfrozen in warm water baths and immediately filtered through $0.45 \mu m$ cellulose acetate filters. pH was measured at room temperature with a standard combination pH electrode, calibrated with buffer solutions at pH 4 and 7. Samples were analysed for major and trace elements by ICP-MS/MS in the School of Environment, Earth and Ecosystem Sciences at the Open University, UK. Suprapur and DI blanks were used to quantify the level of contamination during the analysis process and were found to be negligible. Elements were analysed using a triple quad set-up with different collision gas modes (no gas, O_2 , and NH_3) to minimise polyatomic and isobaric interferences. This allows for lower detection limits and improved accuracy across the range of elements analysed.

4.4.6 Weighted Ash Fraction (WAF) Correction.

Matrix glass samples from both the 2021 and 2022 eruptions were analysed for major and trace elements via JEOL JXA-8230 SuperProbe electron probe micro-analyser (EPMA) at the Institute of Earth Sciences, University of Iceland (Caracciolo et al., 2025) and LA-ICP-MS/MS (Agilent 8800) at the Open University using analytical techniques outlined in Jenner and O'Neill (2012) for trace elements. The Ag analysis was done using a line scan on matrix glasses with the same approach as described in Wieser et al. (2020) for Se analysis in melt inclusions. The ZrO interference correction was done as described in Reekie et al. (2019), with reference material analyses for Ag from Jenner et al. (2015). These analyses were undertaken to determine an ash composition for each eruption (see electronic supplement sheets S6 and S7). Presumed ash compositions were used to perform subsequent weighted ash fraction corrections on all filter pack samples.

To constrain the concentration of elements in the non-silicate aerosol phase (i.e., not contained in ash or dust), a weighted ash fraction (WAF) correction was applied to filter pack samples in this study. We assume using a mass balance equation that the concentration on the filter, $[A]_{filter}$ in ppm is derived from two components, silicate ash and dust $[A]_{ash}$, and non-silicate aerosol $[A]_{aerosol}$ (see eq. 4.1).

$$[A]_{filter} = [A]_{ash} * X_{ash} + [A]_{aerosol} * (1 - X_{ash}) \quad (4.1)$$

Where X_{ash} is mass fraction of silicate ash on the total mass of the filter and $X_{aerosol}$, the mass fraction of aerosol phase on the total mass of the filter, where $X_{aerosol} = 1 - X_{ash}$.

For refractory elements, we assume that the concentration in the aerosol phase is zero ($[A]_{aerosol} = 0$), allowing equation 4.1 to be simplified to:

$$X_{ash} = \frac{[A]_{filter}}{[A]_{ash}} \quad (4.2)$$

Using the average of four refractory reference elements (Fe, Mg, Mn, Ti), it is then possible to derive X_{ash} for each filter pack sample. Using an average of four major elements as our reference elements is beneficial as their higher concentrations (relative for example, to REE) in silicate material allow smaller ash concentrations to be resolved. Weighted ash fractions for each element in each sample (WAF) can then be calculated using eq. 4.3 and inputting the X_{ash} calculated for each sample using the refractory reference elements:

$$WAF = 100 * \frac{X_{ash} * [A]_{ash}}{[A]_{filter}} \quad (4.3)$$

Note that this means that whilst the overall mass fraction of ash on the filter may be low (< 1%) the WAF (contribution from ash for a specific element on the filter) may still be high, particularly for refractory elements (generally > 90%).

4.4.7 Emanation Coefficients and Enrichment Factor Calculations.

Emanation coefficients (ϵ_x) describe the degree to which an element is degassed from silicate melts into a vapour phase:

$$\epsilon_X = ([X]_i - [X]_f) / [X]_i \quad (4.4)$$

where $[X]_i$ is the initial concentration of X in the melt, and $[X]_f$ is the final degassed concentration of element X in the melt. In this work, emanation coefficients (ϵ_x) are calculated using the measured composition of the volcanic plume (gas and PM), combined with the composition of degassed matrix glasses:

$$\epsilon_X = ([X/Y]_{plume} * Y_{degassed}) / ([X/Y]_{plume} * Y_{degassed} + X_{MG}) \quad (4.5)$$

where X is the element of interest, and Y is S. X_{plume} is the concentration of element X measured on particulate filters (corrected for ash, as above); Y_{plume} is the total S measured on filter pack particulate and gas filters; and $Y_{degassed}$ is the concentration of S degassed during subaerial eruption. $S_{degassed}$ was determined by comparison of the average S content of melt inclusions (960 ppm) and matrix glass compositions (120 ppm), which are presented in Pfeffer et al. (2024) to give a degassed total of ~ 800 ppm). X_{MG} is the concentration of element X remaining in the degassed matrix glass (See the Electronic Supplement Sheet S6).

Note also that emanation coefficients are calculated using silicate-corrected plume composition data, and therefore these emanation coefficients are relative, i.e., during the ash-correction, elements used to calculate X_{ash} are assumed to be only present in a silicate phase, and therefore these elements have emanation coefficients of zero (or close to zero) but may partition into the gas phase to a limited extent. Emanation coefficients for the Fagradalsfjall 2021 and 2022 eruptions are included in the electronic supplement Sheet B3. Enrichment factors (EF) describe the degree to which an element X is enriched in one phase relative to another, as calculated below. In this work we calculate EF both for the volcanic plume and snow compositions relative to the basaltic glass composition, using Mg as a refractory reference element:

$$EF_{Mg} = ([X]_{Plume/Snow} / X_{Basalt}) / ([Mg]_{Plume/Snow} / [Mg]_{Basalt}) \quad (4.6)$$

Where $X_{plume/snow}$ are the concentrations of the element X in measured plume and snow samples and X_{basalt} is the concentration in basaltic glass sampled from the same eruption.

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Chapter 5

Hybrid particulate matter generated by lava-ignited wildfires at the Litli-Hrútur 2023 eruption, Iceland

Laura Wainman, Evgenia Ilyinskaya, Melissa Anne Pfeffer, Penny E. Wieser, David Damby, James B. McQuaid, Celine Mandon, Enikö Bali, Josefa Sepulveda-Araya, Richard Walshaw, Caleb Hall, Stuart Micklethwaite, Zabeada Aslam, Samantha J. Hammond, Barbara Kunz, Frances Jenner, Andri Stefánsson, Sæmundur A. Halldórsson, Jóhann Gunnarsson Robin, Alessandro Aiuppa, Tamsin A. Mather.

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- Lava flows at the 2023 Litli-Hrútur eruption in Iceland ignited extensive moss wildfires.
- We collected samples of endmember and mixed volcanic and wildfire emissions, including gas and particulate matter (PM).
- Mixing between emissions resulted in agglomeration and scavenging of volcanic aerosols by wildfire PM to form hybrid PM.
- Hybrid PM had altered physicochemical characteristics relative to end-member volcanic and wildfire emissions.
- Modified physicochemical characteristics could result in new transport pathways for toxic metals and gaseous pollutants.

Abstract.

Lava flows from the Litli-Hrútur 2023 eruption ignited the largest moss wildfires since modern record keeping in Iceland began. Volcanically ignited wildfires present a cascading and more complex hazard than standalone volcanic eruptions and are likely to become more frequent globally due to climate change. Both volcanic eruptions and wildfire events generate well-characterized air pollution hazards through the emission of gas and particulate matter, but the physicochemical consequences of mixing between end-member emission types during compound events remain poorly understood. In this study, we collected samples of end-member volcanic, wildfire, and mixed plume particulate matter during the Litli-Hrútur 2023 eruption and wildfires. Geochemical and morphological analysis showed that wildfire smoke and lava flow outgassing have distinctive chemical signatures and particulate matter (PM) size distributions, but that when mixing occurs between them, either directly at the lava-moss burning interface or during downwind transport, it can result in the formation of hybrid PM. This hybrid PM may be formed through mechanical interactions via well-established processes such as agglomeration and particle scavenging, although these interactions are unique in the context of a compound volcanic-wildfire event as they occur between emissions from two different sources. We demonstrate that the formation of hybrid PM via these mechanisms may result in altered physicochemical characteristics, and suggest that this may have consequences for depositional processes and atmospheric and environmental transport pathways of key species when compared to stand-alone volcanic eruptions.

5.1 Introduction

The likelihood of compound volcanic-wildfire events is increasing globally due to continued planetary warming and changes in global weather patterns (Mansoor et al., 2022). Compound volcanic-wildfire events can occur when an eruption happens coincidentally to an existing wildfire or, depending on the style of eruption, a wildfire may be ignited by volcanic products, such as lava flows, incandescent ballistics, or pyroclastic flows (Quah et al., 2023). Extended periods of hot and dry weather due to climate change mean that some of the environments (e.g., forests, peatbog, grassland, and steppe) surrounding active volcanoes are becoming more vulnerable to ignition by all causes, including volcanically triggered events (Fink and Ajibade, 2022). Although on a regional scale, the forecast of wildfire modification due to global changes can be ambiguous,

for example in Iceland where an increase in frequency of extreme weather includes both heavy precipitation and extended dry periods (Icelandic Met Office, 2018), impacting both vegetation production and fuel load. Several volcanically ignited wildfires have been documented to date during flank eruptions at Kīlauea (Hawai‘i) between 1983 and 2018 (Meredith et al., 2022), at Pacaya Volcano (Guatemala) in 2010 (Wardman, 2012), at the eruption of Stromboli (Italy) in 2019 (Turchi et al., 2020, Iacono et al., 2025), at the Tajogaite eruption on La Palma in 2021 (Shatto et al., 2024), and most recently at the eruptions in Iceland on the Reykjanes Peninsula between 2021-2025 (Schiffmann et al., 2025). It is likely that other volcanic-wildfire events have also occurred across the globe but are undocumented in the scientific literature.

One of the primary hazards associated with compound volcanic-wildfire events is the simultaneous emission of wildfire smoke and volcanic aerosols, both of which can individually worsen air quality on a regional scale (Volcanic eruptions: Kajino et al., 2004; Schmidt et al., 2015; Whitty et al., 2026; Wildfires: Selimovic et al., 2019; Adachi et al., 2022; Holder et al., 2023). Wildfire emissions contain reactive gases (CO , CO_2 , CH_4 , volatile organic compounds – VOCs, and nitrogen oxides - NO_x) and particulate matter (PM), including black and brown carbon (Selimovic et al., 2019; Holder et al., 2023; Wilson et al., 2025), whilst volcanic eruptions can emit significant quantities of silicate ash, gases (including H_2O , CO_2 , SO_2 , HCl , HF), PM and trace metal species (Nriagu, 1989; Delmelle, 2003; Mather et al., 2003; Aiuppa, 2009). The end-member compositions of these emissions have been well constrained individually; however, to date very few studies have investigated the processes that occur during compound events when volcanic and wildfire emissions mix in the atmosphere. Atmospheric mixing and the co-presence of volcanic and wildfire emissions are likely to result in mechanical interactions and chemical reactions and thus potentially facilitate the formation of hybrid PM. In this study, we consider hybrid PM to be that which has altered physical or chemical properties as a consequence of mechanical interactions and/or chemical reactions that occur upon mixing between emissions from different sources. Such physicochemical alterations could include, but are not limited to, changes in bulk PM size distribution (e.g., via scavenging or agglomeration effects), as well as alterations to element water solubility or changes in element speciation behaviour. Such changes could have consequences for the environmental reactivity and mobility of key pollutant species, as well as their bioavailability. Given that exposure to volcanic and wildfire emissions separately has been linked to negative health effects in humans (including an increased prevalence of respiratory and cardiovascular disease, as well as higher rates of overall morbidity and mor-

tality (Reid et al., 2016; Stewart et al., 2021), understanding and mitigating human exposure to hybrid volcanic-wildfire emissions is of critical importance for protecting population health during compound volcanic-wildfire events. Furthermore, extreme environmental change in Earth’s deep past, associated with extended episodes of volcanism, have in some cases shown evidence of increased wildfire occurrence, emphasising the importance of understanding the environmental consequences of these interactions on a planetary scale (e.g., Chu et al. (2020)).

In this study, we investigate the air quality impacts of a compound volcanic-wildfire event at the Litli-Hrútur 2023 eruption and lava-ignited wildfires on the Reykjanes Peninsula in Iceland. We examine the atmospheric processes that occurred during the simultaneous emission of gases and PM from the volcanic vent, lava flows, and wildfire vegetation burning. We focus on the formation of hybrid PM as a result of mechanical interactions between volcanic and wildfire particles and gaseous species in the mixed plume and suggest that this hybrid PM may have distinct physicochemical characteristics compared to end-member volcanic and wildfire emissions. We propose that this may alter the atmospheric transport and environmental dispersion pathways of key elements, with possible implications for regional air quality and human exposure to harmful pollutant species. Given the increasing likelihood of future volcanically ignited wildfire events globally, future volcanic hazard mitigation planning could integrate the unique air quality threat posed by compound-volcanic wildfire events.

5.1.1 The Litli-Hrútur 2023 Eruption and Wildfires

The effusive Litli-Hrútur eruption began on 10th July 2023 and lasted three and a half weeks before ceasing on 5th August 2023. The eruption occurred to the northeast of the previous Geldingadalir (2021) and Meradalir (2022) eruptions (Figure 5.1d). The eruption generated a total lava volume of approximately 15.9 million m^3 covering an area of $\sim 1.5 km^2$. The eruption began with multiple effusive fissures stretching over 1 km in length, before ultimately focusing into a single crater. The lava composition was similar to the end of the previous eruption in 2022, suggesting it derived from a similar magmatic source at depth (Caracciolo et al., 2025).

The occurrence of the eruption in July-August 2023 coincided with an extended period of hot and dry weather in Iceland (Veðurstofa Íslands, 2023). Climate-related forecasts over the next few decades for Iceland suggest more frequent extreme weather, including both heavy rainfall and dry spell periods. The extended dry period in June 2023 may, therefore, have contributed

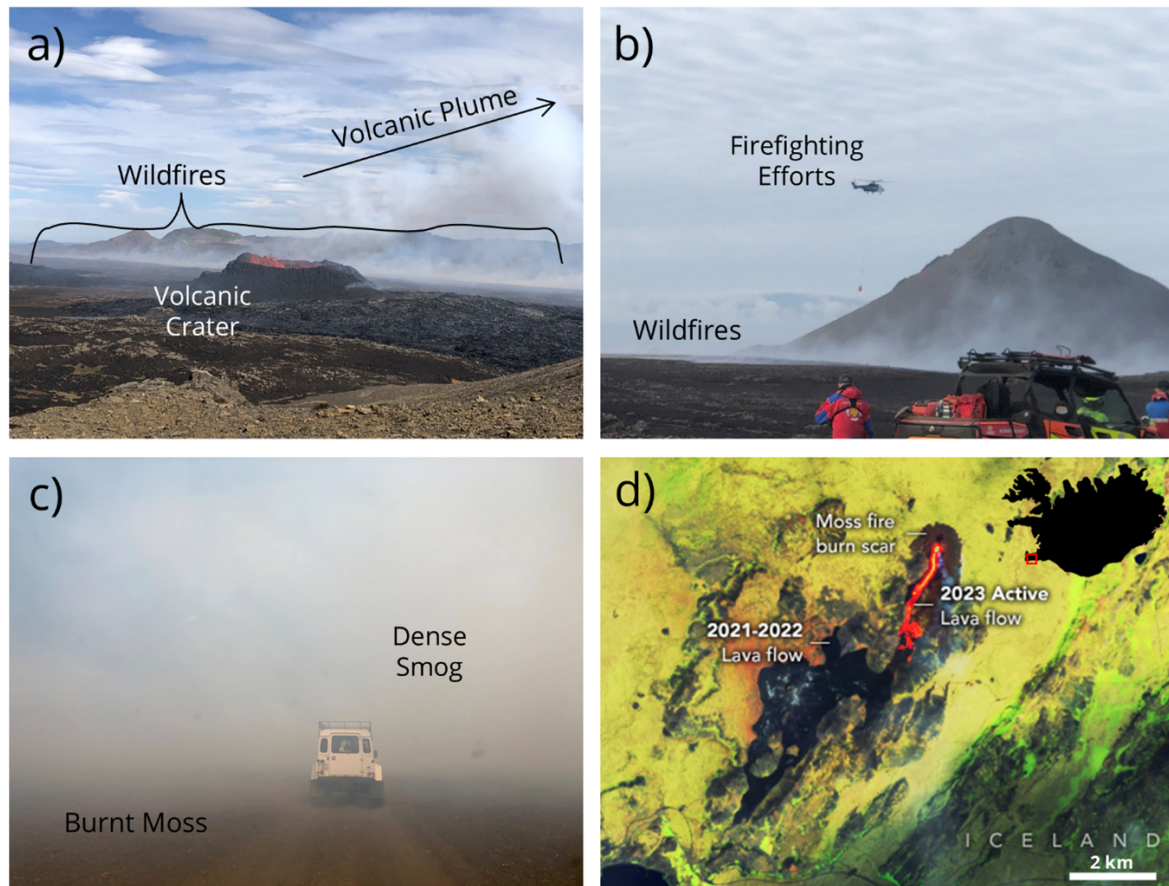


Figure 5.1: The Litli-Hrútur 2023 Eruption and Lava-Ignited Wildfires. a) Photograph of the Litli-Hrútur eruption crater. Fire fountaining is visible over the volcanic crater rim. The volcanic plume can be seen as degassing occurs from the vent, is advected upwards due to buoyancy, and is dispersed downwind. Wildfire smoke can be seen in the background at the edge of the lava field, where it ignited the moss which covers the peninsula. b) Aerial firefighting efforts to contain the extent of the wildfires. Buckets of freshwater were dropped using helicopters for fire suppression. c) The thick smog around the eruption site was created from mixing between wildfire and volcanic emissions. Either side of the road areas of scorched earth from moss that has already burnt can be seen. d) Satellite image adapted from Landsat 9 – OLI-2 on 17th July 2023 showing the extent of moss burning and lava flows across the Reykjanes Peninsula, Iceland, during the Litli-Hrútur eruption (from NASA Landsat Image Gallery; Voiland, 2023). Photos in a), b), and c) taken by L. Wainman.

to the occurrence of extensive wildfires during the July 2023 eruption, compared to only very minor wildfires during the previous eruptions in 2021 and 2022 (Schiffmann et al., 2025). The vegetation surrounding the eruption site, which includes grasses, dwarf shrubs, herbs and mosses, was potentially drier as a result and thus readily ignited by advancing lava flows when the eruption occurred (Fig 5.1b). Once ignited, the smouldering spread rapidly through the moss with some areas of open flame burning. This resulted in a total burn area of $\sim 2.5 \text{ km}^2$, with the smoulder front being up to 1 km from the active lava flows in some cases, and making it the largest moss wildfire since modern record keeping in Iceland began in 2006 (Figures 5.1c and 5.1d and Figure 5.2; Icelandic Institute of Natural History, 2023; Schiffmann et al., 2025).

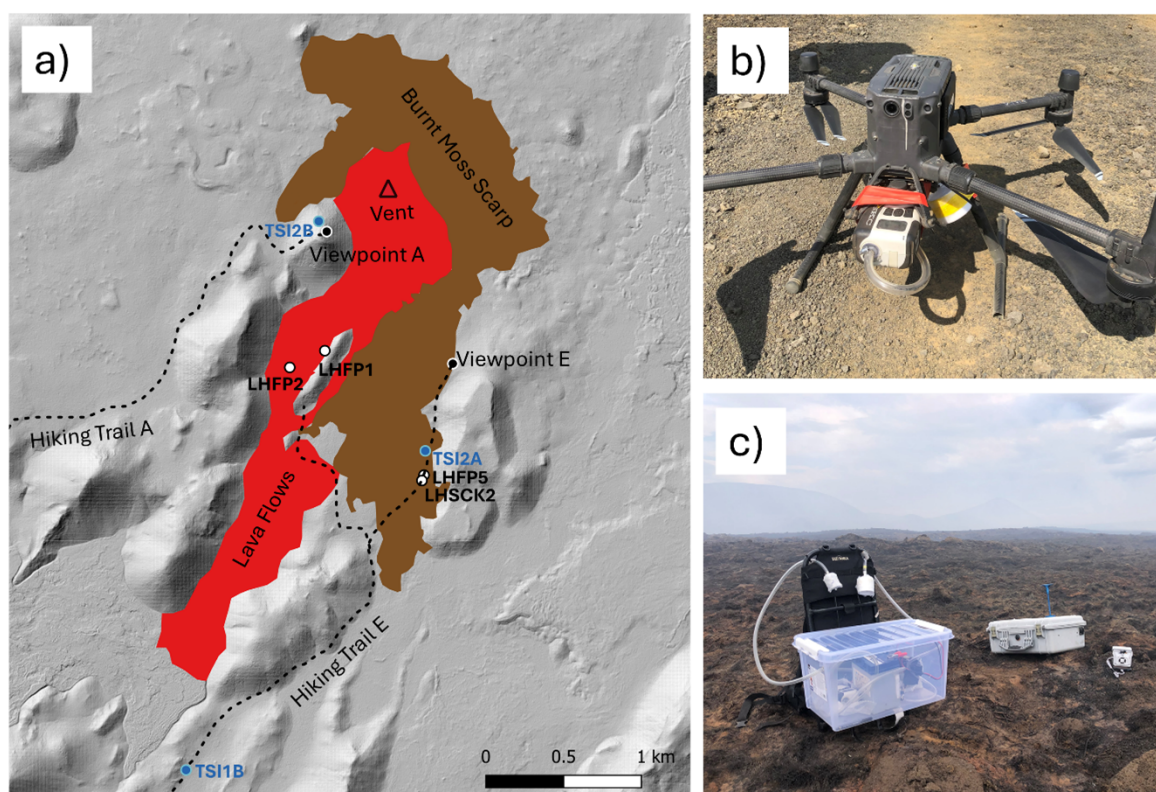


Figure 5.2: The Litli-Hrútur Eruption Map and Sampling Set Up. a) Map of the Litli-Hrútur Eruption. Red infilled area shows the final extent of lava flows and the triangle marks the location of the main eruptive crater. Brown infilled area shows the total area of moss burned by lava-ignited wildfires based on satellite imagery and Figure 4a from Schiffmann et al. (2025). Dashed lines show the official tourist hiking trails to the eruption viewpoints. Note Hiking Trail E runs directly through an area of burnt moss. White circles show the locations of filter pack and cascade impactor samples and blue circles show the locations of optical particle spectrophotometer (OPS) measurements labelled according to the sample names outlined in Table 5.1. b) UAV-mounted sampling set up with filter pack, pump, and tubing mounted on the underside of the UAV. c) ground-level sampling on the Hiking Trail E path during active moss burning in the area. A filter pack (LHFP5), a cascade impactor (LHSC2), and an OPS measurement (TSI1B) were collected simultaneously at this location. Photos b) and c) taken by L. Wainman.

5.2 Methods

5.2.1 Sampling Approaches

Filter Packs

Filter packs mounted on (i) UAV (uncrewed aerial vehicle, DJI Matrice 300 RTK; Wainman, 2024) and (ii) ground-level apparatus were used to collect in-situ samples of gases and aerosol PM from volcanic and wildfire emissions, respectively. Sampling altitude with the UAV ranged between 50 and 80 m above the flight take-off point. Where multiple flights were used to collect one sample, the pump was turned off whilst the UAV was grounded to minimise the uptake of ground-based dust. The UAV sampling set-up consisted of a 4-stage Teflon (Dupont) filter pack holder secured to the UAV “leg”, connected via PVC tubing to a pump (SKC Leland Legacy) mounted on the body of the UAV (Figure 2b). The combined weight of the filter pack and pump (and on-board multi-GAS; see Section 5.2.3) was just under the payload capacity of the UAV (Max payload: 2.7 kg). Care had to be taken to ensure a balanced weight distribution on the UAV to avoid issues upon take-off and landing. The ground-level filter pack sample (LHFP5) was collected along Hiking Trail E, used by tourists to reach Viewpoint E (Figure 5.2c). This was done using a portable backpack frame with the same filter pack and pump set-up as used for the UAV sampling. Further details on the filter holder configuration and filter preparation via base treatment prior to sampling are provided in the supplementary document. Note that throughout the sampling process all team members wore half-face respirators with combined gas, vapour, and particulate cartridges (e.g., 3M 6000 Series).

5.2.2 Cascade Impactors

The use of cascade impactors is similar to that of filter packs, where the impactor is connected to an air pump which draws air through a series of stages containing PTFE filters for sampling. SKC Sioutas cascade impactors consist of four stages plus an after stage and can thus resolve particles into a series of five size bins of decreasing particle diameter ranges from stage A ($> 2.5 \mu\text{m}$), B ($2.5 \mu\text{m} - 1 \mu\text{m}$), C ($1 \mu\text{m} - 0.5 \mu\text{m}$), D ($0.5 \mu\text{m} - 0.25 \mu\text{m}$), to the final after stage E ($< 0.25 \mu\text{m}$). A cascade impactor was used to collect a size-resolved PM sample at ground level along the tourist Hiking Trail E (Figure 5.2a). This cascade impactor sample (LHSC2) was collected simultaneously with the filter pack sample LHFP5. See electronic supplement sheet C2 for cascade impactor trace element data.

Sample ID	Sample Type	Sample Location	Sampling Date	Filter Set Up	Flow Rate (L/min)	Sample Duration (mins)	Volume Pumped (L)	Mass % Filter for SEM Analysis***
LHFP1	Filter Pack	UAV Lava-Moss Contact	13/07/2023	PM + 3G*	10.1	1**	10.2	7
LHFP2	Filter Pack	UAV Above Lava Flow	13/07/2023	PM + 3G	9	43.5	312.1	13.5
LHFP5	Filter Pack	Ground-level Hiking Trail E	16/07/2023	PM Only	9	35	315.1	8
LHFP8	Filter Pack	UAV At-Vent	19/07/2023	PM Only + MG^	9	61	549.6	0
LHSC1	Impactor	UAV Lava-Moss Contact	13/07/2023	PM Only (5 Stages)	9	12.2	109	0
LHSC2	Impactor	Ground-level Hiking Path	16/07/2023	PM Only (5 Stages)	9	35	315.1	0
LHSC3	Impactor	UAV At-Vent	16/07/2023	PM Only (5 Stages) + MG^	9	30	270.3	0

Table 5.1: Filter Pack and Cascade Impactor Sample Overview and Metadata.

*PM + 3G refers to the filter set up containing one PTFE PM filter + 3 base-treated gas filters on the subsequent stages.

**The limited sampling duration reflects a technical issue with the pump set-up where the tubing became twisted and thus cut off the flow of the pump.

***The % (by mass) of each filter cut out for SEM analysis is included and was corrected for when processing the ICP-MS results.

^Simultaneous on-board MultiGAS during sample collection. For the samples with on-board MultiGAS SO_2 timeseries was used to correct the total volume pumped for the time spent in the plume. Where on-board MultiGAS was not available the total volume pumped was used instead.

5.2.3 MultiGAS

A multi-GAS instrument from the University of Palermo (Aiuppa, 2005; Liu et al., 2020) was installed on the UAV for time-series measurements of major gas concentrations (time resolution 1 Hz). This aerial multi-GAS, used previously during eruptions in Iceland (Halldórsson et al., 2022), contains SO_2 and H_2S electrochemical sensors (City Technology; T3ST/F-TD2G-1A and T3H-TC4E-1A, calibrated for 0 to 200 ppmv and 0 to 50 ppmv respectively, see Liu et al. (2020)), and an infrared spectrometer for CO_2 (Microsensorik Smartgas Modul Premium2, range 0 to 5000 ppmv).

Time-averaged in-plume SO_2 concentrations for filter pack and impactor samples were calculated using the multi-GAS SO_2 timeseries where sample collection had on-board multiGAS, excluding data < 0.5 ppmv (the baseline between in-plume peaks in SO_2) within the known flight-time window. The time-averaged SO_2 concentrations should be viewed as minimum values as some in-plume measurements were made when SO_2 concentrations were above the maximum detection limit of the sensor (saturation occurred at ~ 220 ppmv, note post-saturation measurements are also associated with higher uncertainty whilst the sensor returns to a reliable response following saturation). The total time filter pack and impactor samples spent inside the aerosol plume (defined as $SO_2 > 0.5$ ppmv) was used to correct the total volume pumped for the in-plume volume sampled where possible. See electronic supplement sheet C4 for raw MultiGAS measurements.

5.2.4 Optical Particle Spectrophotometer

As part of the emergency air quality monitoring campaign on 16th July an optical particle spectrophotometer (OPS; TSI 3330) was deployed at several locations around the eruption site to rapidly assess ground-level airborne concentrations of PM_{10} and $PM_{2.5}$. The OPS used is a reference grade instrument which measures number concentrations of particles between 0.3 and 10 μm across 16 size bins, with a maximum particle count of 3000 particles cm^{-3} (Vasilatou et al., 2021). OPS measurement locations around the Litli-Hrútur eruption site are shown in Fig. 5.2a and measurement details are included in Table 5.2, with photographs of the deployed OPS included in Supplementary C Figures C.1 and C.2. The OPS was used at ground level and was considered representative of the potential exposure for tourists hiking along the path to reach the eruption viewpoint.

Sample ID	Sample Location	Sample Duration	Sample Type
TSI1B	Hiking Trail E	15 mins	Far-field Mixed
TSI2A	Hiking Trail E Moss Burning	45 mins	Moss Burning
TSI2B	Viewpoint A	15 mins	Near-field Mixed

Table 5.2: Optical Particle Spectrophotometer Measurements*.

*Measurements were collected on 16th July 2023 as part of an emergency air quality monitoring campaign with the Icelandic Meteorological Office. See Figure 5.2a for exact sample locations. The 15-minute average time series for OPS measurements are shown in Figures 5.6, 5.7, and Supplementary C Figure S3.

Concentrations of $PM_{2.5}$ and PM_{10} were calculated by manually reprocessing the raw particle count data, downloaded from the OPS instrument, and following a series of assumptions. The standard approximation of spherical particles of uniform density was applied. We also chose to calculate a volume weighted diameter (D_{pv}) for each size bin, rather than a geometric diameter, for consistency with the OPS software (AIM Software) and Crilley et al. (2018). Bin cutoffs are lower size bounds (Bin 1: 0.3- 0.374 μm , Bin 17: $> 10 \mu\text{m}$). Particle count concentrations were then converted to particle mass measurements following Eq. 1 – Eq 3. in Crilley et al. (2018). Changes in the assumed particle density can result in significant variations in the particle mass measurement outputs so we therefore perform our conversion with an average density of 1.7 g/cm^3 , a maximum density of 2.3 g/cm^3 (volcanic glass and dust, see Butwin et al. (2020)) and a minimum density of 1.1 g/cm^3 (wildfire smoke), with sulfate aerosol also falling between these two values (1.7 g/cm^3). Note also that the OPS used was not configured for a size bin cutoff at 2.5 μm (Bin 10: 2.156 μm - 2.685 μm), and thus we include Bin 10 in our $PM_{2.5}$ calculation, meaning this represents a slight overestimation. See electronic supplement sheets C5-7 for raw particle number count data.

5.2.5 Sample Analysis

Filter Extraction and Compositional Analysis

Details of the two-stage filter extraction method are provided in the supplementary document and follow the procedures outlined in Ilyinskaya et al. (2021) and Wainman et al. (2024). PM filter samples and blanks were analysed for major and trace elements by ICP-MS/MS in the School of Environment, Earth and Ecosystem Sciences at the Open University, UK. Synthetic calibration standards were doped with the same solution matrix as samples to eliminate ionisation effects (particularly with samples containing propan-2-ol). Ionisation effects were monitored

by running an internal standard throughout all measurement sessions. Elements were analysed using a triple quadrupole set-up with different collision gas modes (no gas, O_2 , and NH_3) to minimise polyatomic and isobaric interferences (Balcaen et al., 2015; Cox et al., 2019). This allows for lower detection limits and improved accuracy across the range of elements analysed. Field, laboratory, and filter blanks were used to quantify the level of contamination at all stages of the sampling and extraction process and were found to be negligible (see Supplementary A).

SEM Imaging and EDS Analysis

The sections of filter that were not subject to the 2-stage extraction for ICP analysis (7-14 wt% of the initial filter) were examined using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) at the Leeds Electron Microscopy and Spectroscopy Centre (LEMAS), University of Leeds, UK. These small sections of filter were mounted on an aluminium stub with a sticky carbon backing, and graphite glue was used to tack down filter edges. Mounted filters were coated with 15 nm of Pt, where Pt was chosen over C so that C-compounds in the sample could still be qualitatively identified using EDS analysis. The PTFE filter used to collect PM is composed of C, O, and F (blank filter EDS spectra shown in Supplementary C Figure C.4).

SEM imaging was performed on a W-filament Tescan VEGA3 XM coupled with an X-max 150 SDD EDS detector at LEMAS at the University of Leeds, UK. An accelerating voltage of 20 kV was used for the silicate PM and 15 kV for the non-silicate organic PM, with a beam intensity between 10 and 13. Secondary electron (SE) imaging was used as it provided the greatest contrast between the particles and background filter, where SE imaging provides high-resolution details on surface topography. By contrast, it was harder to differentiate between particles and the background filter when using Backscattered Electron (BSE) imaging as the particles and filters often had similar C-rich compositions.

Point-by-point EDS analysis was conducted and processed using the Aztec 3.3 Software (Oxford Instruments, UK), with a process time of 4 and an acquisition time between 45 and 120 seconds. Over 50 particles per sample were imaged and analysed via EDS to provide context to the morphological data collected using SE imaging. Interaction volumes for PM of different compositions (sulfate and chloride aerosol, basaltic glass, and an organic matrix representative of the moss fragments) were modelled using the CASINO software (Hovington et al., 2006) and

varied between $\sim 1 \mu\text{m}$ and $3.5 \mu\text{m}$ (see Supplementary C Figures C.5a-C.5d). As such, when analysing particles $< 3 \mu\text{m}$ in diameter via point EDS analysis the interaction volume of the beam sometimes exceeded the size of the particle. This meant that the EDS spectra showed peaks for C, O, and F which reflected interactions from the background filter. Combined with the fact that samples show significant topography (Figure 5.3), EDS data is considered qualitatively.

TEM Imaging and EELS Analysis

Following SEM analysis, a single moss fragment was identified in sample LHFP1 for further analysis using Transmission Electron Microscope (TEM) Electron Energy Loss Spectroscopy (EELS). A section of this fragment ($\sim 10 \times 18 \mu\text{m}$) was cut out from the filter using a Focused Ion Beam (FIB) instrument (FEI Helios G4 CX DualBeam, LEMAS, University of Leeds, UK). This fragment was then soldered to a needle and transferred to a TEM stub, to which it was then soldered using a Pt strip. The FIB gallium beam was then used to mill two sections of the sample down to the required thickness of $\sim 100 \text{ nm}$, where electron transparency is needed to perform subsequent TEM-EELS analysis. The limited structural integrity of the moss particle meant that the milling process was especially delicate and that the end thickness of the sample was slightly higher in some sections (101-141 nm).

The moss fragment was then analysed by EELS on a TEM (FEI Titan3 Themis 300) at LEMAS, University of Leeds, UK. Several transects were performed along the milled sections at discrete points from the edge to the interior of the moss particle (at $\sim 0, 0.5 \mu\text{m}$, and $2 \mu\text{m}$ depths). Mass fractions were measured for 10 different elements, including S, Cl, K, Fe, Ca and Al.

5.3 Results

5.3.1 Particle Morphologies and Mixing Interactions

The PM collected on filter packs around the eruption site have distinctive morphologies and size distributions depending on whether the sample was collected above an outgassing lava flow, in regions of smouldering moss, or in areas of mixing between emissions, respectively (see Figure 5.3 for SEM-SE images of PM). PM from outgassing lava flows (Fig 5.3a – 5.3c) was dominated by silicate material and generally comprised of shards or blobs smaller than $30 \mu\text{m}$ in diameter. Figure 5.3a shows a shard of basaltic silicate glass from sample LHFP2, which was collected above an outgassing lava flow. Figures 5.3b and 5.3c show an augite crystal and

glassy bead with prismatic and blob-like morphologies, respectively. This material was collected in sample LHFP1 at the lava moss-contact. The EDS spectra for the augite crystal in Figure 5.3b (Supplementary C Figure C.6) also contained peaks in S and Cl, possibly representing the smaller non-silicate aerosol component outgassed from the lava which is coating the surface of the particle, although the interaction volumes (1-3 μm , See supplementary C Figure C.5) meant that it was not possible to perform EDS analysis on these sub 1 μm particles, despite their known abundance in volcanic plumes (Martin et al., 2008; Martin et al., 2012). The background filter of sample LHFP1 also showed EDS peaks in S and Cl, indicating a widespread dispersal of these small-size-fraction S and Cl-rich secondary volcanic aerosols across the filter (Supplementary C Figure C.7).

Figures 5.3d-5.3e show examples of the particles generated by the moss-wildfire burning. These are characterised by large ($> 100 \mu\text{m}$ length) moss fragments with fibrous textures (Figure 5.3d-5.3e) which have likely been disarticulated upon burning and atmospheric transport. Point EDS analysis showed that these particles are C and O-rich, but some also had minor peaks in S and Cl (e.g., Supplementary C Figure C.8). Fragments of additional biological material were also present in this sample, which was collected above areas of active smouldering and burnt soil. Figure 5.3f shows the siliceous test of a *Testate* amoeba, which is a unicellular amoeboid protist that is commonly found in freshwater environments, including lakes and rivers, as well as peat bogs, moss, and soils (Opravilová and Zahrádková, 2003). The tests are very resistant even after the amoeba has died, so it is possible that the test was remobilised from the soil into the atmosphere during the wildfire burning along with other organic material (Perron et al., 2022).

Figures 5.3g-5.3i show volcanic and wildfire particulates that have interacted upon emission directly at the lava-moss burning interface. Figures 5.3g-5.3h show the moss fragments associated with multiple similarly sized silicate fragments to form a larger agglomeration of mixed particles. These agglomerations have total diameters $> 60 \mu\text{m}$ which is much greater than the $< 30 \mu\text{m}$ diameters generally seen for individual silicate shards. The size difference between the larger moss fragments ($> 100 \mu\text{m}$ length) and smaller silicate shards can also be seen in Figure 5.3i in sample LHFP1, containing mixed volcanic and wildfire PM collected above burning at the lava-moss interface. Differences are also seen between the composition of an unused blank filter and the background of the filter collected at the moss-lava interface which had a higher relative C peak and the appearance of being covered in a sticky film.

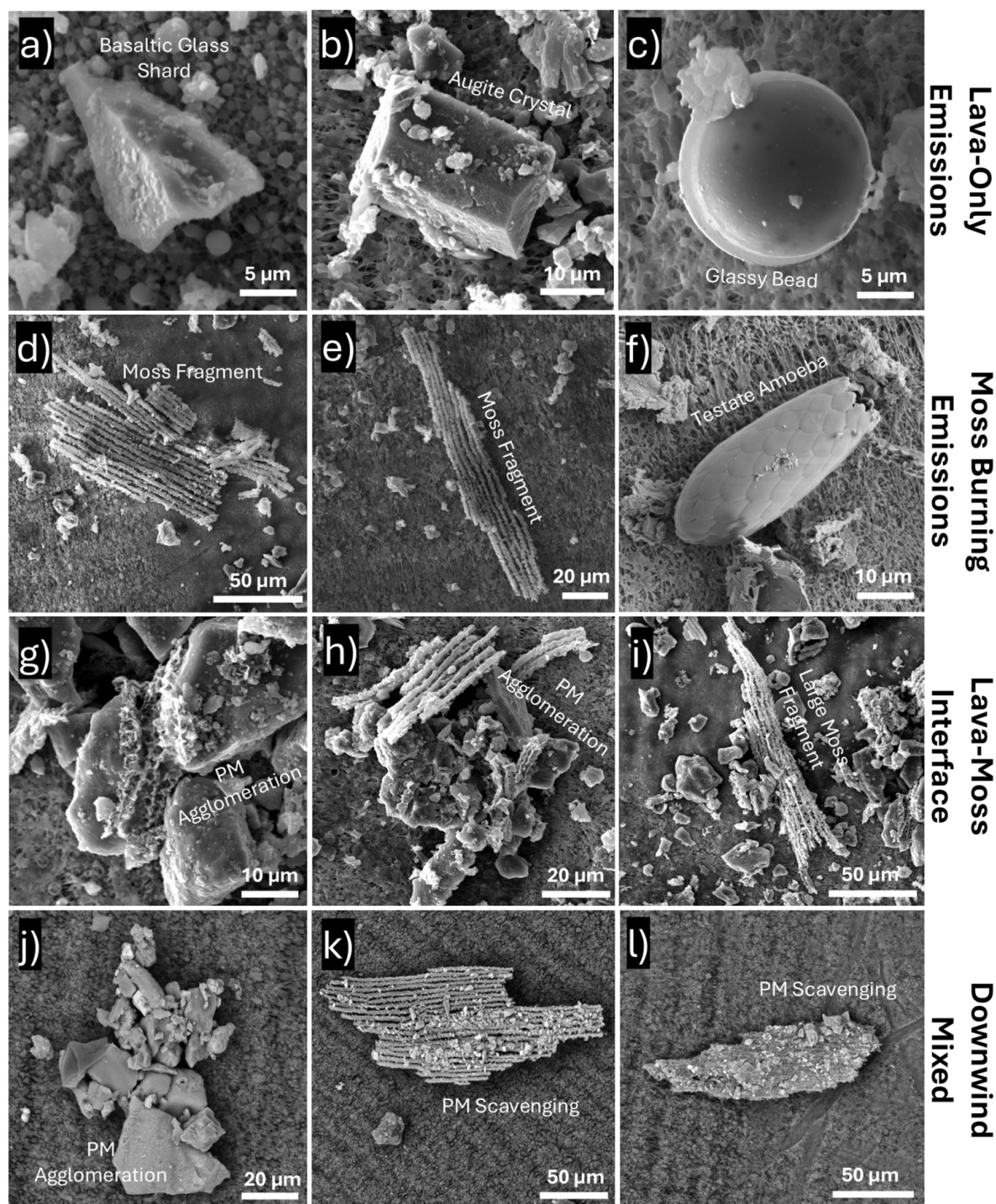


Figure 5.3: SEM-SE Images of Lava, Wildfire, and Hybrid PM from filter pack samples. a) Angular silicate shard from outgassing lava sample LHFP2. b) Prismatic Fe silicate particle identified as augite by EDS from the mixed lava-moss sample LHFP1. c) Al-Ca silicate blob also from LHFP1. d-e) Fibrous C-rich moss fragments from mixed moss-lava sample LHFP1, similar to images in Robinson (1971). Mosses were likely disarticulated during burning and some fragments displayed S and Cl peaks in EDS analysis. f) Test from a Testate amoeba from sample LHFP1, remobilised from the soil during wildfire burning. g) Moss fragment binding together two silicate shards (LHFP1). h) Agglomeration of silicate shards and C-rich moss fragments (LHFP1). i) Larger moss particle surrounded by smaller silicate PM (LHFP1). j) Agglomeration of silicate shards in downwind ground-level sample LHFP5 from Hiking Trail E. k-l) Large moss particles with smaller silicate shards stuck between fibres of the moss particle.

Agglomeration is especially pronounced in sample LHFP5, which was collected on Hiking Trail E, downwind of both the volcanic vent and the area of lava-moss burning at the time of sampling. Figure 5.3j shows a cluster of silicate fragments of varying sizes that have clumped together to form a larger agglomeration, possibly during atmospheric transport and collisions. Fig 5.3k-5.3l show larger moss particles with many smaller silicate shards and S and Cl-rich particles stuck to/in between the C-rich fibres that comprise the moss particle. Across this sample (LHFP5), the majority of large fibrous moss fragments were similarly covered in smaller volcanic aerosol particulates.

5.3.2 Particle Coating and Gaseous Interactions

As highlighted above, some of the moss particles that were burnt directly at the interface with advancing lava flows (LHFP1) also had minor peaks in S and Cl when analysed by EDS point analysis (Supplementary C Figure S8). SO_2 and HCl are major components of volcanic degassing (Aiuppa, 2009; for the Fagradalsfjall eruptions see Halldórsson et al. (2022) and Wainman et al. (2024)), and so these peaks in S and Cl may be indicative of the organic moss particles interacting with volcanic gases as it is co-transported in the mixed plume. To investigate this possibility further, we used the FIB to isolate a section of one moss particle from LHFP1 (lava-moss interface sample) that showed EDS peaks in S and Cl. This fragment was then transferred to the TEM instrument where we performed EELS analysis across two transects from the surface to the interior of the moss particle at three distinct points: 1) Moss surface, as close as possible to the edge without touching the Pt bar soldered across the top, 2) Moss sub-surface, ~ 500 nm depth from the surface, 3) Moss interior, $\sim 2 \mu\text{m}$ from the moss surface layer. EELS analysis reported the mass fraction of 10 different elements, including refractory elements Al, Ca, and Fe, as well as the relatively more volatile elements S, Cl, and K.

The mass fractions of the refractory elements Al, Ca, and Fe remain within analytical error across all three locations from the surface-to-edge transect, suggesting there is no significant variation in the behaviour of these elements throughout the width of the moss particle (Figure 5.4 and Supplementary C Table 1). By contrast, mass fractions of S and Cl, which are potentially indicative of interactions with volcanic gases, SO_2 and HCl , are within error of each other at the particle surface and sub-surface, but mass fractions from the interior are significantly lower (See Figure 5.4 and Supplementary C Table 1). The mass fractions of S and Cl do not show a single discrete layer solely on the surface of the moss particle, but also appear elevated within

the subsurface. The mass fraction of K, which is known to be a volatile trace element with a tendency to form chlorides in volcanic gases (Mather et al., 2012; Mason et al., 2021), follows a similar pattern to S and Cl, where the mass fraction of K is highest at the surface of the moss particle, also within error of the subsurface, but is significantly higher than in the mass fraction of K in the interior of the moss particle.

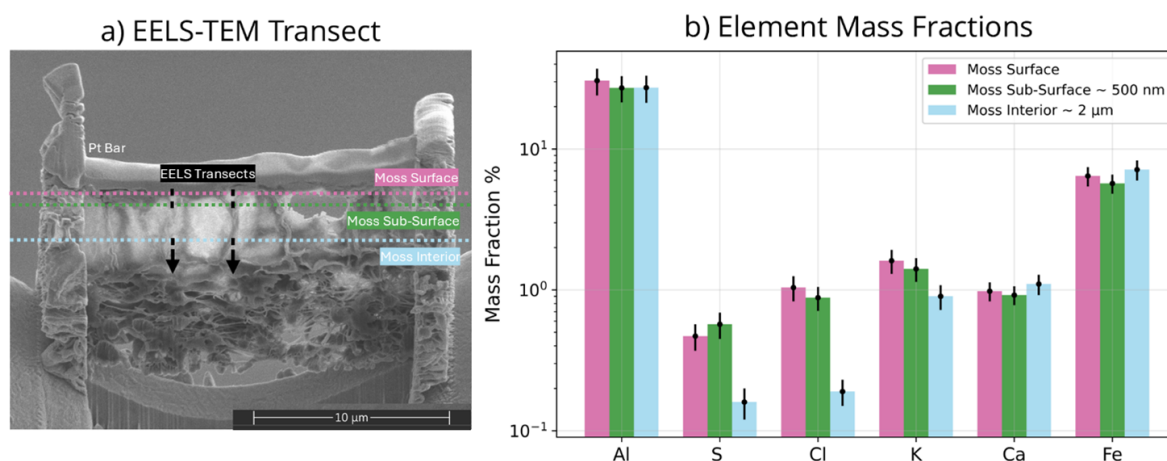


Figure 5.4: TEM Image and EELS Transects with Mass Fraction % for a Selection of Elements. a) Image of the moss fragment that was cut out from SEM mounted sample LHFP1 using a FIB, before being milled down to electron transparency (approximately 100 nm). Schematics of the TEM-EELS transects are shown, which were performed across two sections of the fragment at three discrete depth locations: 1) Surface, 2) Sub-surface (~ 500 nm depth), 3) Interior (~ 2 μm). b) Mass fractions for a selection of refractory (Al, Ca, Fe) and volatile (S, Cl, K) elements. Black lines show the mass fraction analytical error bars.

5.3.3 Trace Element Signatures

PM samples collected by filter pack at the lava-moss interface (LHFP1), above an outgassing lava flow (LHFP2), and on the downwind hiking path, where volcanic and wildfire emissions were mixing in the atmosphere (LHFP5), all have distinct trace element signatures. Figure 5.5a shows the concentrations of a range of trace elements collected at the lava-moss interface (LHFP1), normalised to the concentration of the same elements collected above an outgassing lava flow (LHFP2). Elements are ordered on the x-axis by increasing values to the right, where all elements have higher concentrations in the lava-moss interface sample compared to the lava-only outgassing emissions. The elements which are most enriched in the lava-moss interface sample compared to the lava-only outgassing are thus likely derived from an additional vegetation burning contribution to the overall aerosol composition and include Mg, Ca, Zn, Sn, Ba, K, P, and Sb. Ca, Mg, Ba, K, and P are essential macronutrients in plants, whilst Zn is an additional

micronutrient (Grusak et al., 2016). Sn and Sb can be toxic in plants in high concentrations but are commonly taken up from soils, particularly if soils are contaminated by transport or industrial pollution or if leaching has occurred from sulfide-rich rocks (Tang et al., 2022). Elements on the left-hand side of Figure 5.5a by contrast, show lower enrichment in the lava-moss interface emissions relative to stand-alone lava outgassing and include elements which are known to be hosted in both the primary (La, Ce, Ta) and secondary (Tl, Ag, Se, Cs, Te, Cd, Cu, As, Pb) volcanic aerosol phase. The slightly greater enrichment of elements found in the primary volcanic aerosol (silicate ash; La, Ce, Ta) compared those in the secondary volcanic aerosol (volatile trace elements; Tl, Ag, Se, Cs, Te, Cd, Cu, As, Pb) suggests a somewhat greater ash component was collected on the LHFP1 PM filter compared to LHFP2, possibly resulting from sampling at different positions along the lava flow; Sample LHFP1 was collected above an actively burning A'ā lava front, which possibly had a greater emission of silicate PM compared to LHFP2 which was collected above a more effusively outgassing Pāhoehoe lava flow.

Figure 5.5b shows trace element concentrations collected in sample LHFP5 on Hiking Path E, normalised to the concentration of the same elements collected above the outgassing lava flow sample LHFP2. Element concentrations in the downwind mixed sample (LHFP5) are much lower than in both the outgassing lava sample and at the lava-moss interface. This is most likely because of mixing with the ambient atmosphere and downwind dilution of the mixed volcanic-wildfire plume. In Figure 5.5b the elements on the x-axis are presented in the same order as in Figure 5.5a for comparison. Generally, elements follow a similar trend as Figure 5.5a with increasing enrichment over the lava outgassing sample towards the right-hand side of the plot. Nonetheless, some elements deviate from the trend of increasing concentration towards the right in Figure 5.5b. For example, Cs, Cu, As, Pb, La, Ce, Sn, and Sb are higher in concentration in the downwind mixed sample compared to the lava-moss interface sample than might be expected based on Figure 5.5a showing a general trend of increasing enrichment towards the right. This suggests that the two samples, at the lava-moss interface and the downwind mixed plume, are not simply related by homogeneous downwind atmospheric dilution, which would preserve this increasing-rightward pattern, but that other processes, such as selective deposition or scavenging, may be contributing to a fractionation in the trace element concentrations in the downwind plume.

Alongside distinctive geochemical compositions, PM from the lava-moss interface and in the

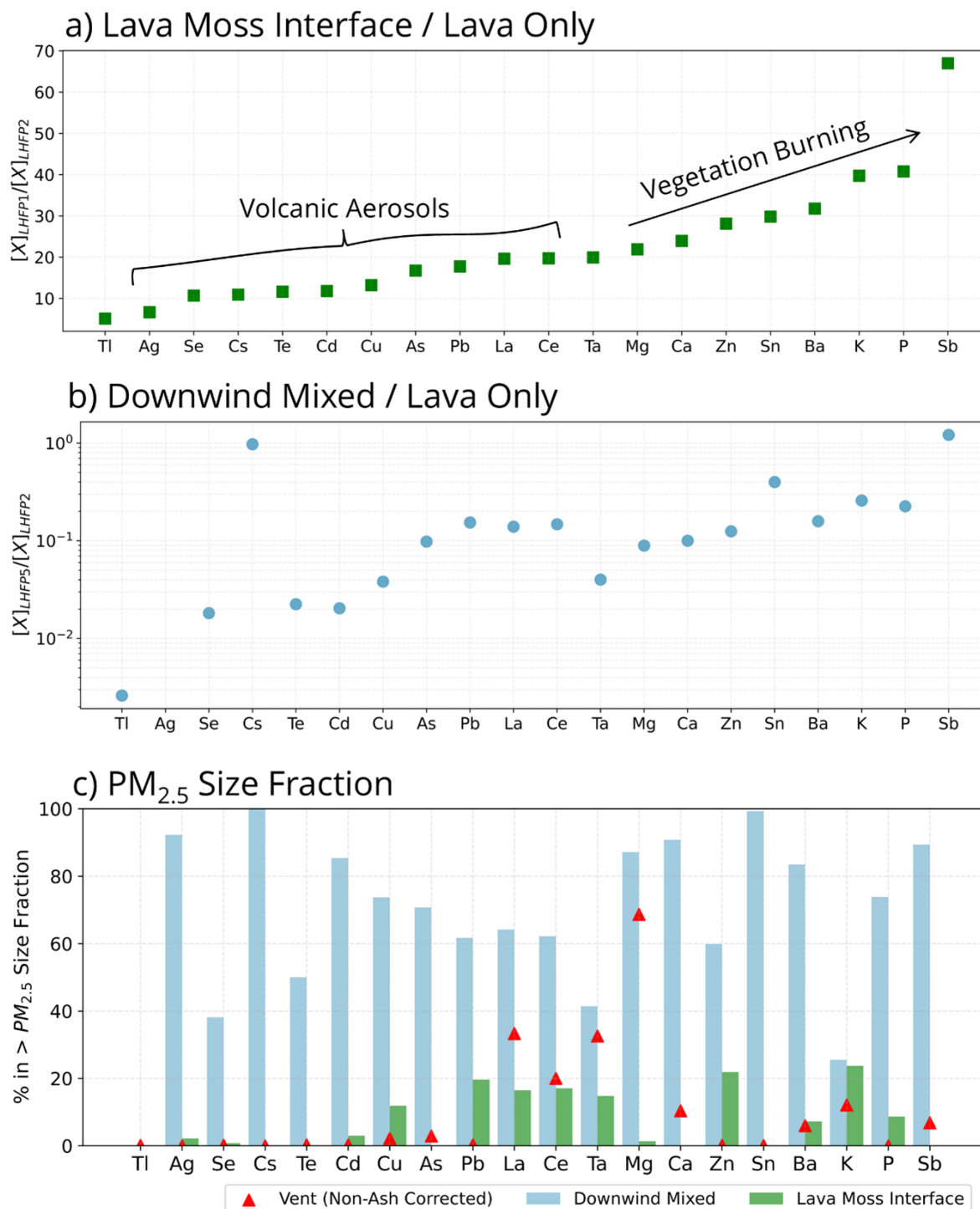


Figure 5.5: Trace Element Signatures and Size Distributions in PM samples. a) Element filter concentrations in sample LHFP1 (lava-moss interface) normalised to element concentrations in sample LHFP2 (lava outgassing). Elements are ordered on the x-axis from left to right by increasing enrichment in the lava-moss interface sample compared to the lava outgassing sample. b) Element filter concentrations in sample LHFP5 (mixed downwind sample, Hiking Path E) normalised to element concentrations in sample LHFP2 (lava outgassing). Elements are ordered on the x-axis as in panel a). c) Proportion of each element hosted by mass in the > 2.5 μm component, as measured using a cascade impactor in samples from the lava-moss burning interface (Green bars; LHSKC1), in the downwind mixed sample (blue bars; LHSKC2), and from an end-member volcanic vent sample (red triangles; LHSKC3). Note the most refractory elements such as Ce, La, Mg, Ba, and Ca are likely to be under sampled by the SKC impactors (Supplementary B).

downwind mixed plume sample show distinctive element concentrations associated with particle size distributions. Figure 5.5c shows the percentage of each element by mass collected in the $> PM_{2.5}$ size bin using a cascade impactor. Elements at the lava-moss burning interface (green bars) are predominantly contained within the $< 2.5 \mu\text{m}$ fraction (no element is more than 25% by mass in the $> 2.5 \mu\text{m}$ impactor stages), and it is only a subset of elements which have any component in the $> 2.5 \mu\text{m}$ size bin (Ag, Cd, Cu, Pb, La, La, Ta, Mg, Zn, Ba, P, K). Elements collected in the downwind mixed emissions on Hiking Trail E show, by contrast, much higher proportions in the $> 2.5 \mu\text{m}$ size bin across nearly all elements: Cu, Pb, La, Ce, Ta, Zn, Ba, K, and P, which had $< 25\%$ in the $> 2.5 \mu\text{m}$ component at the lava-moss interface all have over 25% in the $> 2.5 \mu\text{m}$ component in the Hiking Trail E sample. In addition, elements such as Ag, Se, Cs, Te, Cd, As, and Sn, which had negligible $> PM_{2.5}$ components in the lava-moss interface sample, have between 30 – 100% by mass in the $> PM_{2.5}$ component in the downwind mixed plume sample. The proportion of each element hosted in the $> 2.5 \mu\text{m}$ size fraction from a volcanic vent cascade impactor sample is also presented in Figure 5.5c (red triangles) to allow comparison with a volcanic endmember. Within the volcanic vent sample, the trace elements fall into two distinct categories: 1) volatile trace elements which are hosted almost entirely in the $< 2.5 \mu\text{m}$ fraction and 2) refractory trace elements which are hosted in the primary silicate ash and have a greater proportion by mass in the $> 2.5 \mu\text{m}$ fraction (Martin et al., 2008; Mather et al., 2012). Supplementary C Figure C.9 presents a comparison of ash corrected vs non-ash corrected at-vent element concentrations to further highlight which elements are predominantly derived from the primary silicate ash phase.

5.3.4 Bulk Size Distribution and OPS Reprocessing

During the air quality monitoring campaign on the 16th of July 2023, we carried out an exploratory assessment using an OPS to measure concentrations of PM_{10} and $PM_{2.5}$ at different locations around the eruption site. Figure 5.6 shows a timeseries of $PM_{2.5}$ and PM_{10} concentrations over a 15-minute sampling window recorded on Hiking Trail E and Figure 5.7 shows $PM_{2.5}$ and PM_{10} timeseries over a 15-minute window at Viewpoint A (see Figure 5.2a for sampling map). Figure 5.8 and Figure 5.9 show 15-minute average box plot distributions of $PM_{2.5}$ and PM_{10} concentrations, respectively. The traffic light system used in Figures 5.8 and 5.9 follows the classification of health hazard level used by the Icelandic Environment Agency for 1 hr exposure limits (Supplementary C Table S2; Icelandic Environment Agency, 2025). Whilst

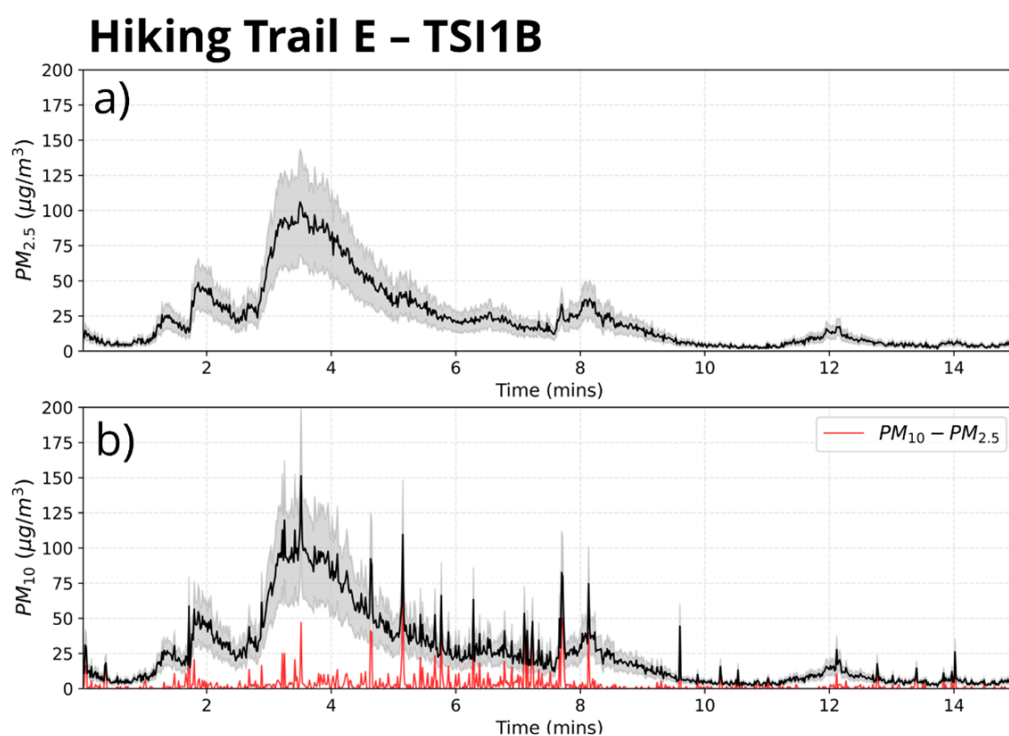


Figure 5.6: Timeseries of OPS PM data collected at Hiking Trail E (TSI1B) across a 15-minute sampling window. Solid black line shows concentrations with an assumed uniform density of 1.7 g/cm^3 (sulfate) and the shaded area shows upper and lower estimates with assumed densities of 1.1 g/cm^3 (smoke) and 2.3 g/cm^3 (glass), respectively. Red line shows $PM_{10} - PM_{2.5}$ to isolate the coarser fraction contribution to PM_{10} . Other assumptions are outlined in Section 5.2.4. Raw particle count data is included in the electronic supplement sheet C5

1 hr exposure limits do exceed our sampling window (15 mins), they were used for reference as they are the closest existing air quality thresholds, are most representative of the acute nature of potential exposure where tourists were hiking for several hours, and the most relevant for informing Icelandic civil protection agencies.

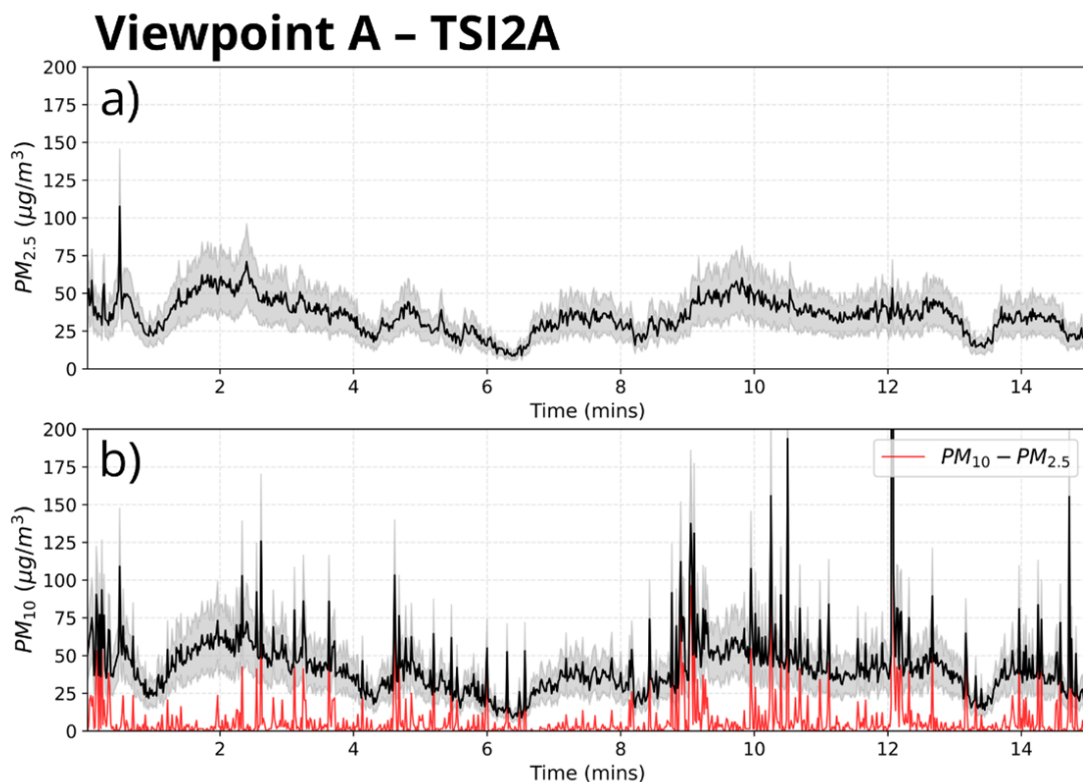


Figure 5.7: Timeseries of OPS PM data collected at Viewpoint A (TSI2B) across a 15-minute sampling window. Solid black line shows concentrations with an assumed uniform density of 1.7 g/cm^3 (sulfate) and the shaded area shows upper and lower estimates with assumed densities of 1.1 g/cm^3 (smoke) and 2.3 g/cm^3 (glass), respectively. Red line shows $PM_{10} - PM_{2.5}$ to isolate the coarser fraction contribution to PM_{10} . Other assumptions are outlined in Section 5.2.4. Raw particle count data is included in the electronic supplement Sheet C6.

$PM_{2.5}$ concentrations varied significantly between Hiking Trail E and Viewpoint A. Over the 15-minute sampling window, Hiking Trail E had lower average $PM_{2.5}$ concentrations, whilst at Viewpoint A $PM_{2.5}$ concentrations were generally higher over the 15-minute sampling window (See Figure 5.8 and Table 5.3). Based on the Icelandic Environment Agency 1 hr exposure thresholds this places Hiking Trail E within the Yellow category, whereas Viewpoint A falls one category above, in Orange. The distribution of $PM_{2.5}$ concentrations also varied between sampling locations; at Hiking Trail E there is a wider range of values, although most fall within the lower end of the distribution ($< 10 \text{ g/m}^3$ see Figures 5.6 and 5.8). This suggests the mean and median values are pulled up by discrete but short-lived peaks in concentration, and such

	Hiking Path E		Viewpoint A	
	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
Mean	22.6	25.2	35.5	43.3
Median	15.8	17.2	34.9	39.4
IQR	23.5	27.1	14.5	19.5
Pearson R Coefficient	0.97 p < 0.05		0.37 p < 0.05	

Table 5.3: Statistical details for OPS measurements.

peaks can be seen in the timeseries shown in Figure 5.6. The largest peak in $PM_{2.5}$ at Hiking Trail E reaches $> 100 \text{ g/m}^3$, with a total of ~ 4.4 minutes (29% of sampling period) spent in the Orange or Red exposure thresholds over the 15-minute sampling window. At Viewpoint A, by contrast, the distribution of concentrations is tighter, not decreasing below 8 g/m^3 across the whole sampling period, and with most of the values falling in the Orange category (See Figures 5.7 and 5.8). This suggests that $PM_{2.5}$ values at Viewpoint A were instead more consistently elevated rather than occurring in discrete peaks, with 12.2 minutes (81%) of the 15-minute sampling period exceeding the Orange exposure threshold.

PM_{10} concentrations show similar variations between Hiking Path E and Viewpoint A, where average concentrations on Hiking Trail E are lower compared to Viewpoint A. These values place them in the Dark Green and Light Green thresholds, respectively. PM_{10} concentrations also show similar distributions to $PM_{2.5}$ at both Hiking Trail E and Viewpoint A. Hiking Trail E generally has lower values punctuated by very high peaks (the highest peak in PM_{10} is coincident with the highest peak in $PM_{2.5}$ and reaches 110 g/m^3). As shown by the red line on Figure 6, the baseline PM_{10} concentrations at Hiking Trail E are mostly comprised of the $< 2.5 \text{ }\mu\text{m}$ fraction ($PM_{2.5}$), which is then punctuated by discrete and generally small peaks containing a coarser ($2.5 \text{ }\mu\text{m} - 10 \text{ }\mu\text{m}$) component. Viewpoint A by contrast, has consistently higher but less variable PM_{10} concentrations (See Figure 5.7 for 15-minute concentration time series). Figure 5.7b shows that baseline PM_{10} concentrations at Viewpoint A are still dominated by the $< 2.5 \text{ }\mu\text{m}$ fraction, but there are larger and more regular peaks in the coarser PM_{10} fraction ($2.5 \text{ }\mu\text{m} - 10 \text{ }\mu\text{m}$). Between Hiking Trail E and Viewpoint A the degree of correlation also varied between $PM_{2.5}$ and PM_{10} : at Hiking Trail E $PM_{2.5}$ and PM_{10} show a strong positive degree of correlation whereas at Viewpoint A there is only a weak positive correlation (Table 5.3). Figure C.3 in Supplementary C shows $PM_{2.5}$ and PM_{10} concentrations measured further along Hiking Trail E in an area of active moss burning (TSI2A). This measurement shows

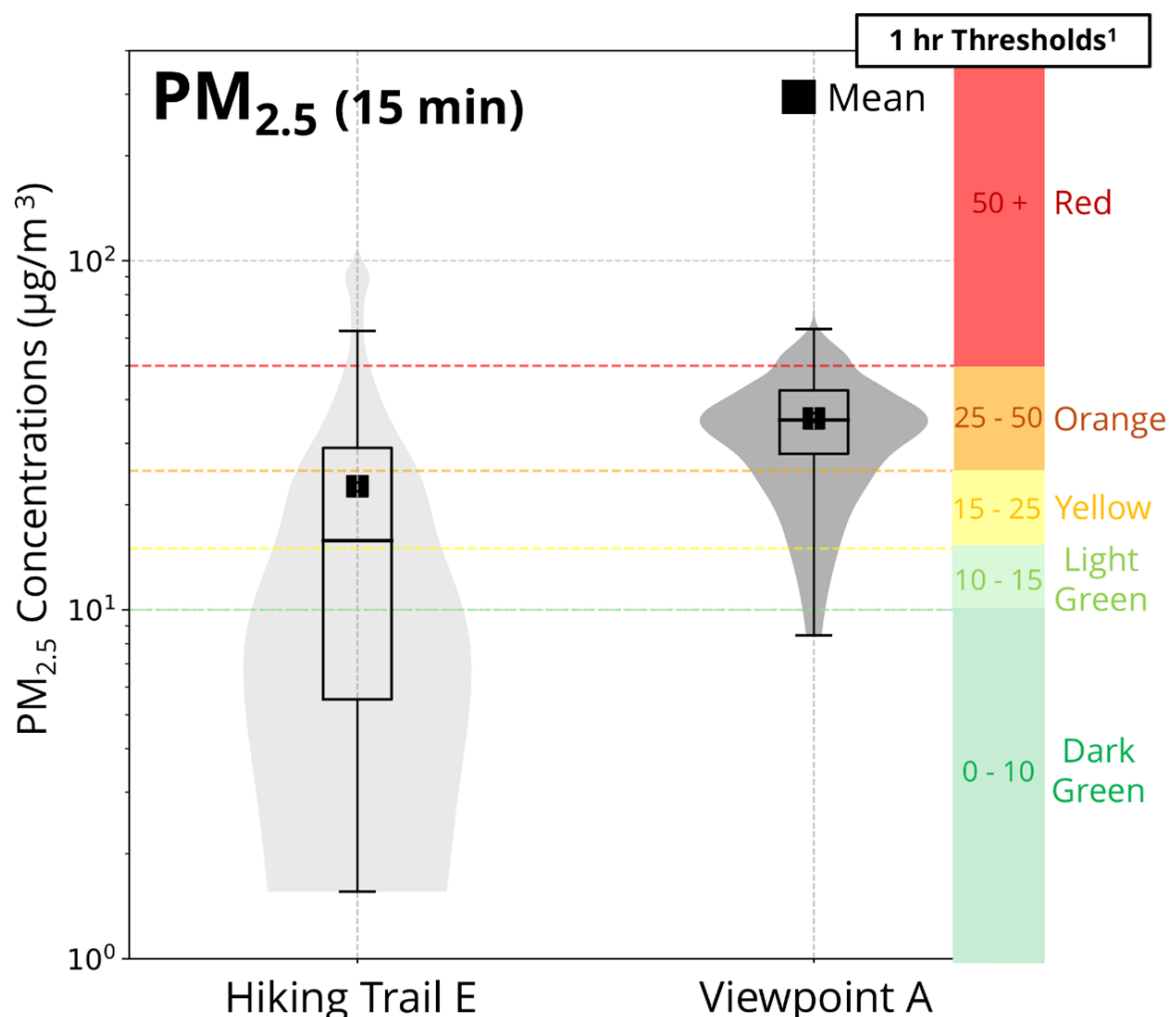


Figure 5.8: $PM_{2.5}$ Concentrations at Hiking Trail E and Viewpoint A. Concentrations were measured during a 15-minute sampling window with an optical particle spectrophotometer and calculated with an assumed uniform density of 1.7 g/cm^3 . Box and Whisker plot shows the median, first quartile (Q1; 25th percentile), third quartile (Q3; 75th percentile), minimum (Q1 $- 1.5 \times \text{interquartile range, IQR}$) and maximum (Q3 $+ 1.5 \times \text{IQR}$). The filled black square shows the mean concentration over the 15-minute sampling interval. Shaded violin plots show the distribution of the concentration data across the 15 minutes, smoothed by a kernel density estimation, which represents the probability of a given value. The right-hand traffic light system corresponds to the air quality classification scheme used by the Icelandic Environment Agency for 1 hr exposure thresholds (Icelandic Environment Agency, 2025; full details in Supplementary C Table 2). Raw instrument particle count data are included in the electronic supplement Sheets C5 and C6 and concentration time series are included in Figures 5.6 and 5.7.

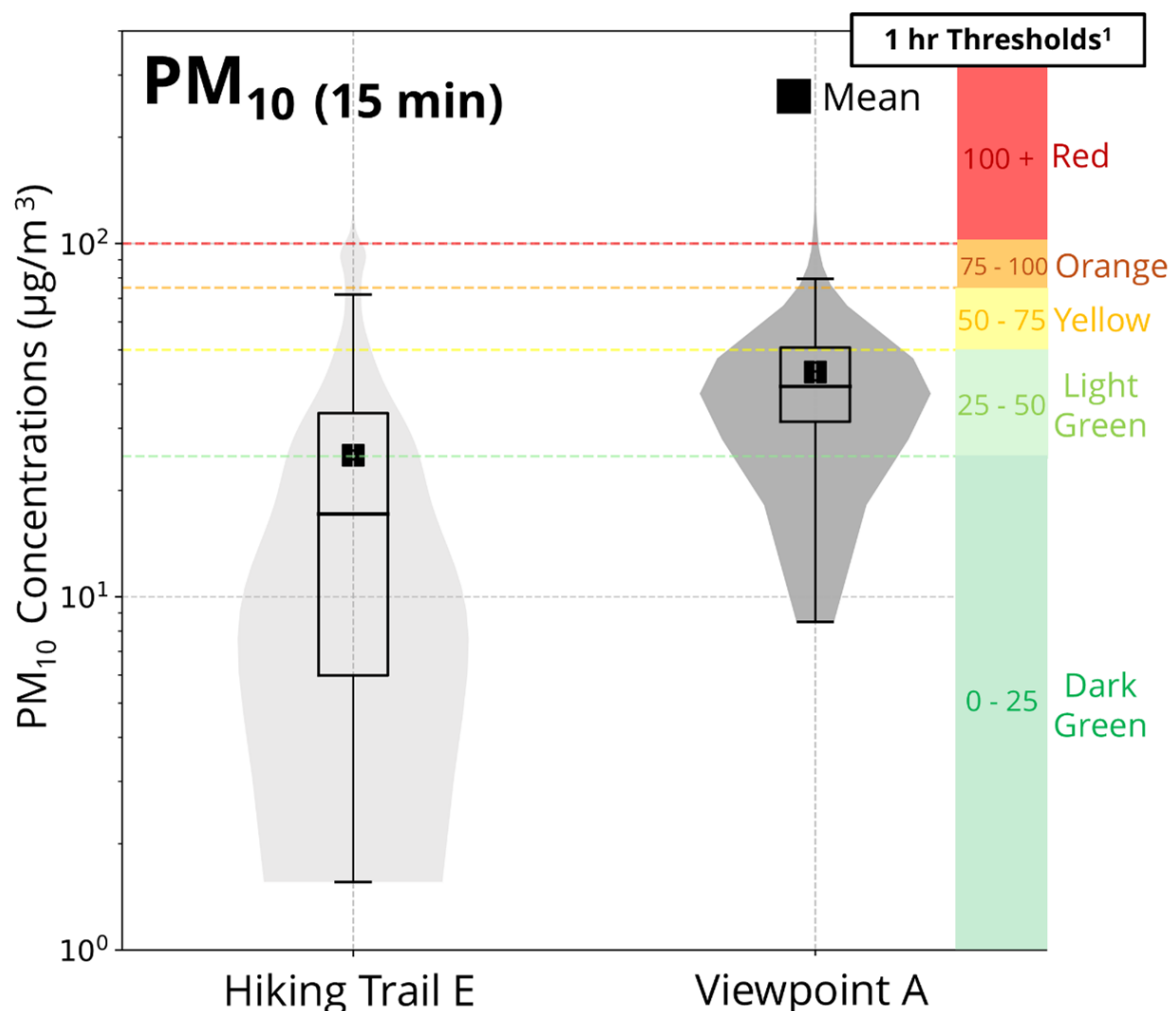


Figure 5.9: PM_{10} Concentrations at Hiking Trail E and Viewpoint A. Concentrations were measured during a 15-minute sampling window with an optical particle spectrophotometer and calculated with an assumed uniform density of 1.7 g/cm^3 . The Box and Whisker plots show the median, first quartile (Q1; 25th percentile), third quartile (Q3; 75th percentile), minimum ($Q1 - 1.5 \times \text{Interquartile Range, IQR}$) and maximum ($Q3 + 1.5 \times \text{IQR}$). The filled black squares show the mean concentration over the 15-minute sampling interval. Shaded violin plots show the distribution of the concentration data across the 15 minutes, smoothed by a kernel density estimation, which represents the probability of a given value. The right-hand traffic light system corresponds to the air quality classification scheme used by the Icelandic Environment Agency for 1 hr exposure thresholds (Environmental Agency of Iceland, 2023; full details in Supplementary C Table S2). Raw TSI particle counts are included in the electronic supplement Sheets C5 and C6 and concentration time series are included in Figures 5.6 and 5.7.

exceptionally high concentrations of $PM_{2.5}$ (average of 805.6 g/m^3) and PM_{10} (average of 848.3 g/m^3), with concentrations of both $PM_{2.5}$ and PM_{10} remaining in the Red category throughout the sampling window. Whilst collecting these measurements, the OPS was placed on the ground within 2-3 m of actively smouldering moss and directly downwind of the resulting smoke. This measurement therefore, represents endmember at-source concentrations of PM_{10} and $PM_{2.5}$ during moss wildfire burning, rather than what is likely to be inhaled by people (or animals) following dilution during downwind transport.

5.4 Discussion

5.4.1 Formation of Hybrid Particulate Matter

Lava flow outgassing and wildfire burning produced physically and chemically distinct emissions of gas and PM, however, upon mixing between end-member emissions, either directly at the burning interface or during downwind atmospheric transport, mechanical interactions between gaseous and particulate species resulted in the formation of hybrid PM with altered physico-chemical characteristics. In this section, we discuss the primary mechanisms that contributed to the formation of hybrid PM and highlight how these processes may have resulted in the alteration of the physical and chemical characteristics of some hybrid PM compared to endmember volcanic and wildfire emissions.

Directly at the lava-moss burning interface, SEM imaging showed that fibrous moss fragments can, in some instances, stick together with similarly sized silicate shards to form larger particle clusters with increased diameters relative to the individual particles. Figures 5.3g – 5.3h show examples of these clusters of volcanic silicate shards, held together by carbonaceous fragments of partially combusted moss. The process of particle clustering is well documented in volcanic settings, for example, as volcanic ash aggregation in explosive plumes (Brown et al., 2012) and via aerosol coagulation (Ammann and Burtscher, 1993). In both instances, aggregation and coagulation contribute to particle growth and an increase in the overall PM size distribution. The clustering of volcanic silicate PM with the partially combusted moss particles observed for some particles in this study likely occurred via Brownian motion and impaction close to the emission interface. Whilst this represents a similar process to those already documented, it remains unclear whether this is a process of agglomeration, where particles are held together by weaker physical forces, or, if similarly to ash clustering in explosive volcanic plumes, it is driven by aggre-

gation and particles are held together by stronger chemical bonds. Nonetheless, the observation of clustering between two separate emission sources is unique to this compound volcanic-wildfire event. It is, however, important to note that the Litli-Hrútur compound volcanic-wildfire presented in this study represents only one example and may be specific to the regional vegetation of Iceland. Burning of other types of organic matter (e.g., forests or grasslands) may result in differing clustering mechanics. Moreover, it is possible that there may be some electrostatic effects on the filter, whereby deposited particles have a tendency to attract other transported particles and thus form "post-depositional" clusters. However, this particle clustering behaviour is only significantly observed in the mixed pollution samples, and thus still highlights the importance of clustering processes between mixing emission types. Future studies using different filter materials may be used to evaluate this process further.

TEM-EELS analysis (Section 5.3.2) also suggests that there may be interactions between volcanic gaseous species, such as SO_2 and HCl , and the moss PM as it is burnt at the interface with the advancing lava flow. A moss particle from the lava-moss burning interface showed higher concentrations of S and Cl nearer the surface relative to the interior, which had negligible mass concentrations of S or Cl (Figure 5.4). We interpret the enrichment of S and Cl only at the surface of the moss particle to suggest that they were most likely derived from an external airborne source, rather than through uptake from the soil, especially as terrestrial mosses have a particularly high airborne adsorption capacity (Varela et al., 2023). Mosses can take up species from the atmosphere either via precipitation (wet deposition) or by capturing airborne particles (dry deposition) on their highly porous surfaces (Varela et al., 2023). Nonetheless, without a sample of unburnt moss which grew in proximity to the previous eruptions, there remain two possible scenarios to explain the peaks in S and Cl: 1) volcanic gases and volatile trace elements are taken up prior to the wildfires when the moss was growing in proximity to previous active eruptions, or 2) interactions with volcanic gases and aerosols occurred after burning and subsequent plume mixing during atmospheric transport. The EDS peaks in S and Cl on the background filter of sample LHFP1 favour the latter possibility as they must have occurred syn-transport in the mixed plume, although they do not exclude an additional contribution of S and Cl taken up in the moss whilst it was growing. Both possibilities demonstrate that mosses (or possibly vegetation more generally) in volcanic environments may provide an additional pathway for the uptake and mobility of metal and trace pollutant species (e.g., Arndt et al., 2017), or in the atmosphere if fragments of this moss are remobilised in the plume upon burning. Notably

several metals, such as Al, Fe, and Ca, also showed no significant variation from the surface to the interior of the moss particle during the TEM-EELS transects, whilst K, which was the only more volatile trace element we measured, showed a pattern similar to S and Cl, with much higher concentrations in the surface and subsurface compared to the interior. We hypothesise that this means the mosses are interacting not only with the primary volcanic gases SO_2 and HCl , but also the secondary volcanic aerosols which contain volatile volcanic trace elements. Moss-based biomonitoring is a well-documented approach for characterising anthropogenic heavy metal pollution around active smelting and industrial sites (Steinnes et al., 2003; Olise et al., 2019). Factor analysis of different metals measured via moss-biomonitoring can be an effective way to apportion the contribution of different pollutant sources. Repeated sampling can also provide long-term insights into environmental change as well as capturing punctuated events. Similar approaches could be valuable in assessing the longer-term environmental impacts of volcanic eruptions on a local or regional scale.

As well as occurring directly at the burning interface, mixing and subsequent mechanical interactions can also occur between lava and wildfire emissions during downwind transport in the volcanic-wildfire plume. Comparison of the proportion of elements hosted in the $< 2.5 \mu m$ fraction between the lava-moss interface and downwind mixed samples (Figure 5.5) shows that the proportion of all elements in the $> 2.5 \mu m$ size bin is much greater in the downwind hiking sample relative to the lava-moss interface. Given the ground-based nature of this downwind sample, this observation could represent a preferential sampling of the larger size fraction PM (including hybrid PM formed via agglomeration) which settled out more rapidly from the near vent plume and thus preferentially collected on our ground level filters whilst the smaller size fraction remained airborne at higher altitudes. However, the observed increase in the proportion of elements hosted in the $> 2.5 \mu m$ size fraction could also be explained by particle scavenging, which would also lead to an increase in the overall PM size distribution by the removal of the smaller $< 2.5 \mu m$ fraction. SEM images of the downwind filter showed that the larger partially combusted moss particles did, in some cases, act as “nets” which scavenged and removed the much smaller silicate volcanic aerosols that collected between the fibres of the moss particles (Figures 5.3k – 5.3l). Scavenging is a well-documented process in volcanic plumes, where scavenging of volatiles such as sulfur, halogens, and trace metals, by volcanic ash is a major sink of these elements from explosive volcanic plumes (Rose, 1977; Mather et al., 2003; Witham et al., 2005). Nonetheless, as with the agglomeration processes discussed above, in the context of this

compound volcanic-wildfire event, it is unique in occurring between emissions of different origins.

Furthermore, the agglomeration and scavenging of secondary volcanic aerosols by larger moss particles does not appear to be equally as efficient across the different metal and metalloid elements in our dataset. For example, at the lava-moss burning interface only some elements, such as Cu, Pb, Zn, and K show a significant increase in their proportions in the $> 2.5 \mu\text{m}$ size bin relative to volcanic-end-member emissions. We hypothesise this could suggest that they have a greater affinity to form agglomerations with or being scavenged by the moss, compared with other elements such as Se and Te which have similarly negligible proportions in the $> 2.5 \mu\text{m}$ component compared to volcanic end-member emissions. In the downwind mixed sample, elements such as Se and Te also show a lower relative increase in the proportion collected in the $> 2.5 \mu\text{m}$ size bin, potentially indicating that they have less affinity for being scavenged and collected by the moss particle “nets” during downwind mixing. The fractionation in element concentrations measured in the downwind mixed sample can be partially split by differences in element speciation behaviour (Cu, Pb, Zn, and K have an affinity for forming chlorides, whilst Se and Te more commonly bond with S).

The observed fractionation in element concentrations in the downwind ground-based sample also provides some evidence for the increase in particle size distribution being to a greater extent the result of scavenging instead of preferential sampling of selectively deposited particles. Wainman et al., (2025) suggest that, for the same eruptions in Iceland, under dry background conditions S-bonding elements are likely to be selectively deposited from the plume faster relative to elements with an affinity for Cl. By contrast in the downwind mixed plume sample in this study it is the Cl-bonding elements which show relatively greater enrichment. This provides preliminary evidence not only for scavenging of volcanic PM by larger partially combusted moss particles as a key process in increasing the overall particle size distribution during compound events, but also that the efficiency of the scavenging process, between moss and volcanic particles, may at least in part be based on element chemical speciation. Not all elements are clearly split in their moss scavenging efficiency by a distinction in their speciation behaviour, however. For example, Sn, which generally forms a sulfide, is 100% in the $> 2.5 \mu\text{m}$ size bin suggesting a very strong affinity for scavenging by the moss particles. This emphasises the need to better constrain the mechanisms and underlying controls on processes such as scavenging and agglomeration in volcanic plumes, including for example, the effect of parameters such as element speciation and

element water solubility.

5.4.2 Implications for Transport, Environmental Dispersion, and Human Exposure

In this section, we discuss how the scavenging and agglomeration effects and the resulting changes in PM characteristics, predominantly via increased particle size and removal of the smaller PM size fraction, may have implications for the subsequent transport and dispersion of key pollutant species in the mixed volcanic-wildfire plume. As highlighted above, agglomeration between and scavenging of volcanic aerosols by the larger moss fragments is likely to increase the size of some hybrid particles and contribute to the removal of the smaller volcanic size fraction from the mixed plume. Similarly to the effects of volatile scavenging by larger silicate ash particles and clustering of ash particles in explosive plumes, we propose that interactions with the moss particles are likely to contribute to the enhanced gravitational settling of 1) the larger agglomerated particles and 2) the smaller volcanic PM size fraction which are scavenged by and deposited out with the larger moss particles onto which they are stuck. These scavenging and agglomeration processes, which occur upon mixing between volcanic and wildfire PM, thus potentially provide an additional deposition pathway that is specific to compound volcanic wildfire events. Theoretically, enhanced deposition rates in the mixed near-vent plume could lead to more intense localised air and environmental pollution but reduced long-range transport relative to a non-wildfire-inducing volcanic eruption. Given the preliminary observation that moss particle scavenging efficiency of volcanic PM may vary between different trace elements (Figure 5.5), this pathway could also lead to a fractionation in element transport distances, where the elements which are most efficiently scavenged by the moss particles, such as Ag, Cs, and Sn, have the greatest reduction in long-range transport during compound volcanic wildfire events. By contrast, elements such as Se and Te which are less efficiently scavenged by the moss particles may experience a relatively greater degree of long-range dispersion. Crucially, this could have implications for the suite of metals to which people may be exposed in a compound volcanic-wildfire event compared to a volcanic eruption with no simultaneous wildfire.

The exposure risk for tourists and frontline workers in the vicinity of the eruption/wildfire burning area also varied locally around the eruption/wildfire site, depending on topography, wind direction, and proximity to the different emission sources. For example, OPS measurements at

Viewpoint A and Hiking Trail E highlight the considerable local variability in PM concentrations, where Viewpoint A was in closer proximity to both wildfire burning and emissions from the volcanic vent and lava flows and thus had, on average, higher PM concentrations. Viewpoint A also had a topographic high to the rear which may have contributed to the build-up of airborne pollution within the relative topographic low of the Viewpoint due to orographic effects. By contrast, Hiking Trail E was further from the volcanic PM sources and sat within a wider and flatter plain where gusts of wind may have flushed the pollution more regularly in between high concentration peaks. In comparison to a stand-alone wildfire, it is also possible that ignition by a lava flow may alter the burn dynamics relative to a fire ignited by other sources and thus result in a different overall particle size distribution (e.g., smouldering fires generally produce coarser PM with a larger mean diameter - Pokhrel et al., 2020).

OPS measurements also show that for both locations $PM_{2.5}$ was on average in a more hazardous air pollution category (Yellow/Orange) than PM_{10} (Light Green/Dark Green) and thus may have been the predominant contributor to ground-level exposure risk. Scaling up $PM_{2.5}$ exposure (29% exceeding the orange threshold) along Hiking Path E for a 8- 10 hr round trip (and assuming only half of this time was within dispersion distance of the volcanic/wildfire air pollution) corresponded to nearly an hour and a half of exposure to $>$ Orange $PM_{2.5}$ threshold concentrations where “Strenuous work or outdoor exercise should be avoided” (Supplementary C Table 2; Icelandic Environment Agency, 2025) on the day when we collected data. This means that even based on a preliminary examination of $PM_{2.5}$ concentrations the Icelandic Civil Defence closure of the area due to elevated gas and smoke pollution was likely very well justified on this day. Whilst this exposure is ultimately still relatively short-term, acute exposure to $PM_{2.5}$ has been associated with serious health problems, including heart and lung conditions, asthma attacks, and respiratory symptoms, particularly in vulnerable populations such as children or the elderly (Chen et al., 2024; Faherty et al., 2025). For frontline construction (Sigtryggisdóttir et al., 2025) and emergency response workers (such as search and rescue and the police) who were more regularly in the proximity of the eruption site, exposure to high levels of $PM_{2.5}$ may have been more severe, although this would require consistent longer-duration OPS monitoring to sufficiently inform health advice. In these conditions, the widespread use of respiratory protection, effective at filtering out small particle size fractions, could be a suitable intervention to reduce exposure to both the wildfire and mixed volcanic plume. Whilst advice around respiratory protection is relevant during stand-alone volcanic eruptions, it may need to be strengthened

during compound volcanic-wildfire events where ground-based pollution is likely to be higher due to the additional contribution of volcanically-ignited wildfires. Such advice could be included in future health protection guidance for compound volcanic-wildfire air pollution events (Stewart et al., 2021).

5.5 Conclusions

The Litli-Hrútur 2023 eruption ignited the largest moss wildfires on record in recent Icelandic eruptive history. This triggered a compound volcanic wildfire event with the simultaneous emission of volcanic gases and PM, as well as smoke from the moss wildfires. We collected samples of endmember and mixed volcanic and wildfire emissions and demonstrated that lava outgassing and wildfire smoke were associated with PM with distinctive chemical signatures and size distributions. Where emissions mixed, either directly at the lava-moss burning interface or during downwind plume transport, mechanical interactions between PM and gaseous species and the formation of hybrid PM with altered physicochemical characteristics were observed. Agglomeration and scavenging of volcanic aerosols by the larger fibrous moss fragments were identified as the primary interaction processes and resulted in an increase in the diameter of some particles relative to those in end-member emissions and the removal of the smaller PM size fraction. PM scavenging efficiency did, however, vary between different volatile trace elements. Whilst scavenging and agglomeration are well-constrained processes in volcanic plumes; in this compound volcanic-wildfire event they were unique in occurring between emissions from two different sources. These processes thus potentially provide an additional deposition pathway for volcanic aerosols during compound volcanic-wildfire events and may have implications for the transport and exposure risk to certain volcanic heavy metals. Compound volcanic wildfire events therefore, present a unique air pollution hazard that influences the issuing of health advice, including emphasising the importance of using respiratory protection to minimise acute exposure to dangerous pollutants (McDonald et al., 2020; Stewart et al., 2021; National Collaborating Centre for Environmental Health (NCCEH), 2025).

In this study, we focus only on the mechanical interactions between volcanic and wildfire PM. However, it is also possible and likely that mixing between volcanic and wildfire emissions may result in chemical reactions between volcanic and wildfire species. For example, the combustion of organic material during wildfires results in the emission of trace, greenhouse, and chemically

reactive gases such as CO_2 , CO (during incomplete combustion), CH_4 , SO_2 , NH_3 , VOCs, and NO_X species which could have implications for reactive gas phase chemistry if they mix with volcanic gases such as SO_2 , HCl , and HF. Identification of these chemical reactions and their implications for atmospheric chemistry remains the exciting remit of future studies. Future work may also consider the toxicological implications of hybrid PM formation in compound events, whether via mechanical interactions or still unknown chemical reactions. Altered physicochemical characteristics may have implications for the respiratory penetration depth and/or PM toxicity relative to end-member emissions (Tomasek et al., 2016). Constraining the toxicological implications is therefore crucial to correctly inform future health advice. Finally, we emphasise that this work is timely, given that current planetary warming means the severity and frequency of wildfire events, including those ignited by volcanic eruptions, are likely to increase globally over the coming decades.

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Chapter 6

Discussion and Conclusions

In this Chapter, I outline the key conclusions of this thesis and suggest potential avenues for future research.

6.1 Technological Advances

Technological advances have provided a wealth of new opportunities to understand trace element behaviour in volcanic plumes, including innovation in sampling platforms and the development of new analytical workflows. These advances have been utilised throughout this thesis and were fundamental to the collection and analysis of several datasets presented in this work.

6.1.1 UAV Sampling

Many previous studies have used filter packs to collect PM from volcanic plumes, but have primarily done so using a ground-based approach (e.g., Martin et al., 2009; Moune et al., 2010; Mather et al., 2012). Ground-based sampling relies on the volcanic plume grounding in an accessible location, which is most likely to occur close to the crater rim before buoyancy lofts the plume upwards, or under specific topographic and meteorological conditions downwind (e.g., orographic controls on plume fumigation around Masaya; Delmelle, 2003). It also relies on the conditions of the plume and the surrounding volcanic environment being safe enough to access the crater or area of plume grounding for a sufficient duration to collect a sample. These considerations can significantly limit the number and type of samples collected (depending on the volcano and eruption style), and can heighten the risk posed to researchers. For example,

at the Fagradalsfjall 2021-2023 eruptions, which were the focus of this thesis, the relatively flat topography surrounding the eruption sites and prevailing wind conditions at the time of sampling meant that for most sampling days, the highly-concentrated near-vent plume would have been completely inaccessible if using only ground-based equipment. Sampling at the Fagradalsfjall 2021-2023 eruptions thus required cutting-edge UAV-mounted technologies, which were used throughout this thesis in addition to selected ground-based approaches (see Section 2.1).

In Chapter 3, I used UAV sampling (set up shown in Figure 2.2) to collect filter pack samples directly above outgassing lava flows. This was advantageous as it meant that samples were collected directly above the red-hot core of the lava flow rather than at the more isolated and cooler margins, which may have had different outgassing dynamics relative to the rest of the flow. These cooler, more crystalline margins would have been the only option if solely using ground-based sampling approaches. Performing UAV sampling above lava flows also allowed the sampling team to stand ~ 100 m away and thus avoid coming into close proximity with the active lava front.

In Chapter 5, UAV sampling was also used to collect mixed emission samples directly at the lava-moss burning interface. Placing a ground-based filter pack directly in front of a dynamically moving lava flow would have been far too dangerous, but it was successfully carried out using a UAV that hovered directly above the interface, which could be adjusted remotely as the lava flow advanced. The ability to rapidly adjust sampling location based on changing conditions is a particular strength of UAV-mounted sampling, especially for maintaining the filter pack position within the plume, which may vary due to changes in prevailing wind direction or the strength of at-vent emissions (although live-streamed telemetry SO_2 data would enhance this further; see future work outlined below).

In Chapter 4, I also used UAV sampling to collect samples of the volcanic plume downwind. Direct constraints on the downwind plume composition are perhaps some of the most challenging to collect using only ground-based approaches due to the difficulty of accessing the buoyant downwind plume. Ground-based sampling approaches have been used to indirectly infer the composition of the airborne plume downwind e.g., precipitation samples which have fallen through the plume (Moune et al., 2006; Calabrese et al., 2011) or biomonitoring of surrounding vegetation (Martin et al., 2010; Mather et al., 2012; Arndt et al., 2017), however, such approaches rely on the assumption that trace elements are deposited homogeneously from the plume downwind.

As discussed in Chapter 4, isolated downfall samples are likely unrepresentative of the bulk eruption cloud due to differentiation in depositional mechanisms acting on the plume and the complex interplay between background meteorological conditions and trace element behaviour. In being able to directly access the buoyant airborne plume as it is dispersed downwind and conduct in-situ sampling, UAV platforms offer the ability to track the compositional evolution of the volcanic plume at unprecedented spatial and temporal resolution.

In Chapter 4, this downwind sampling capability was utilised, although only within the first 1 km of plume dispersion due to UAV battery life constraints. The resulting samples, collected at high spatial resolution in the near-vent downwind plume, highlighted a fractionation in the plume composition, primarily via the preferential gravitational sedimentation and scavenging by silicate particles, which occurred within the first few hundred meters away from the vent. Previous studies have often inferred “at-vent” compositions using ground-based samples collected at 100-200 m distances from the crater (e.g., Moune et al., 2010; Mather et al., 2012; Martin et al., 2012) compared to the < 50 m achieved by UAV sampling used in this thesis. However, the near-vent heterogeneous element deposition reported in Chapter 4 of this thesis could imply that some elements were potentially undersampled and underreported by ground-based approaches (e.g., in Chapter 4, within 500 m $> 10\%$ of refractory elements had been lost from the plume compared to $< 5\%$ of some of the most volatile elements). UAV technologies thus offer opportunities for more direct, dynamic, and higher resolution sampling of volcanic plumes, with great potential applicability for understanding the downwind dispersion behaviour of volcanic trace elements (Wainman, 2024; Thivet et al., 2024).

Suggestions for Future Work and Best Practice

Whilst recent advances in UAV technology have unlocked new possibilities for sampling volcanic plumes, there remain several areas of improvement that would optimise their use in volcanic environments. Firstly, focusing on the construction of the UAV itself, improved battery lifetimes and payload capacities, particularly for rotary-style UAVs, would significantly improve their performance in sampling volcanic plumes and in the range of samples that could be collected. Longer battery lifetimes would also prevent the need for multiple flights to one sampling location. This approach was used frequently in this thesis to ensure element concentrations were above detection limits, but repeated take-offs and landings introduced uncertainty due to potential contamination. Longer UAV battery lifetimes would also increase the distance over

which sampling could occur relative to the take-off point (limited to around 1 km on the DJI Matrice 300 RTK model used in this thesis). Higher payloads would also mean that a greater number of instruments could be mounted on the UAV simultaneously (e.g., filter pack, Cascade impactor, multiGAS, and OPS), thus allowing for more robust comparisons between sampling methods and the generation of more coherent datasets.

Optimisation of sampling equipment is another avenue that would allow for a greater number of instruments to be mounted on the UAV. For example, the set-up used in this thesis relied on the use of a heavy external pump to generate airflow through the filter pack, which took up nearly half of the overall payload capacity (see Figure 2.2). Future setups could therefore consider a smaller pump (as done by Galle et al. (2021)), although there may be a trade-off with flow rates and total sampling volume, or a pump that does not contain its own battery but may be plugged into the UAV power system (e.g., the Sniffer 4D, see Thivet et al. (2024)). The setup used in this thesis also relied on excessive amounts of duct tape, cable ties, and jubilee clips (and hope), which simultaneously prevented easy access to sampling equipment (needed to check the multiGAS SD card) and caused several issues with loose tubing hitting the rotary blades, causing the UAV to crash. Other recent studies have overcome some of these issues by live-streaming data via telemetry (Galle et al., 2021; Thivet et al., 2024); however, this feature was broken in the MultiGAS unit used in this thesis. Future work could also consider improvements to the mounting apparatus of sampling equipment on the UAV (e.g., through bespoke 3D printing of parts).

Mounting a greater array of sampling instruments on UAV platforms is also an exciting area of current development (e.g., Galle et al., 2021; Thivet et al., 2024). At the Litli-Hrútur 2023 eruption, I experimented with conducting vertical transects of the volcanic plume at around 200 m downwind using the compact multiGAS unit (outlined in section 2.1.3) simultaneously with a handheld OPS. This vertical transect approach helped other researchers to identify the optimal height for collecting gas bag samples for CO_2 carbon isotope analysis by identifying the altitude range with the highest CO_2 concentrations; however, the OPS lacked the measurement precision to resolve differences in in-plume particle size distributions, primarily due to instrument drift. Future attempts to conduct vertical transects of an effusive volcanic plume in this way (especially with equipment such as the Sniffer 4D which has been built to be specifically compatible with DJI UAV models and simultaneously collects PM, major gas, VOCs, and other gas data within

one sampling unit; Thivet et al., 2024) could provide useful insights into potential stratification processes within the plume or the deconvolution of gaseous and PM components. Another beneficial advancement in UAV filter pack sampling of effusive plumes would be the development of sealed filter packs with automatic opening/pump start-up upon entering the volcanic plume. This would significantly reduce potential contamination of the filter pack (e.g., by remobilised dust) during take-off and landings. Automated technologies have already been employed when using fixed-wing drones to collect ash from explosive volcanic plumes using custom-built collectors (Liu et al., 2020; Thivet et al., 2024 and references therein). Similar approaches could therefore be implemented in sampling effusive volcanic plumes with relatively little modification, e.g., where the filter opens once a baseline SO_2 concentration is reached, which indicates the UAV has entered the volcanic plume. This automated sampling approach would also remove the need to manually calculate “in-plume sampling durations” and thus provide more streamlined major gas and trace element data.

6.1.2 Microscopy

In Chapter 5 of this thesis, I also explore the use of high-resolution microscopy (SEM and TEM) for geochemical and morphological analysis of mixed volcanic and wildfire PM, collected via filter pack sampling at the Litli-Hrútur 2023 eruption. Physicochemical analysis of PM using SEM imaging and EDS analysis is a well-established approach that has been used extensively by previous studies, particularly to characterise the primary silicate ash phase (Moune et al., 2010; Martin et al., 2012; Trejos et al., 2021) and the respirable risks of volcanic ash (Horwell et al., 2003; Hillman et al., 2012). Fewer studies have used SEM or TEM to image and analyse the smaller secondary non-silicate volcanic aerosol, largely because of the difficulties of performing EDS analysis on sub-micron PM (outlined in Section 2.2.2; Martin et al., 2012; Mandon et al., 2019). The detection of some trace elements using SEM-EDS analysis can also be challenging where element concentrations are $< 0.1\text{--}0.5\text{ wt}\%$, where elements have potential spectral overlaps, and if the surface topography of the sample reduces signal strength. These difficulties mean that only a few studies have robustly imaged or constrained compositional data for the smallest volcanic aerosol fraction (e.g., Delmelle et al. (2007) on the surface of ash particles using X-ray photoelectron spectroscopy and atomic force microscopy, Pfeffer et al. (2006) using TEM, and Moune et al. (2010) using SEM). The presence of this sub-micron aerosol phase, potentially as a coating on larger particles, has more commonly been inferred indirectly through S and Cl

spectral SEM-EDS peaks (Mandon et al., 2019).

In Chapter 5 of this thesis, some moss particles showed anomalous EDS peaks in S and Cl, which I inferred to indicate potential interactions with or coating by volcanic aerosols, rich in SO_2 and HCl gases (Wainman et al., 2026). To test this possibility further, I developed an approach using TEM to perform geochemical EELS transects from the edge to the interior of the moss particle at nm scale resolution. This was advantageous over SEM analysis because the higher spatial resolution of TEM analysis could distinguish between the element concentrations in the interior and at the edge of the moss particle, whereas the interaction volumes associated with EDS analysis would sample the edge and interior simultaneously and report this as a single bulk composition. TEM analysis did require prior cutting and milling using a focused ion beam (FIB), which was challenging given the weak internal structure of the moss particle, causing it to partially disintegrate upon being cut out of the filter for TEM-EELS analysis. Nonetheless, the EELS transects performed in Chapter 5 of this thesis were sufficient to suggest a potential surface enrichment of S and Cl, which may have resulted from interactions during mixing with volcanic aerosols. This TEM-EELS workflow thus offers a new possibility for studying the smallest size fraction volcanic aerosols, which until now have been the most elusive.

Suggestions for Future Work

Continued development of the TEM workflow, outlined above and in Chapter 5 of this thesis, could provide an alternative approach to analysing the smallest volcanic aerosols, both as a coating on larger particles (especially relevant for ash-aerosol interactions, where volatile species may be adsorbed to the surface of the ash; Delmelle et al., 2007; Ayris and Delmelle, 2012) and as standalone submicron PM. The workflow presented in Chapter 5 is still under development, having only been performed on a single particle in one volcanic context, but future studies may refine this approach by applying it to a range of different volcanic and/or mixed PM and in varied volcanic environments. Potential applicability includes, for example, where volcanic emissions may have mixed and interacted with PM from other sources, such as from wildfire burning (Wainman et al., 2026) or with anthropogenic emissions (discussed further in Section 6.5 below). Future studies investigating such processes could also consider the use of X-ray Photoelectron Spectroscopy (XPS; Delmelle et al., 2007) to determine the bulk surficial composition (i.e., the top 1-10 nm) of collected hybrid volcanic-wildfire and/or volcanic-urban PM and thus if mixing between emission sources has resulted in coating interactions.

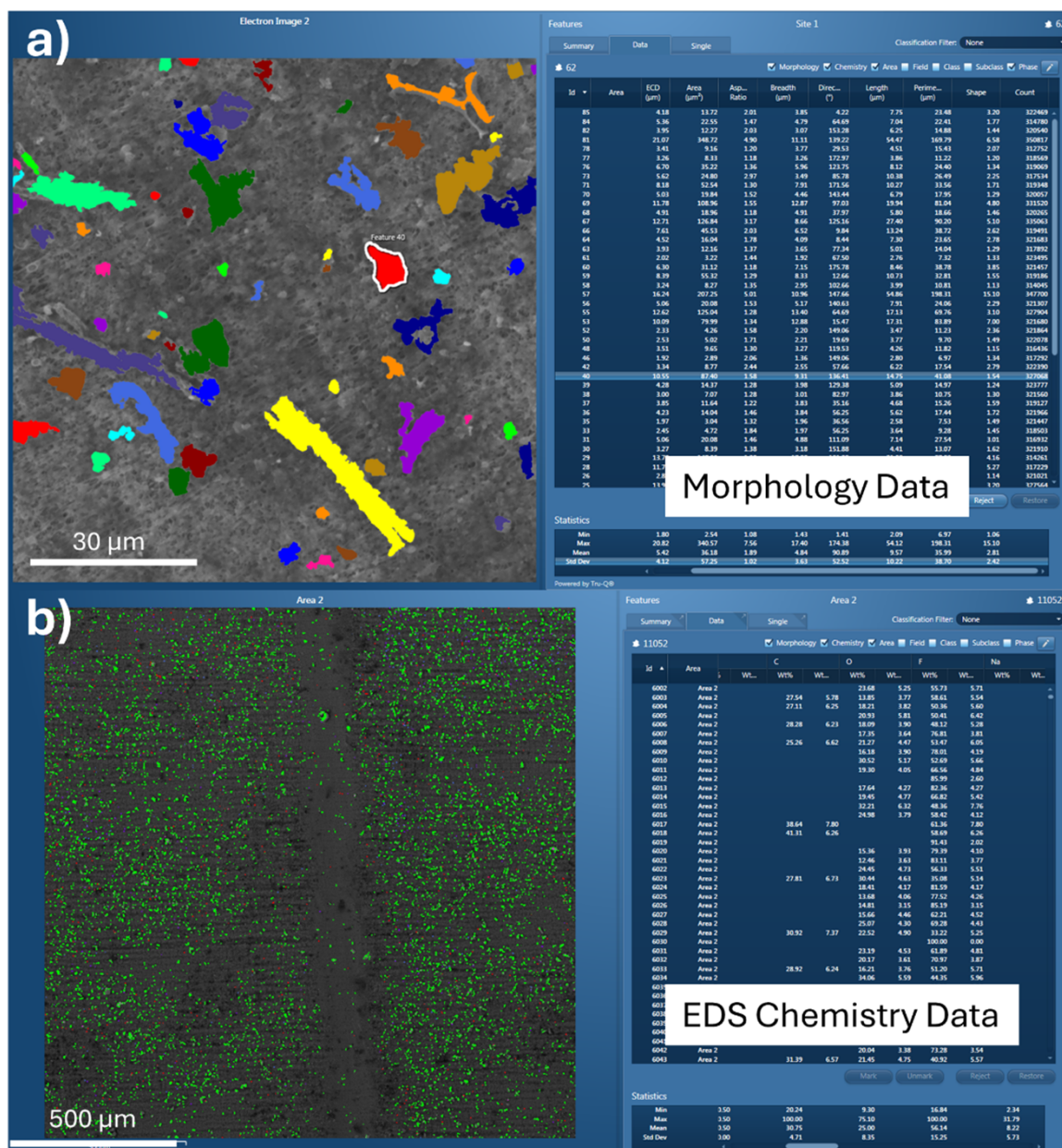


Figure 6.1: Automatic classification of volcanic PM using Aztec Feature. a) Particle detection over a single field of view based on grayscale differences between PM and the background filter. Once detected, morphological data is estimated (e.g., area, aspect ratio, diameter). b) Automatic detection applied across 49 fields of view ($\sim 2 \text{ mm}^2$) containing over 11,000 particles. Shows an initial screening step where true particles (green) are being separated from artefacts (purple and red) generated by false detection of the filter pores. Artefacts and true particles are distinguished based on their size and EDS chemistry spectra (e.g., filter pores have characteristic wt% of C, O, and F).

Another approach that was tested but not completed within the scope of this thesis was the use of the SEM software Aztec Feature (Oxford Instruments) to automatically detect and classify PM collected on PTFE filters. Aztec Feature uses grayscale colour band differences on SEM images to automatically detect particles (see Figure 6.1) and produces particle-by-particle morphological data (e.g., estimated particle area, aspect ratios, diameter etc). Automated point EDS analysis can then be performed across the field of view at the detected location of each particle. Combined with morphological parameters, geochemical data can then be used to generate a catalogue of end-member particle types. Once this “recipe” of different PM endmembers has been constructed, it can then be used to automatically detect and classify PM across an entire section of the filter based on the specified groupings (e.g., Group 1: silicate PM, Group 2: organic moss PM, Group 3: non-silicate Cl-rich aerosols). During preliminary testing, I used Aztec Feature to automatically detect and classify over 150,000 particles (in $\sim 8hrs$) on a PTFE filter collected in the mixed volcanic-wildfire plume at the Litli-Hrútur 2023 eruption. Compared to most current studies, which use SEM-EDS analysis to manually classify volcanic PM (often at most a few hundred to a few thousand particles and requiring extensive instrument and manual processing time, e.g., Moune et al., 2010; Mandon et al., 2019), automated classification offers a clear advantage in generating much larger and more statistically robust datasets. This rapid classification and apportionment of PM could be especially useful in an operational capacity. For example, at the Litli-Hrútur 2023 eruption, it took several months to produce the results presented in Chapter 5, whereas with automated classification using the Aztec Feature software, a sample could theoretically be collected during an eruption, run overnight, and reported the next day to civil protection agencies. Refinement of this automated SEM apportionment approach, possibly using machine learning techniques, should therefore be a priority for future work, with a clear potential for operational impact.

6.2 Element Speciation

A central theme that runs throughout this thesis is the importance of speciation in controlling trace element emission, transport, and deposition behaviour from the volcanic plume. In Chapter 3, I model the speciation behaviour of an array of different trace elements in the vent emissions of the Fagradalsfjall 2021 eruption using thermodynamic modelling with the HSC chemistry software (Wainman et al., 2024). Element speciation at the Fagradalsfjall 2021-2023

eruptions shows a stronger affinity for S and OH complexes, with relatively fewer elements complexing as chlorides compared to arc settings (Mandon et al., 2019; Mason et al., 2021). Speciation results for the Fagradalsfjall 2021-2023 eruptions are therefore highly consistent with the thermodynamic speciation modelling performed by Mason et al. (2021) for the Kīlauea 2018 eruption, another S-rich fissure eruption. The consistency between modelled element speciation at the Fagradalsfjall and Kīlauea eruptions provides further support for the framework outlined by Edmonds et al., 2018, which explains the characteristic differences in trace element fluxes between arc and hotspot/rift tectonic settings based on melt compositions, slab enrichment, and characteristic element speciation affinities. Scholtysik and Canil (2021) expanded this framework further by outlining two groups of elements based on their affinity for complexing with S (Zn, As, Pb, $\pm$ Cd, $\pm$ Bi) and Cl (Rb, Cs, Ag, $\pm$ Cd, $\pm$ Bi). These groupings are in good agreement with results from the Fagradalsfjall 2021-2023 eruptions for those elements which characteristically form chloride complexes (from Wainman et al. (2024): Ag, Rb Cu, Cs, Mn, Fe and Mg) and sulphides (Pb, Sn, As, Se, and Te) although neglect that under certain temperatures and melt compositions elements such as Zn, Cd, and Ag may remain in their elemental forms.

The temperature dependence of element speciation for a given melt condition is explored further in Chapter 3 of this thesis, with only a small number of elements (As, Te, Se, and Mn) showing consistent speciation across the whole 400 – 1200 °C temperature range. Most elements instead undergo speciation transitions with decreasing temperatures (e.g., Pb complexes as a sulphide at high temperatures but as a chloride below 600 °C under Fagradalsfjall input conditions). The sensitivity of element speciation behaviour to melt composition, oxygen fugacity, and temperature was also explored further in Chapter 3 of this thesis through comparing modelled element speciation at the vent (high temperature, S-rich degassing regime) to element speciation downflow in an outgassing lava flow as it cools, oxidises through mixing with air, and undergoes fractional degassing (Sigmarsson et al., 2020). Fractional degassing (decreasing S/Cl and S/F downflow due to the higher melt solubilities of Cl and F and preferential outgassing of S at the vent) has been observed previously during the Holuhraun 2014-2015 eruption (Sigmarsson et al., 2020), at Mt Etna (Aiuppa, 2009), and in lava flows at Piton de la Fournaise (Toutain et al., 1990). The work presented in Chapter 3 is, however, the first to link fractional degassing and element speciation affinities to an overall fractionation in element outgassing as lava flows age and cool (Wainman et al., 2024). In Chapter 3, a model for the fractional degassing of major gas and trace element species is presented based on an observed transition from an S-dominated regime

at the vent to a Cl-dominated degassing regime in the relatively young lava flows over which samples were collected in this thesis. A further transition from Cl to F-dominated degassing was hypothesised based on thermodynamic modelling, where some elements (Rb, Cs, and Ce) were modelled to undergo a transition from chlorides to fluorides with decreasing lava temperatures. Levillayer et al. (2025) followed up on the process of fractional degassing at the Fagradalsfjall eruptions, presenting element degassing concentrations from the cooled post-eruptive crater several months after the end of the eruption. They reported a relative increase in the emission of fluorine ($\text{Cl}/\text{F} < 1$) and Mo and Ru, both of which have been thermodynamically modelled to complex as fluoride compounds. This observation therefore lends further support for the fractional trace element degassing model presented in Chapter 3 of this thesis (Figure 3.6; Wainman et al., 2024).

In Chapter 4 of this thesis, I also highlight the relationship between element speciation and the affinity of different trace elements for wet and dry depositional processes. Broadly, those elements which have an affinity for complexing with S are lost more rapidly from the plume via dry depositional processes, likely due to preferential scavenging by larger ash particles, whereas elements which preferentially complex with Cl are lost to a greater extent via plume wash out and plume rain out due to their higher solubility in water. This observation is in agreement with previous studies that have reported the preferential wet deposition of gaseous HCl over SO_2 and H_2S due to the higher water solubility of HCl (Kawaratani and Fujita, 1990). The work presented in Chapter 4 also builds on the framework presented by Ilyinskaya et al. (2021), which explains the difference in deposition behaviour between refractory and volatile trace elements in the Kilauea 2018 eruption plume as a consequence of their speciation, solubilities, and affinity for plume rain out in the humid atmosphere. The framework for meteorologically dependent deposition presented in this thesis (discussed further in Section 6.4) now extends this to present a more complete picture of heterogeneous trace element deposition, with speciation being understood as one of the central parameters controlling trace element deposition behaviour.

6.2.1 Suggestions for Future Work

Thermodynamic modelling of element equilibrium speciation was performed in this thesis using the HSC Chemistry software (Chapter 3, Section 3.3.6). This software uses experimentally constrained thermodynamic parameters and solves a series of mass balance and mass action equations to determine the species present at given input conditions. However, the underlying

thermodynamic data (Gibbs energy (ΔG), enthalpy (ΔH), entropy (S), and heat capacity (C_p)), used in the software are often not well defined at the high temperature conditions of volcanic plumes ($> 800^\circ\text{C}$ directly at the emission interface, although cools rapidly to $\sim 300\text{--}400^\circ\text{C}$ within a few meters of the vent) and so relies on extrapolations of lower temperature datasets (or may even be missing data for some species entirely), creating a significant uncertainty with modelling element speciation at the high temperatures associated with volcanic vents. Further to this, Mandon et al. (2025) suggested that elements in the volcanic plume may exist as a series of hydrated metal-ligand compounds (e.g., $\text{CuCl}n\text{H}_2\text{O}$) rather than simple metal gas compounds (e.g., CuCl). Hydration can significantly impact gas species thermodynamic stabilities, but is not currently accounted for in the HSC chemistry software, which could alter thermodynamic modelling results. The expansion and calibration of thermodynamic data sets, specifically for volcanic conditions, is therefore a clear priority for future work and would facilitate deeper study into the effects of temperature, pressure, and melt composition on element speciation in volcanic environments. The additional dataset presented in this thesis for the Fagradalsfjall 2021-2023 eruptions also presents the opportunity to compare element speciation between hotspot (Kīlauea 2018; Mason et al., 2021), rift (Erta Ale; Zelenski et al., 2013) and mid-ocean ridge (this thesis) eruptions. This comparison would build directly on the framework presented by Edmonds et al. (2018), which compared trace element behaviour between only arc and hotspot settings, and thus potentially offers additional insights into the parameters which control trace element emissions at different global volcanoes.

When using the HSC Chemistry software, element speciation is also generally only modelled in the gas phase (as done in this thesis and in recent studies by Mandon et al. (2019) and Mason et al. (2021)). Modelling in the gas phase is suitable for inferring element speciation at the point of emission at the lava-air interface; however, it potentially overlooks the speciation changes that could occur during the subsequent gas-to-particle conversion processes that happen rapidly post-emission and during downwind transport. For example, Mason et al. (2021) demonstrated using thermochemical modelling of the Kīlauea 2018 eruption plume in the gas phase that there was a discontinuity in element speciation at around 14% mixing with the ambient atmosphere. Elements such as Te, Se, As, Sn and Pb, which under magmatic plume compositions were modelled to form $\text{TeS}_{(g)}$, $\text{SeS}_{(g)}$, $\text{AsS}_{(g)}$, $\text{SnS}_{(g)}$, and $\text{PbS}_{(g)}$ respectively, underwent a speciation change at 14% mixing with air to form $\text{TeO}_{2(g)}$, $\text{SeO}_{2(g)}$, $\text{AsO}_{(g)}$ and $\text{AsO}_{2(g)}$, $\text{PbCl}_{2(g)}$ and $\text{PbO}_{(g)}$, and $\text{SnCl}_2\text{O}_{2(g)}$ instead. These downwind low temperature changes in element speci-

ation are perhaps one of the most significant uncertainties when linking element speciation to subsequent downwind transport and deposition behaviour (e.g., as done in Chapter 4). Assuming that element speciation in the downwind aerosol plume is the same as speciation modelled in the gas phase during emission potentially obscures important changes that may occur during the gas-to-particle conversion process and other low-temperature reactions. Such changes could have significant but currently unknown and unaccounted-for effects on aerosol properties, such as water solubility or ash scavenging affinity, and thus significantly impact element deposition processes and element bioreactivity once delivered to the surface. Future work, either through thermodynamic modelling or using experimental fumarole set-ups (e.g., Scholtysik and Canil, 2020; Scholtysik and Canil, 2021), which can more comprehensively constrain element speciation changes during gas-to-particle conversion processes and low temperature reactions in the downwind plume, is therefore critical to improving confidence in linking element speciation to plume transport and deposition behaviours.

6.3 Going Beyond Point-Source Emissions

Previous work considering trace element emissions in effusive eruptions has, for the most part, focused on emissions from the central volcanic vent(s) (Ilyinskaya et al., 2021; Mather et al., 2012; Martin et al., 2012; Moune et al., 2010). The additional outgassing of trace elements from lava flows has received comparatively little attention despite lava flows often being generated extensively during effusive volcanic activity (e.g., at the Kīlauea 2018 eruption, at the Tajogaite 2021 eruption on La Palma and at the Holuhraun 2014-2015 and Fagradalsfjall 2021-2023 eruptions). In Chapter 3 of this thesis, I focus on the emission of trace elements from outgassing lava flows at the Fagradalsfjall 2021-2023 eruptions by collecting filter packs at discrete distances away from the vent downflow. I demonstrated that the geochemical signature of lava flow trace element outgassing evolved with increasing distance from the vent as the lava cooled and aged. This evolution was driven by fractional degassing (Sigmarsson et al., 2020) and resulted in a transition from S-dominated degassing at the vent to increasingly Cl-rich (Wainman et al., 2024) and eventually F-rich (Levillayer et al., 2025) degassing down flow. This highlights that the emission fluxes of volcanic trace elements (i.e., $[X]/[SO_2]$) cannot necessarily be reported as a homogenous value for the whole eruption based on at-vent point source measurements, but instead, depending on the style and extent of generated lava flows, may vary by an order of

magnitude (i.e., $[Cu]/[SO_2]$ at the vent was 1.2×10^{-5} but was 3.0×10^{-4} at the most distal lava flow) within a single volcanic environment.

In Chapter 3, I estimate that the flux of trace elements from lava flow outgassing corresponds to $\sim 10\%$ of the total flux from combined at-vent and lava flow emissions. For effusive eruptions, this means that lava flows may be a non-negligible source of volcanic trace elements to the troposphere and surrounding environment. This is especially pronounced in relatively clean atmospheres such as Iceland, where even the lava flow emission fluxes of certain heavy metals during the Fagradalsfjall (Geldingadalir) 2021 eruption were greater than total emission fluxes for the same metal pollutants in 2021 from anthropogenic sources (Wainman et al., 2024).

The fractional emission of trace elements from lava flows as they age and cool has critical implications for estimating total trace element emission inventories and for constraining and mitigating population exposure to hazardous metal pollutants, where air pollution from lava flows is currently underaccounted for in hazard and mitigation planning. Due to their dynamic nature, large ground-based footprint, and potential for extended outgassing even following the end of an eruption, lava flows could pose a significant, if localised, air quality hazard. For example, whilst the main vent is a static point-source (although new vents may emerge, as in the 2021 Geldingadalir eruption), lava flows are a dynamic and often persistent source of major gas, PM, and trace element emissions. Lava flows reach up to 10's of km from the central vent (with outgassing composition changing as they cool) and thus may significantly extend the total area that is impacted by volcanic air pollution and exacerbate exposure risk further if flows encroach on settled areas and towns, even if the main vent remains distal (e.g., the 2021 Tajogaite eruption, La Palma, or the more recent Sundhnúkur 2024-2025 eruptions on the Reykjanes Peninsula). The emissions produced by lava flow outgassing are also less buoyant and more dispersed than the central point-source volcanic plume. Ground-level air pollution impacts in the immediate vicinity of the lava flows will be missed if sampling efforts or air quality modelling forecasts (e.g., using the CALPUFF model; Barsotti et al., 2023; Pfeffer et al., 2024) are only focused on the dispersion of the central volcanic plume (although this can still cause significant ground-level impacts further afield; Whitty et al., 2026).

The impact of lava flow emissions on the ground-level airborne concentrations of trace elements was investigated at the Meradalir 2022 eruption site (Wainman et al., in prep). Figure 6.2 shows a preliminary mixing model that was developed between the airborne plume and emissions from

a nearby lava flow based on measured concentrations. Filter packs were collected simultaneously in the airborne plume at 500 m downwind (mounted on the UAV) and at ground level, directly underneath the UAV sample. Another filter pack was also collected within ~ 5 m of an outgassing lava vent. Figure 6.2 shows measured downwind ground-based element concentrations (black line) and measured concentrations in the airborne plume at varying degrees of dilution (grey lines) downwind. As shown by the cross-cutting relationships between the grey lines and the black line, ground-based element concentrations cannot be accounted for by simple dilution of the airborne plume. The mixing model between the diluted airborne plume (diluted to 25% of measured concentrations) and lava flow outgassing is shown by the green lines on Figure 6.2, where measured concentrations in the lava sample are diluted between 45% and 5% to account for mixing with the ambient atmosphere upon emission. The best-fit agreement between modelled element concentrations (green lines) and measured element concentrations (shown by the solid black line) is achieved when the airborne plume is diluted to 25% of measured concentrations at the vent and mixed with lava outgassing emissions diluted to 30% of measured at-source concentrations. Notably, the concentrations of the elements which mostly commonly complex with S can be accounted for as a direct dilution of the airborne plume, whereas to match measured Cl-complexing element concentrations at ground level, an additional input from outgassing lava flows is required. This fractionation between the main vent plume and lava flow outgassing mirrors the S-rich vent regime and Cl-rich downflow enrichment reported in Chapter 3 of this thesis (Wainman et al., 2024).

This preliminary result also highlights that ground-level trace element concentrations and air pollution impacts may be related both to the main buoyant plume and diffuse outgassing from nearby lava flows to produce a low-level haze (Simmons et al., 2017). From a hazard perspective, considering the additional risk posed by lava flow outgassing to ground-level air quality is particularly important during eruptions such as the Fagradalsfjall 2021-2023, where thousands of tourists visited the eruption site, sometimes coming within 10s of m of active lava flows (Simmons et al., 2017; Donovan et al., 2023). The array of trace elements emitted by these lava flows, and thus the hazard potential for exposed tourists, is also likely to evolve in composition over the course of the eruption due to fractional degassing as the lava flow ages and cools (Wainman et al., 2024).

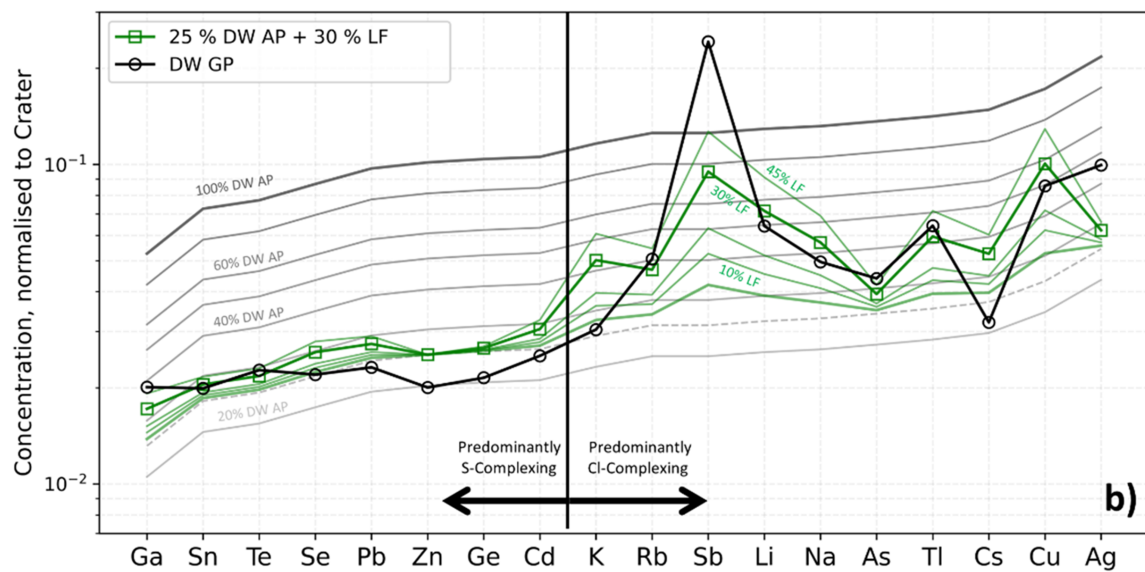


Figure 6.2: Mixing Model of downwind airborne (DW AP) and ground-level plume (DW GP) compositions. Element concentrations are normalised to the main vent samples to investigate relative depletion rates. Solid grey lines show the composition of the 2022 downwind airborne plume, with lighter grey lines showing the downwind airborne plume diluted homogenously between 0-80%. The black line with circles shows the composition of the ground-based plume sample in 2022. Green lines show the composition when an additional component from 2021 outgassing lava flow (LF) is included in the mixing model, between 5-45% dilution.

6.3.1 Suggestions for Future Work

Improved constraints are needed to fully quantify trace element emissions from outgassing lava flows and to better understand their contribution to the local atmosphere and environment. The emission fluxes reported in Chapter 3 provide only a snapshot of lava flow trace element outgassing (i.e., measured on one day and reported in Kg/s). Whilst these emission fluxes are non-negligible relative to fluxes from the main vent, they do not provide an estimate of the total flux of trace elements from lava flow outgassing over the duration of the eruption. Previous studies of the Laki 1783-1784 (Thordarson et al., 1996) and Holuhraun 2014-2015 (Simmons et al., 2017; Donovan et al., 2023) eruptions have estimated that lava flows accounted for between 20% and 0.2% of total SO_2 flux. Such values could be applied to estimating the contribution of lava flow outgassing to total trace element emission inventories, although they would be improved with better constraints on the duration and dynamics of post-emplacement lava flow trace element outgassing. For example, Simmons et al. (2017) demonstrated that lava flows at the Holuhraun 2014-2015 eruptions continued to degass SO_2 for at least 3 months following emplacement, although a clear temporal trend (e.g., an exponential decay in emission rate over time) in outgassing flux was not observed. The longer-term effect of fractional degassing on the assemblage of trace elements outgassed by lava flows also remains uncertain (beyond the F-rich degassing regime reported by Levillayer et al. (2025)). Integrating these changes, both in emission rate and trace element composition, over the total area of the degassing interface and time span of an eruption is a reasonably involved calculation. For eruptions such as Fagradalsfjall 2021-2023, where the lava dynamics, composition, and degassing parameters are relatively well constrained (Halldórsson et al., 2022; Pedersen et al., 2022; Pfeffer et al., 2024; Wainman et al., 2024), it may, however, be possible to produce an initial estimate (Wainman et al., in prep).

Quantification of the total emission inventory for the Fagradalsfjall 2021-2023 eruptions (or other basaltic eruptions) which includes the contribution of trace elements from lava flow outgassing would be valuable, both in constraining localised impacts (i.e., the delivery of trace metals to the surrounding soils) and for tightening global volcanic trace element emission inventories (e.g., estimated by Nriagu (1989) and Mather et al. (2003)). Calculation of global emission inventories to date has largely relied on assuming an annual global volcanic SO_2 flux (as a sum of the at-vent SO_2 fluxes of the major global degassing volcanoes) and using measured $[X]/[SO_2]$ values for each element to estimate total global volcanic flux of each element (Nriagu, 1989; Mather et al.,

2003). Not only does this approach neglect the significant differences in $[X]/[SO_2]$ ratios which have been found between different volcanoes (e.g., arc vs hot spot; Edmonds et al., 2018) and even within a single volcanic setting (e.g., $[X]/[SO_2]$ changes down flow due to fractional degassing; Wainman et al., 2024) but it may also underestimate trace element fluxes due to omitting the additional contribution of lava flows during syn and post-eruptive effusive degassing. On a global scale, this underestimate is likely to be small compared to total global fluxes (especially compared to anthropogenic emissions of heavy metals) and thus non-critical, but for regional-scale inventories, the inclusion of lava flow outgassing contributions could be important when estimating the delivery of metal pollutants to the local atmosphere and environment.

Additional constraints on the dispersal ranges and environmental processing of trace elements emitted by lava flows could also help constrain the localised air quality and environmental impacts associated with effusive eruptions and lava outgassing, which, as discussed above, are likely to have different dispersal characteristics relative to the main vent plume. In addition to the work presented in this thesis, I have also collected an array of moss samples from the area surrounding the Sundhnúkur 2024 lava flows that follow three transects spanning from the lava-moss interface to ~ 1 km distance away. This employs a similar biomonitoring approach to Calabrese et al. (2015) and Arndt et al. (2017), and the aim is to quantify the dispersion distances of trace elements emitted by lava flows through tracking the concentrations of volatile volcanic trace elements in nearby mosses (Wainman et al., in prep). This could have implications for better constraining the exposure of emergency and frontline construction workers who spent extended periods within ~ 1 km of active lava flows during the Fagradalsfjall 2021-2023 eruptions.

6.4 Downwind Transport

The transport and deposition of silicate ash from explosive volcanic plumes has received considerable attention due to its significance as an aviation hazard (Prata and Rose, 2015). The processes and mechanisms that control the transport and deposition of volatile trace elements, hosted in the non-silicate aerosol fraction, are however, less well understood, having been investigated to a lesser extent. Until recently, many studies have assumed that the deposition of volatile trace elements from volcanic plumes is a homogenous process and thus that element ratios in deposited samples (i.e., where precipitation has fallen through the plume) are representative of airborne plume chemistry (Moune et al., 2006; Calabrese et al., 2011; Liotta et al., 2021). This

has only recently been called into question by observations at the Kīlauea 2018 eruption, where Ilyinskaya et al. (2021) suggested that the higher volatility trace elements, which form more soluble complexes, are deposited more rapidly in the far-field plume via rain out processes. It has since also been hypothesised that observed decoupling in ice core deposits between sulfate aerosols, chloride-forming volatile elements, and refractory metals associated with silicate ash may also be the result of downwind meteorologically controlled heterogeneous deposition of volcanic trace elements (Mason et al., 2022; Edmonds et al., 2022). Until now, however, direct observations of heterogeneous trace element deposition occurring in real-time during downwind transport have been lacking, primarily due to the difficulties of collecting in-situ samples of the dispersed volcanic plume.

In Chapter 4, I used cutting-edge UAV sampling platforms (Section 6.1) to collect direct in-situ measurements of the downwind volcanic plume. Using this data I investigated the processes that govern the near-vent transport and deposition of volcanic trace elements, finding a clear fractionation between the behaviour of volatile and refractory trace elements. A significant proportion of the more refractory elements ($> 13\%$ by mass) were lost from the near-vent plume within the first 500 m, whilst a greater proportion of the more volatile elements were subject to longer range transport. The rapid loss of refractory elements from the near-vent plume occurred under both wet and dry meteorological conditions. Under dry conditions, this may be explained by preferential gravitational sedimentation of the larger silicate ash particles (Wesely and Hicks, 2000) and under wet conditions, it was hypothesised to be due to continued gravitational sedimentation as well as the additional impact scavenging of silicate PM by snow falling through the plume (Cheng et al., 2021). This result highlights that even for effusive plumes, which are characterised as “ash-poor”, the deposition of silicate ash may still be a key process within the very near-vent environment for facilitating the delivery of refractory trace elements to the surface.

The preferential deposition of refractory elements from the plume, via both wet and dry depositional processes, does however, contradict observations by Ilyinskaya et al. (2021). Based on observations at the Kīlauea 2018 eruption, they suggested that the refractory elements experienced longer-range transport downwind, primarily due to their lower solubilities and thus less efficient removal from the plume by wet depositional processes. Nonetheless, the observations and framework for meteorologically dependent trace element deposition presented in Chapter 4

of this thesis can be reconciled with observations from the Kīlauea 2018 eruption by Ilyinskaya et al. (2021) with two possible explanations: 1) Samples collected by Ilyinskaya et al. (2021) were all at least 30 km from the vent. As such, most of the larger silicate ash, which hosts the most refractory elements, was likely to have already been deposited (i.e., within the first 1 km, as observed in Chapter 4 of this thesis). Any remaining refractory elements were therefore likely hosted in the accumulation mode PM, which is the least efficiently removed from the atmosphere (Mather et al., 2003). As suggested by Ilyinskaya et al., 2021 the lower solubilities of these accumulation mode refractory elements, which are complexed as oxides and silicates, potentially made them less susceptible to wet deposition in the far-field downwind plume than the more volatile and soluble elements. 2) Alternatively, the filter packs collected by Ilyinskaya et al., 2021 in the downwind plume were all ground-based. It is therefore possible that these ground-based filter packs actually sampled below, or at least in the lower section, of the volcanic plume, which grounded at these high elevation locations due to orographic effects (Delmelle, 2003). As such, if these ground-based filter pack samples actually represent compositions beneath or in the lower section of the plume, then the conclusions of the study may be inverted (and align with observations presented in Chapter 4). This would mean that refractory element concentrations are greatest in the lower section of the plume, due to more rapid sedimentation, whilst the more volatile elements are likely lofted to the much higher altitude portion of the plume, and thus only appear to have lower concentrations downwind because they are not being captured by the ground-based filter packs. By 30 – 100 km downwind, it is highly likely that the volcanic plume will have a very large diameter and thus that decoupling between PM of different size fractions and compositions may have occurred. Investigating the possibility of decoupling or stratification within the volcanic plume is a clear priority for future work and could be conducted using UAV-OPC transects as outlined in Section 6.1 or even atmospheric sampling balloons released upwards through the volcanic plume (e.g., Vignelles et al., 2016).

In Chapter 4 of this thesis, I also explore heterogeneous deposition within the volatile trace element fraction based on element speciation groupings. Under dry conditions, elements which preferentially bond with S (Se, Te, Sn) are lost more rapidly from the near-vent plume compared to those elements which bond with Cl (Cu, Rb, Cu). Previous studies have reported that S-gases are potentially scavenged more efficiently by silicate ash in explosive plumes (Rose, 1977; Witham et al., 2005; Delmelle et al., 2007), and thus it could follow that S-speciated elements may also be preferentially scavenged by ash in the near-vent plume. The underlying mechanism

for possible differences in uptake efficiency remains unconstrained, but is the focus of recent and ongoing investigations into high temperature gas-ash interactions (Ayriss et al., 2013; Ayriss et al., 2014; Delmelle et al., 2018). The observed fractionation between S and Cl-bonding elements is reversed when wet deposition is the primary process acting on the volcanic plume, with Cl-complexing elements then being lost more rapidly from the volcanic plume. There is no discernible size difference between S and Cl-bonding elements (Chapter 4, Figure 4.2), and thus it is unlikely that impact scavenging efficiency (which depends mostly on particle diameter; Cheng et al., 2021) could explain this difference. Previous studies have, however, found that *HCl* gas is more readily lost from volcanic plumes via wet depositional processes due to its higher solubility (Kawaratani and Fujita, 1990; Textor et al., 2003). This may therefore explain the preferential loss of Cl-complexing trace elements due to enhanced solubility-driven processes such as plume rain out (Cheng et al., 2021).

Several recent studies have also investigated precipitation-plume interactions and trace element deposition as rain falls through an effusive volcanic plume (Calabrese et al., 2011; Liotta et al., 2021). These studies notably do not see a clear fractionation between concentrations of volatile trace elements in precipitation samples based on S and Cl speciation groupings, possibly suggesting that scavenging by rain fall is a homogenous process (Calabrese et al., 2011; Liotta et al., 2021). The difference between these observations and the heterogeneous deposition behaviour reported in Chapter 4 of this thesis could be a key difference between rain and snow interactions within volcanic plumes. Rain and snow hydrometeors may result in a different balance of wash out (dependent mostly on particle diameter and thus no expected difference between volatile elements hosted in similarly sized PM) and rain out (solubility dependent and thus could result in a fractionation between Cl and S-complexed elements) processes.

Whilst this model of solubility-driven heterogeneous wet deposition of volatile elements remains relatively untested, it does offer a convincing, if preliminary, explanation for several geochemical signatures recently observed in polar ice cores. Edmonds et al. (2022) hypothesised that the decoupled chloride and sulfate signals in an ice core record from Antarctica, linked to the 17.7-ka eruption sequence of Mount Takahe (McConnell et al., 2017), could be due to the early localised deposition of volcanic chloride aerosols due to preferential loss via wet deposition processes during downwind transport. Using a series of ice cores from Greenland, Hutchison et al. (2024) also observed decoupled deposition of S and Cl between inland and coastal ice core sites following

the Icelandic Eldgjá eruption in 939 CE. They found that nssCl (non-sea-salt Cl) dominated volcanic fallout at the coastal ice core site (which was closest to Iceland) whilst at inland ice cores, nssS (non-sea-salt S) and nssCl were roughly equivalent. They hypothesise that this could be due to more rapid scavenging of the Cl aerosol along the coast due to the wetter local atmospheric conditions (Hutchison et al., 2024). The framework outlined in Chapter 4 provides clear support for these hypotheses by providing the first direct measurement of heterogeneous speciation-driven deposition of trace elements within an effusive volcanic plume as it is dispersed downwind.

6.4.1 Suggestions for Future Work

The work presented in Chapter 4 is one of the first studies to attempt to directly compare trace element deposition under different meteorological conditions using in-situ volcanic plume sampling. The resulting framework, which outlines potential mechanisms of heterogeneous deposition, is however, solely based on data from the Fagradalsfjall 2021-2023 eruptions and thus its applicability to other global volcanoes remains untested (although plausible given the proposed mechanisms are fundamental principles across the fields of atmospheric chemistry and physics). Future studies at other global volcanoes to directly measure trace element deposition are therefore needed to refine and generalise this framework further. More data, for example, from low latitude eruptions would be particularly useful given the pronounced differences in background conditions compared to the high latitude Icelandic atmosphere. Use of emerging UAV sampling should facilitate these studies and further improvements in UAV technologies (e.g., UAVs that could fly despite precipitation) may unlock even more possibilities for directly measuring active depositional processes in volcanic plumes. On a theoretical level, improved constraints on the link between element speciation (facilitated firstly by a better understanding of element speciation changes during downwind transport; Section 6.2) and in-plume aerosol properties (e.g., water solubility, ash adsorption affinity) would also substantially strengthen the framework presented in Chapter 4. Volcanic trace element solubility has been estimated by several previous studies (Mather et al., 2012; Ilyinskaya et al., 2021) and in Chapter 4 of this thesis, but these calculations are based on water extraction solubilities under laboratory conditions, meaning their applicability to volcanic plume conditions (e.g., low pH, high temperatures) is somewhat limited. Improved experimental constraints on volcanic trace element solubilities under plume conditions could therefore provide further insight into the wet deposition behaviours of volatile

volcanic trace elements.

Future work may also consider the impacts of heterogeneous deposition on the delivery of trace elements to the surface, including potential implications for population exposure to heavy metal pollutants. The meteorologically dependent trace element deposition observed at the Fagradalsfjall 2021-2023 eruptions raises the possibility of seasonal variations in trace element deposition around other long-lived degassing volcanoes that are situated in regions with strong seasonal weather variations (e.g., Masaya). Such processes could be investigated through long-term monitoring of hydrological and biological reservoirs, which may experience variable delivery of trace elements between wet and dry seasons (and also via wet and dry transport pathways). Additional ice core datasets could also consider not only sulfate and chloride peaks but also directly compare trace element concentration ratios to better constrain the impact of heterogeneous deposition on far-field trace element dispersion and the atmospheric lifetimes of volatile volcanic trace elements.

6.5 Interactions with Non-volcanic Emissions

In Chapter 5 of this thesis, I explore the interactions that occurred upon mixing between volcanic aerosol and wildfire smoke emissions. Lava-ignited wildfires were generated at the Litli-Hrútur eruption in Iceland in 2023 and, alongside being the largest wildfires in recorded memory in Iceland, they also contributed an additional compounding air quality hazard to the air pollution released by the eruption (Wainman et al., 2026). The work presented in Chapter 5 was conducted as part of an emergency response air quality monitoring campaign, led by the Icelandic Meteorological Office and requested by Icelandic civil defence and health protection agencies. The immediate results of this monitoring survey informed choices made by civil defence and health protection agencies around managing public access to the eruption site and resulted in stronger messaging about the need for respiratory protection given the high levels of PM_{10} and $PM_{2.5}$ air pollution (Chapter 5, Figures 5.6-5.9). Subsequent microscopy and geochemical analysis of the mixed PM revealed extensive interactions between the volcanic aerosols (both the primary silicate and secondary non-silicate fractions) and wildfire PM (composed primarily of partially combusted moss fragments). Interactions included the agglomeration of volcanic and wildfire PM to form larger particle clusters of mixed composition and origin, and the scavenging of smaller volcanic PM between the fibres of the larger moss particles. These interactions

occurred very close to the emission interface, where lava flows were directly burning the moss, and continued hundreds of meters downwind in the mixed plume as it was dispersed. Preliminary results from TEM-EELS transects spanning the edge to the interior of the moss suggested there may also have been interactions between moss PM and the much finer volcanic aerosols. This interaction may account for enrichment of volatile volcanic species (S, Cl, volatile metals) in surface layers of the moss particles, although it remains to be determined if this uptake of volcanic species from the air occurred prior to burning, whilst the moss was still growing or if it occurred post-burning during mixing in the airborne plume.

The interactions between volcanic and wildfire PM identified in Chapter 5 have implications both for understanding the dispersal and delivery of volcanic trace elements to the environment, as well as for constraining and mitigating population exposure to dangerous pollutants. Scavenging and agglomeration processes resulted in increased particle size distributions via particle clustering and the removal of the smaller PM size fraction via scavenging (Chapter 5). Akin to scavenging by volcanic ash (Witham et al., 2005; Delmelle et al., 2007), this could provide an additional deposition pathway for volcanic trace elements in the near-vent environment through enhanced gravitational settling of the larger moss particles. This could increase total particle concentrations close to the eruption site, potentially heightening exposure for visiting tourists and emergency workers; however, it could also reduce the overall downwind dispersal of volcanic aerosols and lessen far-field population exposure. Increased diameters could also reduce the overall respiratory penetration efficiency of some hybrid PM compared to PM from a stand-alone volcanic eruption, although the net health impacts of exposure to hybrid volcanic-wildfire PM with altered physicochemical properties remain very poorly constrained due to lack of observational or experimental data (e.g., toxicology co-exposure studies; Tomasek et al., 2016).

6.5.1 Suggestions for Future Work

Volcanically ignited wildfires are likely to become more frequent over the coming decades due to worsening global warming and changing weather patterns (although impacts will be regionally specific; Mansoor et al., 2022). Future studies on the impacts of compound volcanic-wildfire events, on overall hazard risk (Fink and Ajibade, 2022), ecosystem health (Schiffmann et al., 2025), and air quality (Wainman et al., 2026) are therefore vital for successful preparation and response planning. To date, the work presented in Chapter 5 has been the only attempt to study the physical and chemical interactions that occur upon mixing between volcanic and

wildfire PM and to constrain the air quality impacts of such an event. The scope for future study is therefore extensive. This includes, for example, collecting additional direct measurements of mixed volcanic and wildfire emissions to test if the mechanical interactions identified in Chapter 5 occur in other global contexts. It is highly probable that some of the mixing interactions identified in Chapter 5 are specific both to the volcanic products that cause ignition (including lava flows, ballistics, pyroclastic material) as well as the ecosystem in which the volcanic wildfire occurs (i.e., moss and peat heathlands are likely in high latitudes such as Iceland, whereas forests, grasslands, or even agriculturally managed fields are more common at lower latitudes). The use of fire as a land management tool and/or for agricultural clearing in proximity to active volcanoes (e.g., in Guatemala, smoke from slash and burn fires compounded volcanic air quality impacts during the 1998 eruption of Pacaya; Global Volcanism Program, 1998) could also present a complex case study of geochemical, physical, and human-volcano interactions.

In Chapter 5 of this thesis, mixing between volcanic and wildfire emissions was studied primarily from the perspective of mechanical/physical interactions between particles. Chemical reactions between volcanic gases (SO_2 , CO_2 , HCl , H_2S , HF) and volatile trace elements and the reactive species released during wildfires (NO_X , $VOCs$, CO) are also highly likely to have occurred, with significant implications for regional or even global atmospheric chemistry, but remain unconstrained. For example, organic and sulfate emissions from the 2020 Australian wildfires were found to increase the solubility of HCl gas and thus act as an additional site for Cl activation, which contributed to enhanced ozone destruction in the stratosphere (Solomon et al., 2023). The additional flux of volcanic HCl gas during compound volcanic-wildfire events could potentially enhance this reaction pathway further and lead to worsening outcomes for both stratospheric ozone destruction and tropospheric ozone pollution. Future studies aiming to constrain these chemical reactions during compound events could do so using a variety of approaches: through direct measurements (e.g., using UAV-mounted thermal desorption tubes to measure VOC concentrations or collect gas bag samples), through experimental studies (e.g., chamber experiments could be used to isolate reactions between specific chemical species under UV light), and, perhaps most comprehensively, through modelling. For example, the Unified Model (UM; Walters et al., 2019) can be configured to run both the UK Chemistry and Aerosol scheme (UKCA; Abraham et al., 2012) and the INFERNO (Mangeon et al., 2016) fire model. Although it has not been configured to date, this combined set-up could reasonably be used to simulate a volcanically ignited wildfire event and model the resulting chemical reactions in the

atmosphere. Modelling could be used to explore the effect of vegetation types (contained within the INFERNO model) as well as the implications for atmospheric chemistry, depending on if mixed emissions were constrained locally within the troposphere or if, perhaps due to a larger eruption or thermal lofting from the wildfires, mixed emissions reached higher altitudes and thus had more widespread effects on global stratospheric chemistry.

Finally, the interactions between volcanic and wildfire PM observed at the Litli-Hrútur 2023 eruption and presented in Chapter 5 of this thesis, also highlight the possibility of volcanic aerosols interacting with emissions from other external sources as they are dispersed downwind. Growing urbanisation and industrialisation in proximity to active volcanoes (Chester et al., 2000) means it is increasingly likely that volcanic emissions, whether from passively degassing volcanoes or during discrete events, are likely to encounter and mix with anthropogenic emissions (such as from coal combustion, metal smelting, vehicle emissions, and other industrial processes; Zhu et al., 2020). Volcanic-urban emission interactions were reported by Raga et al. (1999) who found that aerosol compositions in Mexico City were influenced by SO_2 emissions from Popocatepetl volcano (~ 60 km away). They suggested that SO_2 emissions from Popocatepetl may have been incorporated into particulates collected in Mexico City via two possible pathways: 1) adsorption onto existing particulates in the already polluted atmosphere (akin to scavenging of volcanic aerosols by moss PM presented in Chapter 5), or 2) incorporation into cloud and/or fog droplets (similar to the in-plume rain out processes explored in Chapter 4 of this thesis). Mixing between volcanic and anthropogenic emissions is likely to result in a vast number of different physical and chemical reactions, owing to the wide array of reactive species contained within both emission types, with implications for pollutant transport, environmental processing, and health impacts in exposed populations. Volcanic-anthropogenic aerosol interactions have already been demonstrated to span a range of mediums and contexts; Trejos et al. (2021) demonstrated a volcanic contribution to the composition of nanoparticles and ultra-fine road dust in Manizales, Colombia and López-Darias et al. (2025) reported enhanced volatilisation of ammonia compounds as lava flows inundated agricultural soils during the 2021 Tajogaite eruption on La Palma. Such examples highlight the wide variety of interactions that are likely to become more frequent over the coming decades as human industry encroaches on active volcanoes, as well as the importance of cultivating a sustainable relationship between humanity and one of the mightiest forces of the natural world: volcanoes.

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Supplementary A

A.1 Supplementary Note 1: WAF Correction.

To constrain the concentration of elements in the non-silicate aerosol phase (i.e not contained in ash or dust) a weighted ash fraction (WAF) correction was applied to filter pack samples in this study. The ash correction assumes that the concentration of volatile element A, on the filter is derived from two components, silicate ash and dust, and non-silicate aerosol (see eq. A.1). Although the plume was gas-rich with minimal visible ash, the correction accounts for sub-micron ash and dust which may have been collected on the filters.

$$[A]_{filter} = [A]_{ash} * X_{ash} + [A]_{aerosol} * (1 - X_{ash}) \quad (A.1)$$

Where X_{ash} is the proportion of silicate ash phase on the filter and $X_{aerosol}$, the proportion of aerosol on the filter is $1 - X_{ash}$. If element A is a lithophile/refractory element we can assume that the proportion of this element in the aerosol phase is zero ($X_{aerosol} = 1 - X_{ash} = 0$), allowing equation A.1 to be simplified to:

$$X_{ash} = \frac{[A]_{filter}}{[A]_{ash}} \quad (A.2)$$

X_{ash} for each sample may then be calculated by using the average of four refractory elements (Fe, Mg, Mn, Ti). Figure S1 below shows X_{ash} for each eruption year and sample. Multiple elements were tested as potential reference elements, although some (such as Na and K) were excluded on the basis of showing some volatile behaviour (and hence not fulfilling the condition that $X_{aerosol} = 0$). Across all samples used in this study X_{ash} , which is the proportion of ash on the filter was $< 1 \times 10^{-3}$ (see Supplementary A Table S2). Using an average of four major

elements as our reference elements is also beneficial as their higher concentrations (relative for example to REE) in silicate material allow smaller ash concentrations to be resolved. Weighted ash fractions for each element (WAF) can then be calculated for the remaining elements in each sample using eq. A.3 and inputting X_{ash} as calculated above for each sample:

$$WAF = 100 * \frac{X_{ash} * [A]_{ash}}{[A]_{filter}} \quad (A.3)$$

Note that this means that whilst the proportion of ash on the filter may be low ($< 10^{-3}$) the WAF (contribution from ash for that specific element on the filter) may still be high, particularly for refractory elements (generally $< 90\%$). It was not possible to precisely align petrological data from down flow lava samples with individual aerosol samples (i.e collected on the same day or at the same distance from vent), and therefore lava samples were matched temporally as closely as possible to the timing of aerosol sample collection. Applying a generalized ash correction with a single ash composition for all samples (i.e the same for both at-vent and at increasing distance down flow) also does not account for variation in ash composition as the lava flow evolves down-flow. Supplementary figure S7 shows a direct comparison of non-ash corrected and corrected element concentrations, with negligible difference between them.

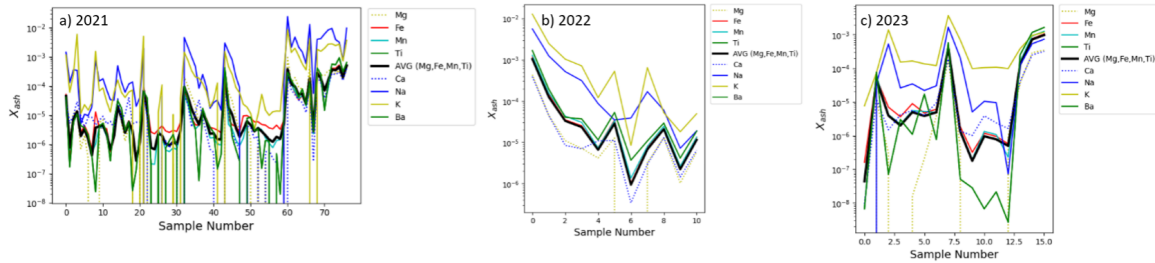


Figure A.1: X_{ash} , the proportion of ash on each filter, calculated using WAF correction outlined above using different reference elements. Results are for all samples collected for each eruption year. Across all samples used in this study $X_{ash} < 10^{-3}$.

A.2 Supplementary Note 2: Emanation Coefficients

Emanation coefficients (ϵ_x) describe the degree to which an element is degassed from silicate melts into a vapour phase:

$$\epsilon_x = \frac{([X]_i - [X]_f)}{[X]_i} \quad (A.4)$$

where $[X]_i$ is the initial concentration of X in the melt, and $[X]_f$ is the final degassed concentration of element X in the melt (originally defined by Lambert et al. (1985)).

In this project, emanation coefficients (ϵ_x) are calculated using the measured composition of the volcanic plume (gas and PM), combined with the composition of degassed matrix glasses:

$$\epsilon_x = \frac{([X]_i - [X]_f)}{[X]_i} = \frac{[X/Y]_{plume} * Y_{degassed}}{[X/Y]_{plume} * Y_{degassed} + X_{MG}} \quad (\text{A.5})$$

where X is the element of interest, and Y is S. X_{plume} is the concentration of element X measured on particulate filters (corrected for ash, as above); Y_{total} is the total S measured on filter pack particulate and gas filters; and $Y_{degassed}$ is the concentration of S degassed during subaerial eruption (determined by comparison of melt inclusion and matrix glass compositions). X_{MG} is the concentration of element X remaining in the degassed matrix glass.

This approach assumes that the concentration of elements in the melt, and their degassing, scales linearly with S or Cl, which is likely to be a reasonable approximation in most cases. Note also that emanation coefficients are calculated using silicate-corrected plume composition data, and therefore these emanation coefficients are relative, i.e., during the ash-correction elements used to calculate X_{ash} are assumed to be only present in a silicate phase, and therefore these elements have emanation coefficients of zero (or close to zero) but may degas in the gas phase to a limited extent.

Emanation coefficients for the Fagradalsfjall 2021 eruption are included in Supplementary Sheet A13.

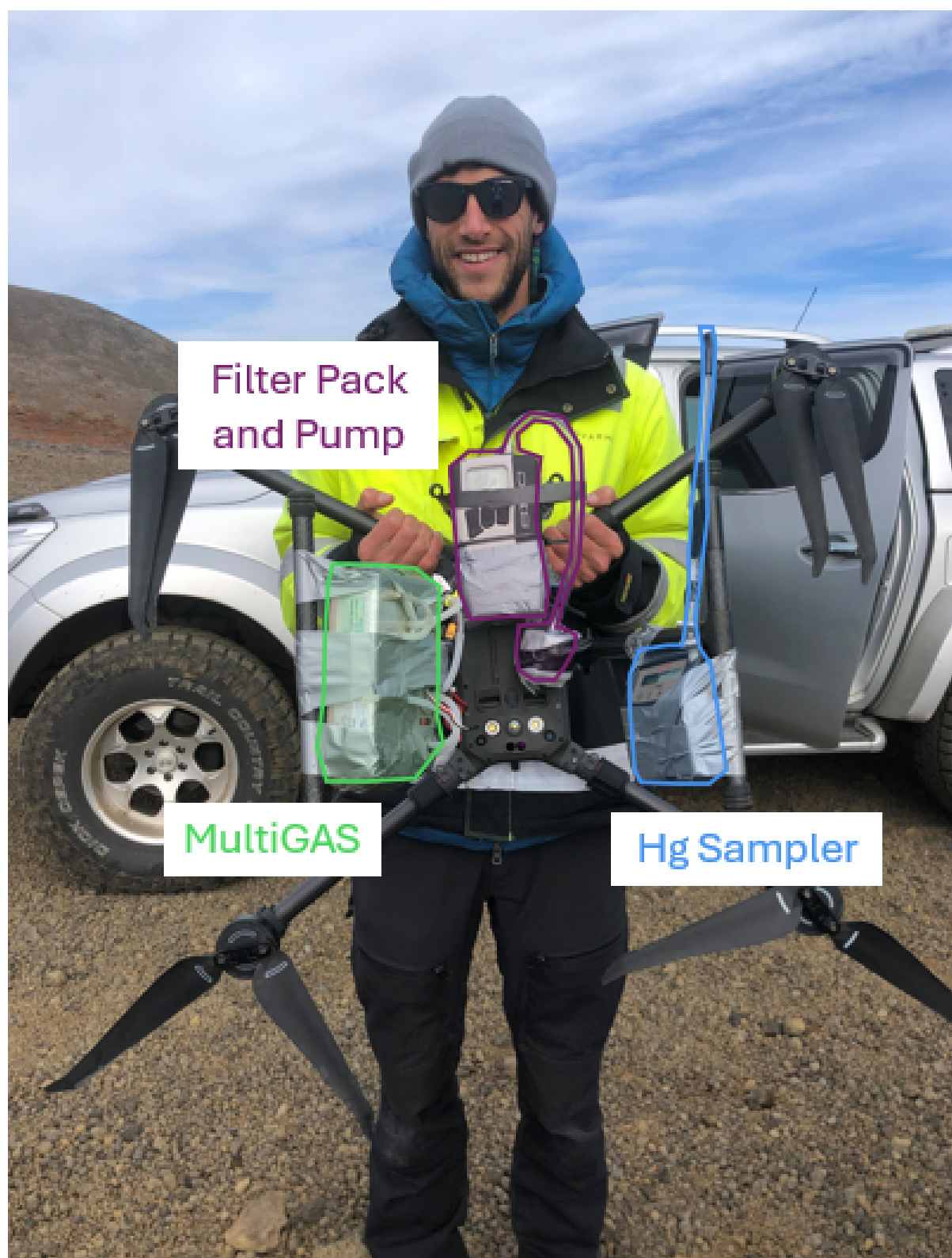


Figure A.2: Instrument Set up on M300 DJI UAV during 2022 campaign. Left to right: MultiGAS ($SO_2/CO_2/H_2S$), Filter pack + Leland Legacy pump, Hg Sampler (data used in Edwards et al. (2024)).

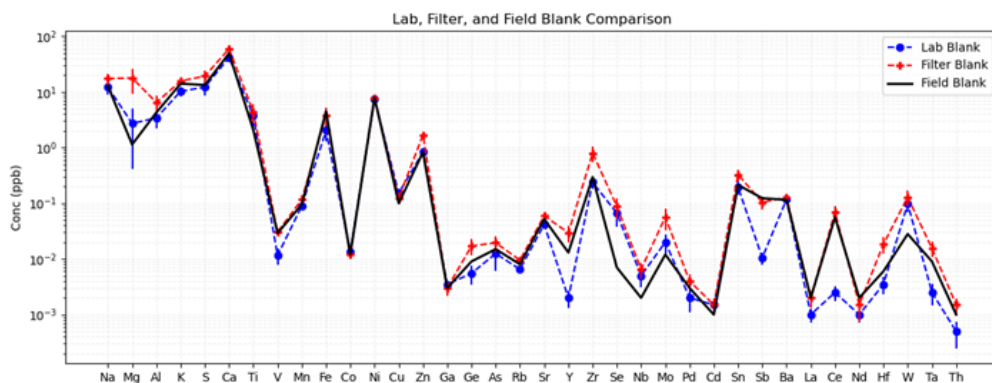


Figure A.3: Lab and filter blanks were averages of multiple blanks run during the extraction process to measure potential contamination either from the PTFE filters or during the extraction process within the lab. The field blank was a PTFE filter from loaded but unused filter pack taken into the field to assess potential contamination from sources in the field – i.e., through handling or dust particles etc.

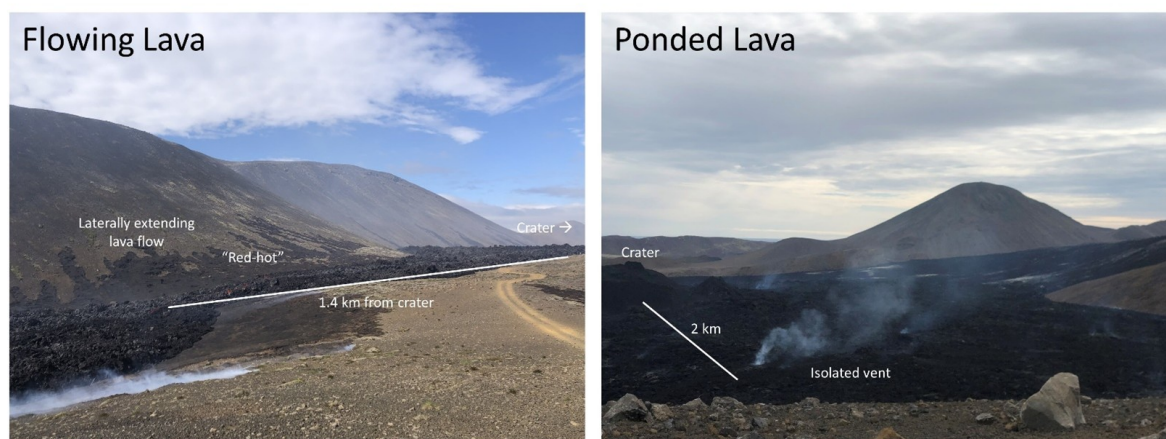


Figure A.4: Annotated photos of example lava flows above which samples were collected. “Flowing lava” shows flow above which sample LHFP4 was collected in 2023 and “Ponded lava” shows the isolated vent above which sample LW17 was collected in 2022.

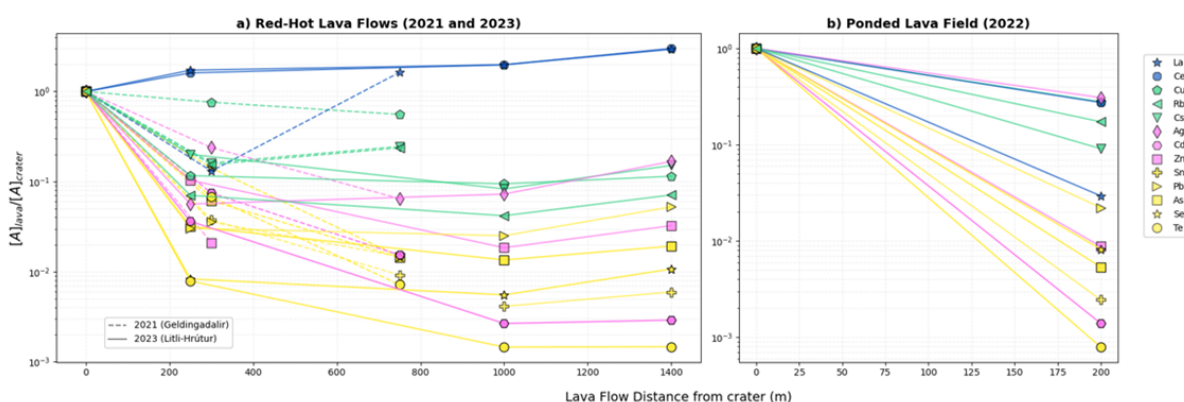


Figure A.5: Ash corrected version of Figure 3.3. WAF correction has been applied to element concentrations $[A]$. Lava flow concentration $[A]_{lava}$ is normalized to source concentration $[A]_{crater}$. The same general trends can be seen as in Figure 3.3, with sulfur-complexing elements depleting more rapidly than chloride, oxide and hydroxide complexing elements.

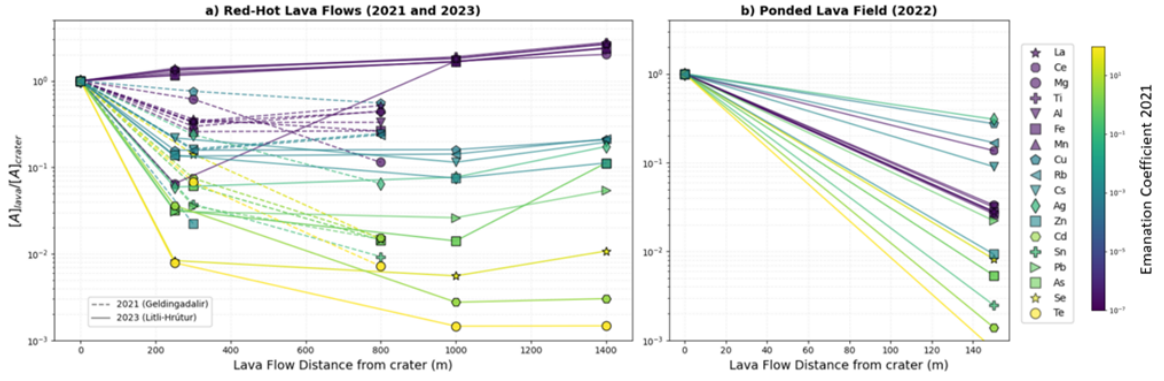


Figure A.6: Figure 3.5 as in main text but elements are coloured by emanation coefficient (coefficients in Supplementary Sheet A13), rather than element speciation behaviour as in main text. Volatility and speciation are closely linked so it is unsurprisingly that element behaviour can be similarly grouped by relative volatility, with the more volatile elements depleting most rapidly as they are more readily volatilised from the melt and lost further upstream. Nonetheless, as discussed in the main text, some element behaviour cannot be explained by volatility alone, but rather by common speciation behaviour between elements of varied volatility.

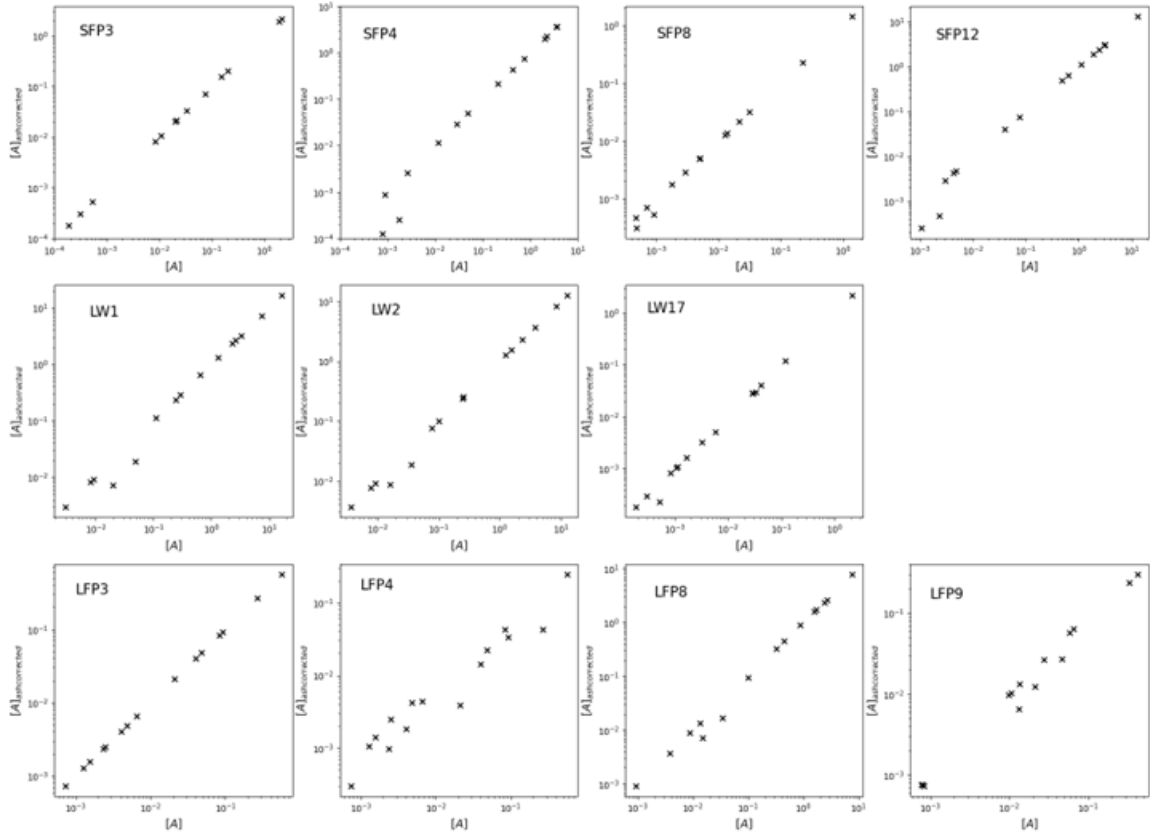


Figure A.7: Comparison of ash-corrected $[A]_{corrected}$ and non-ash-corrected element concentrations. For volatile elements considered in this study, applying an ash correction has a very small effect on element concentrations which mostly plot on a 1:1 line. The most impacted elements are La and Ce which are the two most refractory elements and therefore present in the silicate ash component.

Sample ID	X_{ash}
2021	
SFP3	7.5e-06
SFP4	1.3e-05
SFP8	3.8e-04
SFP12	7.0e-05
2022	
LW1	1.03e-03
LW2	1.25e-04
LW17	6.7e-06
2023	
LHFP3	9.8e-04
LHFP4	7.17e-04
LHFP8	4.04e-04
LHFP9	4.5e-05

Table A.1: X_{ash} on filter pack samples calculated using weighted ash fraction (WAF) correction outlined in Supplementary Note A1.

Sample	Temperature Constraint (°C)			
	Helz and Thornber (1987)	Putirka (2008)	Putirka (2008)	Sugawara (2000) Eq 6a
	MgO SD = $\pm 71^\circ\text{C}$	Eq 15 SD = $\pm 26^\circ\text{C}$	Eq 22 SD = $\pm 29^\circ\text{C}$	SD = $\pm 30^\circ\text{C}$
G20230710-1a	1164	1185	1179	1179
G20230719-1	1164	1185	1180	1180
G20220803-2	1165	1187	1182	1182
G20220805-4	1162	1184	1178	1180
G20210405 -2gr3_glass	1171	1191	1184	1186
G20210405 -2gr4_glass	1164	1184	1175	1178
G20210405 -2gr9_glass	1172	1192	1184	1185
G20210405 -2gr31_glass	1173	1193	1185	1187

Table A.2: Calculated temperatures using a variety of liquid-only thermometers. Calculations were performed using Thermobar (Wieser et al., 2022).

Supplementary B

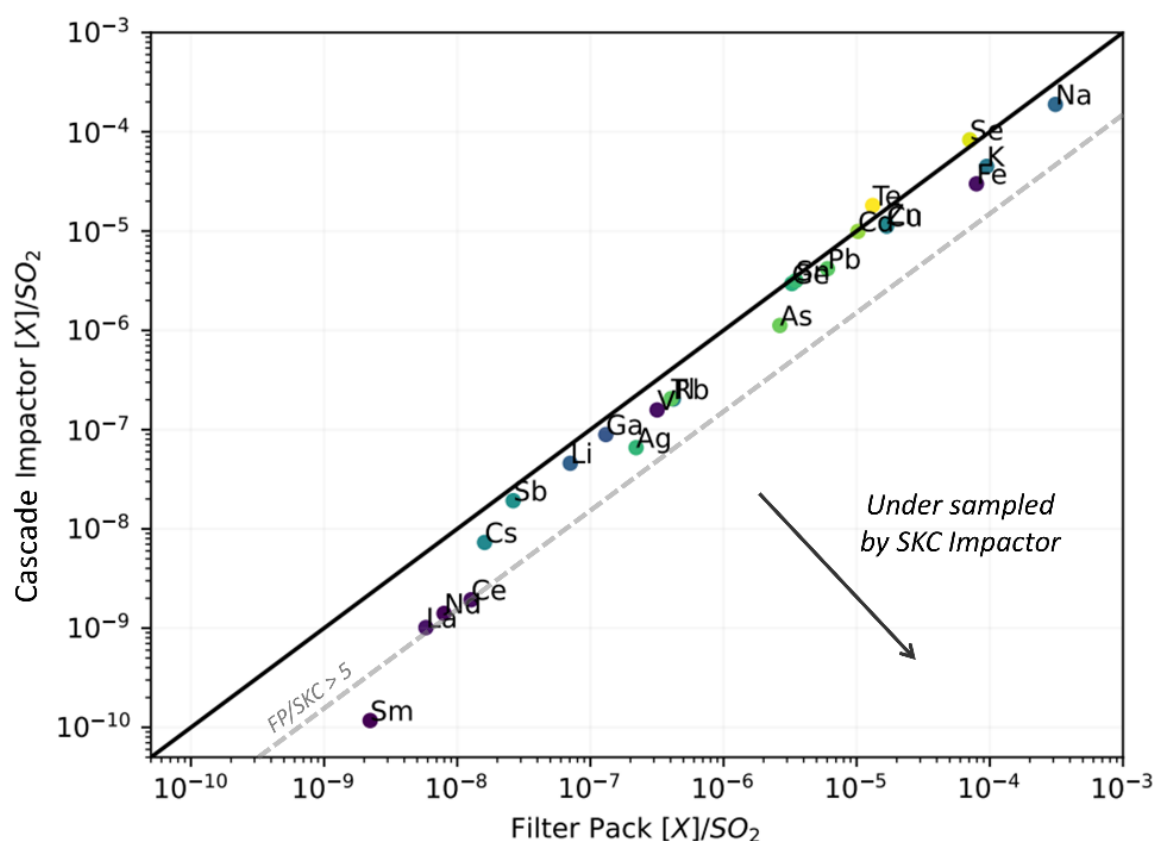


Figure B.1: Comparison of cascade and filter pack sampling element distribution. Y-axis shows $[X]/[SO_2]$ summed across all stages of a cascade impactor sample SMSKC1. X-axis shows $[X]/[SO_2]$ for FP sample SFP12. Both samples were collected in the main plume above the crater during the 2021 Fagradalsfjall eruption within Phase II of the eruption (~ 6 days apart). Dashed grey line denotes the filter pack $[X]/[SO_2]$ being 5 times greater than that of the SKC sample. Elements that lie on the solid black line have a FP/SKC ratio of 1 and are thus sampled equally by both techniques. The cascade impactors are therefore potentially under-sampling PM on the coarsest stages. This can be explained by increased wall deposition in the coarsest stages, which means elements such as Al (which are predominantly recorded in the coarsest PM fraction) being under-reported in cascade impactor samples. See Berlinger et al. (2021) for further discussion of wall deposition in cascade impactors.



Figure B.2: Lava pond with active outgassing vents. Photo (taken by L. Wainman) showing the Meradalir vent during the 2022 Fagradalsfjall eruption, with the surrounding lava pond and outgassing vent in the foreground.

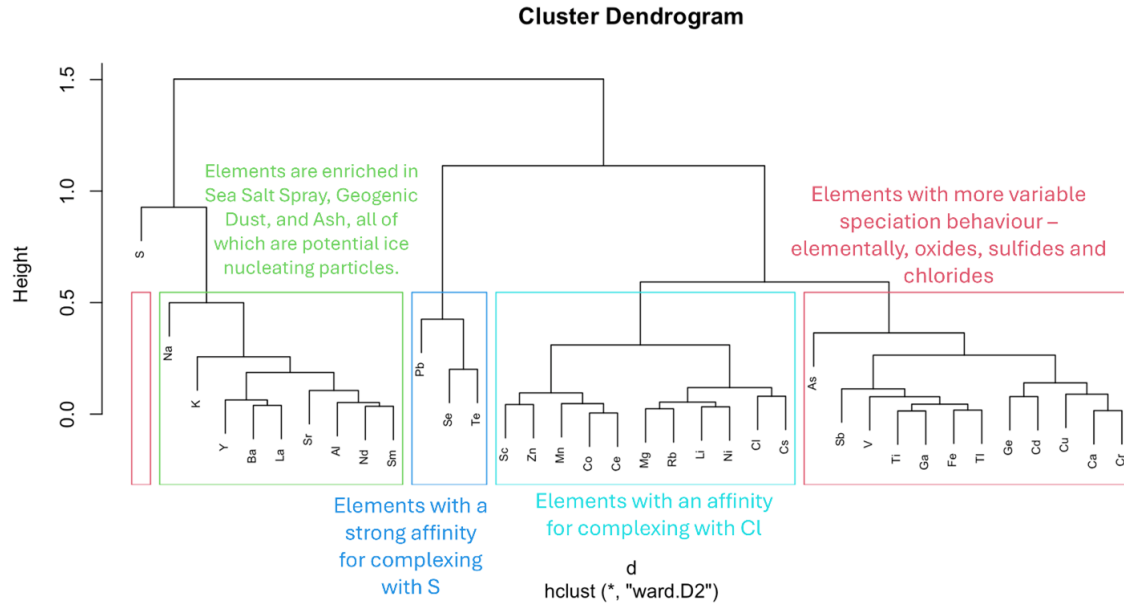


Figure B.3: Cluster analysis of the snow samples collected along a downwind transect at the 2021 eruption. Elements are treated as the observations and the samples as the variables. Snow sample concentrations (ppb) were converted to their standard scores (z-scores). Ag and Sn were omitted as they did not have a complete set of measurements. Then dist function in R was then used to calculate the euclidean distances between all samples and the hclust function for hierarchical cluster analysis.

Note on Cluster Analysis Approach:

We invert the traditional clustering approach to make the variables (the element compositions) the subject of the analysis rather than the samples (which are used here as variables). A clustergram is the visual output of cluster analysis, and groups variables according to their degree of similarity in multivariate space. Agglomerative clustering algorithms group the most related variables first, and then progressively reduce the number of clusters at each hierarchical level from n clusters of size 1, to one cluster incorporating all observations (i.e. a tree structure). The Ward method of minimum variance (Ward, 1963) creates clusters at each step that minimize the increase in the error sum of the squares, and is the approach adopted here.

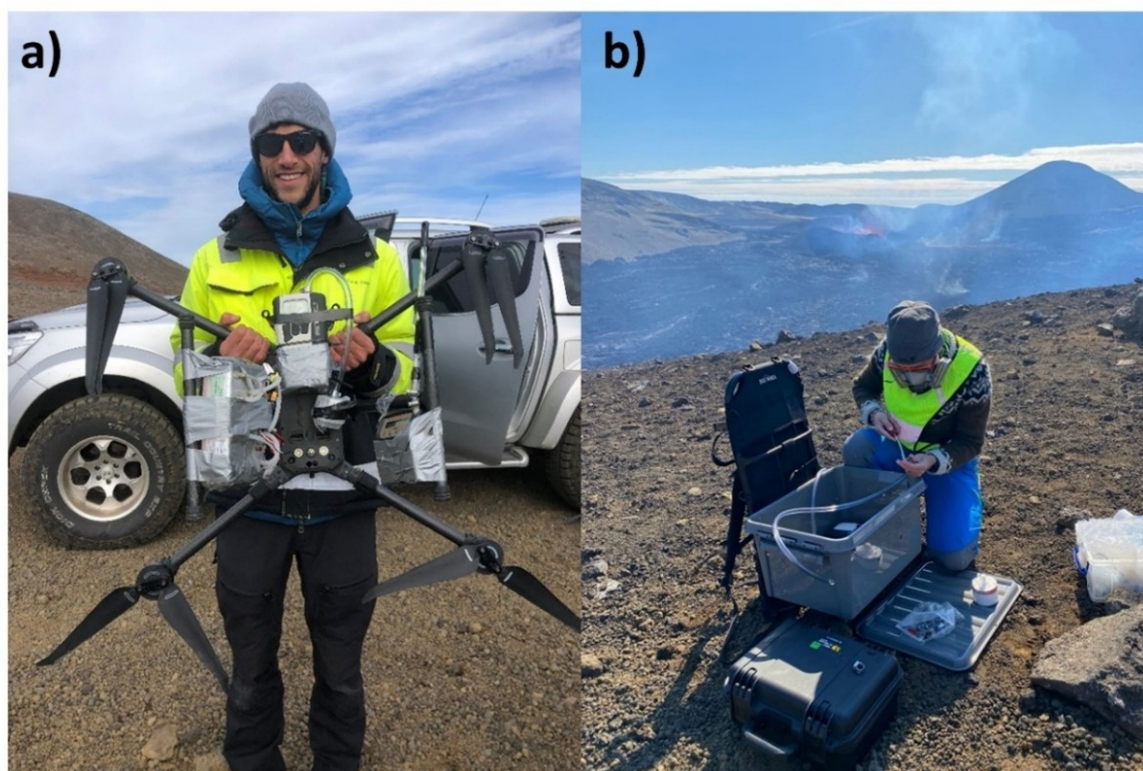


Figure B.4: UAV and Ground-based sampling set up at the 2022 Fagradalsfjall eruption. Both set ups consist of a FP or cascade impactor connected via tubing to a Leland Legacy air pump. Simultaneous MultiGAS measurements were collected with both samples.

Sample ID	Sampling Date	Sample Set Up	Sampling Location	Distance from vent	Total Volume Pumped (L)	Plume Volume Pumped (L)	Plume Sample Duration (mins)	Flow Rate (L/min)	Number of Flights	% flight above SO_2 saturation
SFP4	23rd March 2021	FP (3G + PM) and MG	At-vent	<80 m	117	117	20	6	1	0
SFP12	13th April 2021	FP (PM Only) and MG	At-vent	<80 m	621	493	55	9	4	2
SMSKC1	6th April 2021	SKC Impactor and MG	At-vent	<80 m	423	310	35	9	3	0
LW1	16th August 2022	FP (PM Only) and MG	At-vent	<80 m	850	830	62	13.5	3	9.4
LW2	16th August 2022	FP (PM Only) and MG	At-vent	<80 m	202	176	14	13	1	15
LW3	16th August 2022	FP (PM Only) and MG	Airborne Plume	500 m	629	582	45	13	2	0

Sample ID	Sampling Date	Timestamp	Sample Type	Distance from vent	Latitude	Longitude
S-01	9th April 2021	2021-04-09 T12:17:05Z	Snow	350 m	63.89153201	22.26369001
S-02	9th April 2021	2021-04-09 T12:31:54Z	Snow	650 m	63.88890504	22.26180098
S-03	9th April 2021	2021-04-09 T13:09:19Z	Snow	900 m	63.88591798	22.26417096
S-04	9th April 2021	2021-04-09 T13:26:57Z	Snow	1300 m	63.88216498	22.26290798
S-05	9th April 2021	2021-04-09 T13:56:31Z	Snow	1600 m	63.879019	22.26031302

Table B.1: Sample Overview. Includes FP, SKC, MultiGAS, and snow sample metadata.

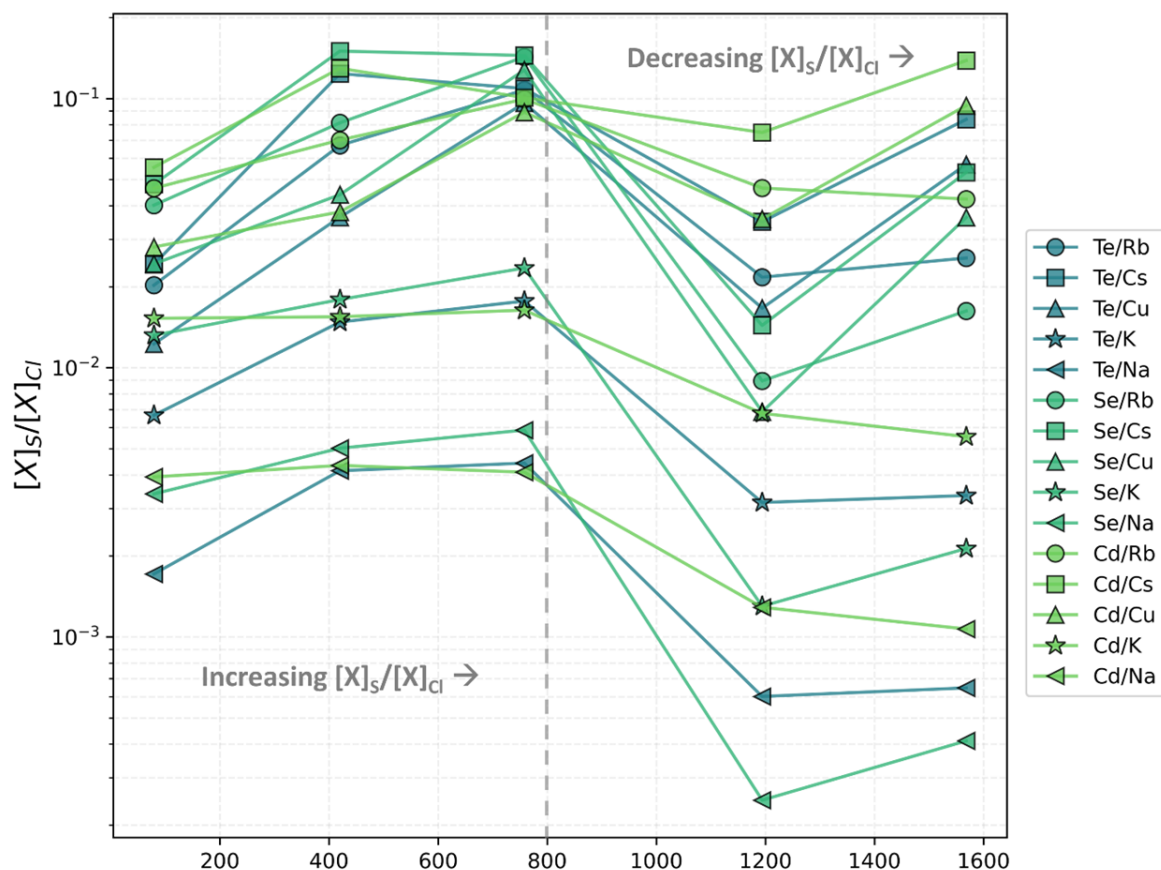


Figure B.5: $[X]_S/[X]_{Cl}$ ratios in snow samples downwind. Element concentration ratios were calculated for a range of S and Cl-complexing elements to assess their relative rates of deposition and depletion from the plume. Assuming that the scavenging rate for Cl species, λ_{Cl} , exceeds that of S species, λ_S , the ratio of the amount of each species deposited D_S/D_{Cl} would be expected to be < 1 but to increase with distance from the vent as the Cl-species are lost more rapidly from the plume. D_S/D_{Cl} is < 1 and shows a generally increasing trend across all elements within the first 800 m away from the vent, consistent with preferential wash out of Cl-complexing elements.

Particle Diameter, d (μm)	Particle Density, ρ_p (kg/m^3)	Settling time
100	1000	88 seconds
100	2000	44 seconds
10	1000	2.4 hours
10	2000	1.2 hours
1	1000	10 days
1	2000	5 days
0.1	1000	2.8 years
0.1	2000	1.4 years

Table B.2: Settling times over 30 m in air for particles of varying diameters and densities calculated using Stoke's Settling Law (eq B.1). Density of air, $\rho_a = 1.204 \text{ kg/m}^3$, $g = 9.81$, dynamic viscosity of air, $\eta = 1.6 \times 10^{-5}$

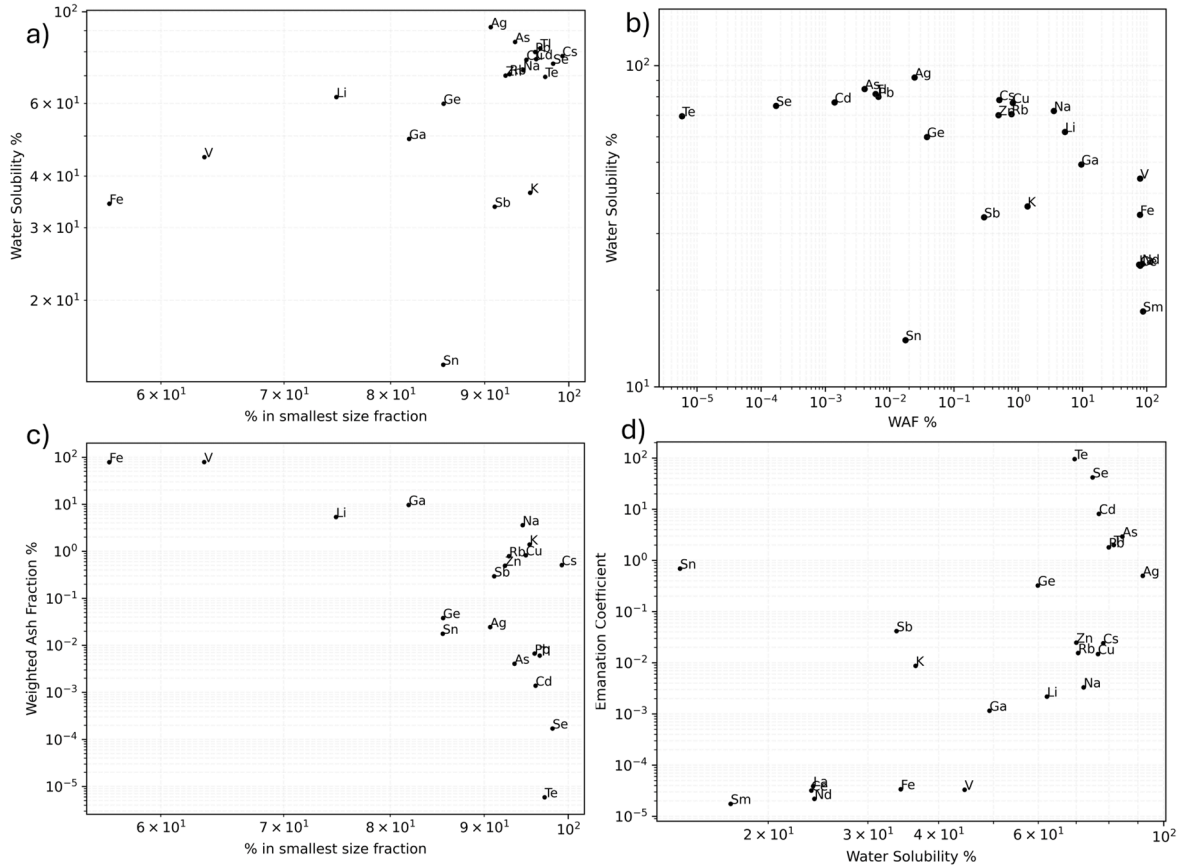


Figure B.6: Comparison of element-by-element PM characteristics. A) water solubility vs mass % of each element in the smallest impactor size bin. Elements which are predominantly hosted in the smallest size fraction generally have relatively higher water solubilities than those which are hosted in the larger size fractions. B) water solubility vs weighted ash fraction (WAF). At WAF > 1 % water solubility begins to decrease. Sn is an exception, having low WAF and also low water solubility. C) WAF vs mass % in the smallest size fraction. Elements hosted in the smallest size fraction generally have the lowest ash contribution (as ash, being formed mechanically, has a larger size distribution than aerosol PM which is formed through gas-particle conversion processes). D) Emanation coefficient (which represents magmatic volatility) vs water solubility. Generally, water solubility increases with increasing magmatic volatility. However, the most volatile elements (Te, Se) are not the most soluble (Ag, Rb, Cs).

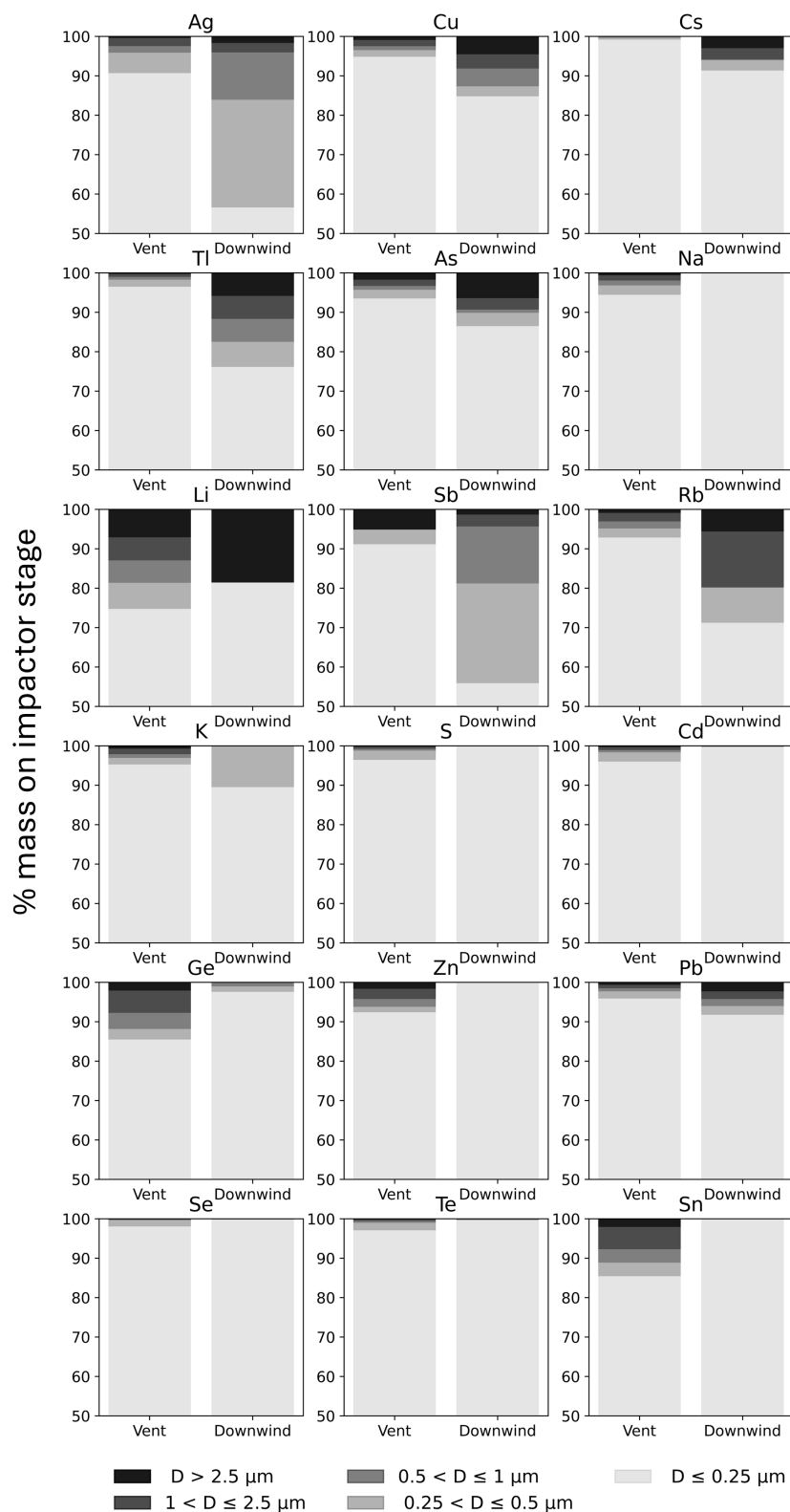


Figure B.7: Comparison of element size distributions in at-vent and downwind impactor samples. Grey scale shows the % mass of each element detected on each stage of the impactor, respectively.

Supplementary C

C.1 Additional Details on Filter Pack Configuration, Pre-treatment and Extraction Procedure

The 4-stage filter packs were used in two different configurations: either containing just one filter for particulate matter (PM collection (PM Only; filter specifications: WTP polytetrafluoroethylene (PTFE) 47-mm diameter, pore size $1.0\ \mu\text{m}$ (WhatmanTM)) or with an additional 3 filters loaded behind the first PM filter for gas collection (PM + 3G, gas filter specifications: Millipore 47-mm diameter absorbent pads). The filters for gas collection were impregnated (5% KOH + 1% glycerol) shortly prior to use (as used in Ilyinskaya et al. (2021) and Mason et al. (2021)). Base treatment of gas filters allows for the capture of acidic gases such as SO_2 , HCl and HF by reaction and conversion to their anions SO_4^{2-} , SO_3^{2-} , Cl^- , and F^- . No gas filters exceeded the saturation threshold of $> 10\%$ of total SO_4^{2-} being present on the final gas filter stage (as defined by Mason et al. (2021) and used by Wainman et al. (2024)). Airflow through the filter pack was generated using an SKC Leland Legacy pump, also mounted on the UAV. The flow rate was set to the highest value that the pump was able to sustain (9 – 10 L/min). The highest sustained flow rate varied according to which filter set up was used (i.e., 1 or 4 filters loaded) and was also sensitive to the curvature of the connective tubing between pump and filter when mounting the equipment on the drone. Immediately after sampling, filter packs were sealed using Parafilm to prevent particle loss and contamination and stored at ambient temperatures during transport. See the electronic supplement sheet C1 for filter pack trace element data.

The filter pack and impactor samples were handled in a Class-10000 (ISO 7) clean laboratory environment at the Institute of Earth Sciences, University of Iceland and the School of Earth and Environment, University of Leeds. Filters were cut into quarters, with 7-14% by mass retained

for SEM analysis (see Section 2.2.2) and the remaining filter material transferred to acid-cleaned 50 ml centrifuge tubes using acid-cleaned metal-free scissors and tweezers to begin the extraction process. Whole gas filters were leached in 20 ml Milli-Q ($> 18.2 \text{ M}\Omega$, MQ) water and $250 \mu\text{l}$ H_2O_2 (to oxidize collected sulfur species to sulfate) and then shaken for 20 mins. 1.5 ml from these solutions was pipetted for anion concentration measurements by ion chromatography (IC) at the Department of Geography, University of Leeds (on Thermo Dionex ICS5000) and Institute of Earth Sciences, University of Iceland (on Thermo Dionex ICS2000).

Material collected on PM filters was extracted using a two-stage sequential leaching method (as used in Ilyinskaya et al. (2021) and Wainman et al. (2024)). The water-soluble PM fraction was first extracted in 20 ml MQ water + $200 \mu\text{l}$ propan-2-ol (to reduce the hydrophobicity of the PM filters), shaken and placed in a sonic bath (20 mins each), before being centrifuged at 3000 rpm for 20 mins. 10 ml of the solution was then pipetted to 15 ml acid-clean tubes for analysis by Inductively Coupled Plasma Mass Spectrometry with tandem mass spectrometry configuration (ICP MS/MS, Agilent 8800) at the School of Environment, Earth and Ecosystem Sciences at the Open University, UK, with a further 1.5 ml pipetted for IC analysis (as described for the gas filters above). The remaining solution and filters were transferred to an acid-cleaned 22 ml PFA vial. 5 ml UPA grade concentrated HNO_3 was added to the PFA beaker and samples dried on a hot plate at 55°C . 1 ml UPA grade concentrated HNO_3 and 1 ml UPA grade concentrated HF were pipetted to the solid residue and refluxed for 3 hr at 110°C with lids on the PFA beakers. The lids were then removed, and samples dried at 55°C . 10 ml UPA grade concentrated HNO_3 was then pipetted to the solid residue and refluxed on a hot plate at $90\text{--}100^\circ\text{C}$ for dissolving the sample back into solution. 10 ml MQ water was pipetted into the PFA beakers and then transferred to an acid-cleaned sample tube for analysis by ICP-MS/MS at the School of Environment, Earth and Ecosystem Sciences at the Open University, UK.

C.2 Weighted Ash Fraction (WAF) Correction Calculation.

Matrix glass samples from both the 2021 and 2022 eruptions were analyzed for major and trace elements via electron probe micro-analyzer (EPMA; JEOL JXA-8230 SuperProbe) at the Institute of Earth Sciences, University of Iceland and LA-ICP-MS/MS (Agilent 8800) at the Open University using analytical techniques outlined in Jenner and O'Neill (2012) for trace elements. The Ag analysis was done using a line scan on matrix glasses with the same approach

as described in Wieser et al. (2020) for Se analysis in melt inclusions. The ZrO interference correction was done as described in Reekie et al. (2019) with reference material analyses for Ag from Jenner et al. (2015). These analyses were undertaken to determine an ash composition for each eruption (see electronic supplement sheets C8 and C9). Presumed ash compositions were used to perform subsequent weighted ash fraction corrections on all filter pack samples.

To constrain the concentration of elements in the non-silicate aerosol phase (i.e not contained in ash or dust) a weighted ash fraction (WAF) correction was applied to filter pack samples in this study. We assume via mass balance that for volatile elements the concentration on the filter, $[A]_{filter}$ in ppm is derived from two components, silicate ash and dust $[A]_{ash}$, and non-silicate aerosol $[A]_{aerosol}$ (see eq. C.1).

$$[A]_{filter} = [A]_{ash} * X_{ash} + [A]_{aerosol} * (1 - X_{ash}) \quad (C.1)$$

Where X_{ash} is mass fraction from silicate ash on the filter and $X_{aerosol}$, the mass fraction from the aerosol phase on the filter. For refractory elements we assume that the concentration in aerosol phase is zero ($[A]_{aerosol} = 0$), allowing equation C.1 to be simplified to:

$$X_{ash} = \frac{[A]_{filter}}{[A]_{ash}} \quad (C.2)$$

Using the average of four refractory reference elements (Fe, Mg, Mn, Ti) it is then possible to derive X_{ash} for each filter pack sample. Using an average of four major elements as our reference elements is beneficial as their higher concentrations (relative for example to REE) in silicate material allow smaller ash concentrations to be resolved. Weighted ash fractions for each element in each sample (WAF) can then be calculated using eq. C.3 and inputting the X_{ash} calculated for each sample using the refractory reference elements:

$$WAF = 100 * \frac{X_{ash} * [A]_{ash}}{[A]_{filter}} \quad (C.3)$$

Note that this means that whilst the overall mass fraction of ash on the filter may be low ($< 1\%$) the WAF (contribution from ash for a specific element on the filter) may still be high, particularly for refractory elements (generally $> 90\%$).

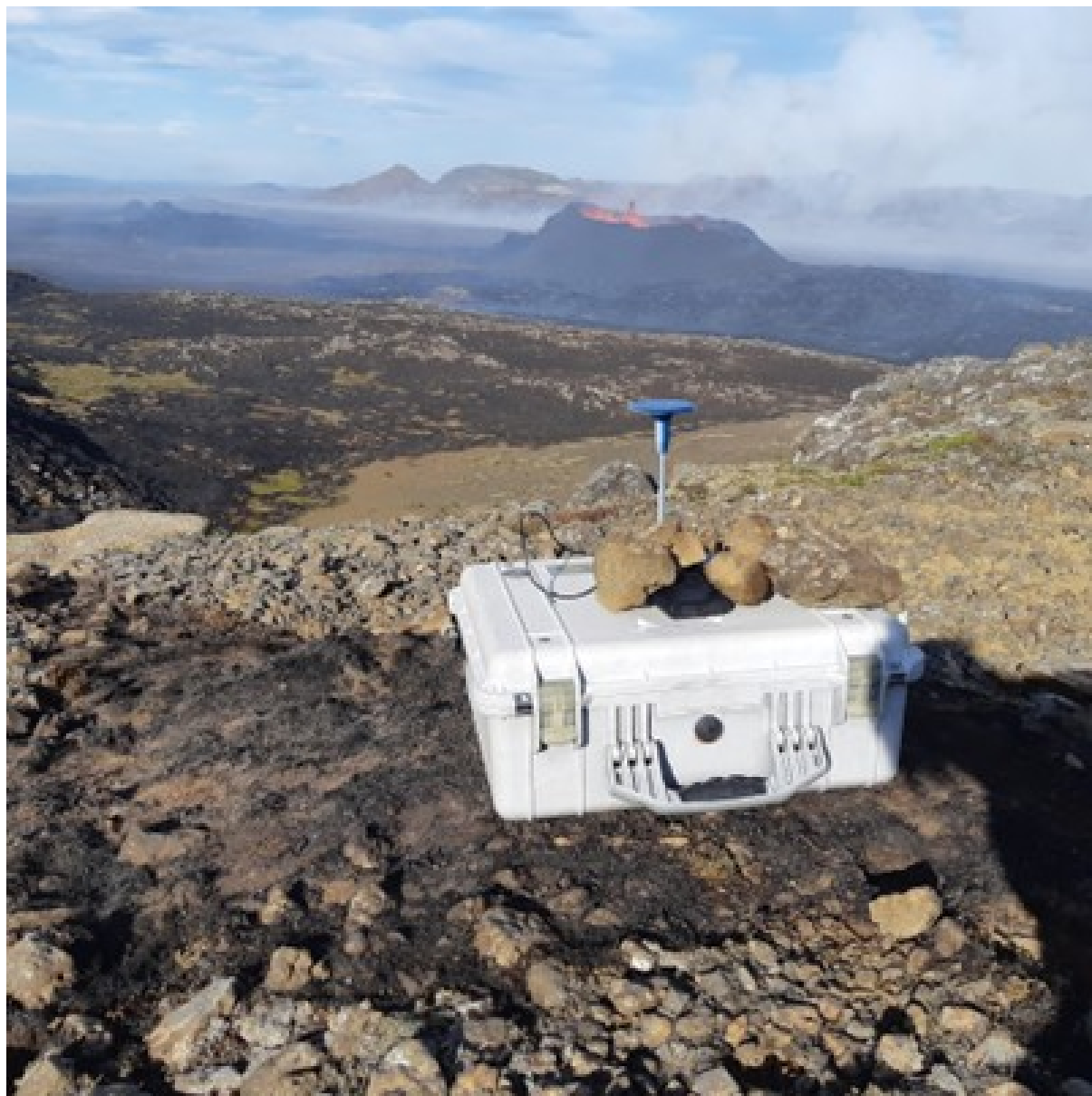


Figure C.1: Measurements using the OPS at Viewpoint A (TSI2B). Viewpoint A overlooked the active eruption crater and ongoing wildfires. Photography by Melissa Anne Pfeffer.

Element	Transect Location and Mass Fraction %		
	Moss Surface	Sub-Surface	Interior
Al	30.6% $\pm$ 6.5%	27.2% $\pm$ 5.8%	27.3% $\pm$ 6.0%
Ca	0.98% $\pm$ 0.2%	0.92% $\pm$ 0.1%	1.1% $\pm$ 0.2%
Fe	6.4% $\pm$ 1.0%	5.7% $\pm$ 0.9%	7.1% $\pm$ 1.2%
S	0.47% $\pm$ 0.1%	0.57% $\pm$ 0.1%	0.16% $\pm$ 0.04%,
Cl	1.04% $\pm$ 0.2%	0.88% $\pm$ 0.2%	0.19% $\pm$ 0.04%
K	1.6% $\pm$ 0.3%	1.4% $\pm$ 0.3%	0.9% $\pm$ 0.1%

Table C.1: Mass fractions of 6 different elements measured via EELS along transects of the moss particle at three different locations.



Figure C.2: Deploying the OPS on Hiking Trail E to collect measurement TSI1B.

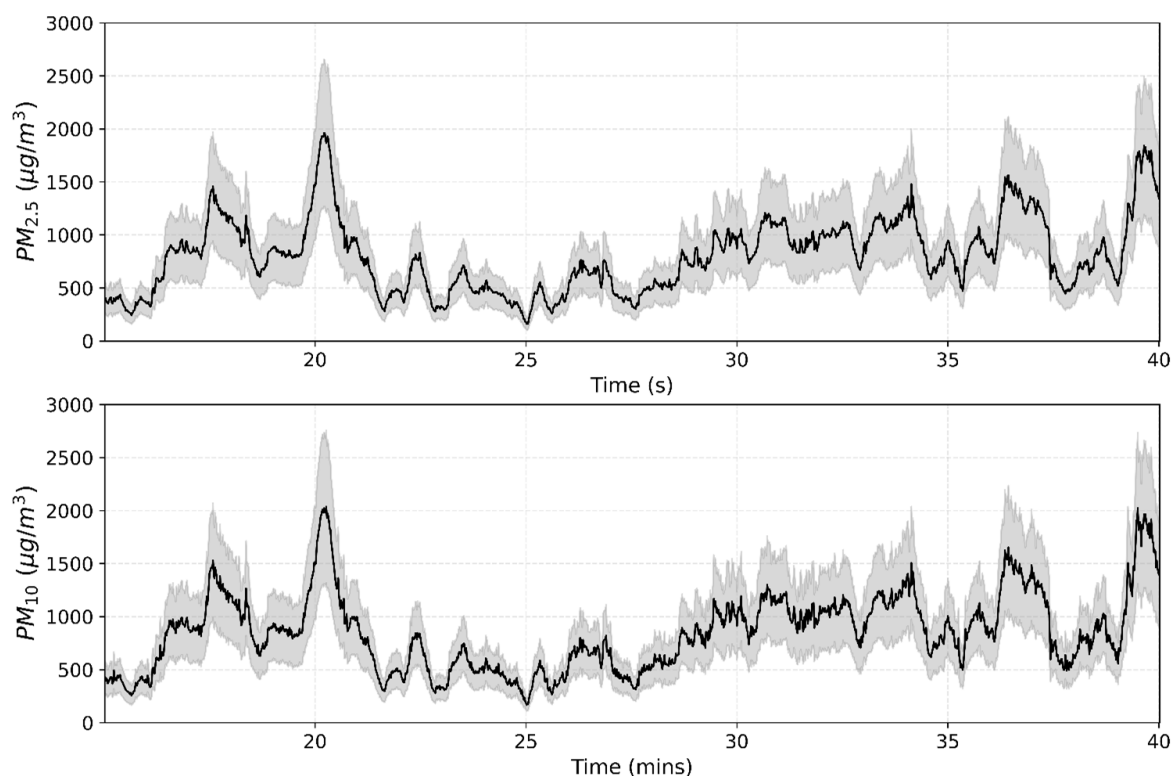


Figure C.3: Timeseries of OPS PM data collected at Hiking Path E next to burning moss (TSI2A) across a 15-minute sampling window. Solid black line shows concentrations with an assumed uniform density of 1.7 g/cm^3 (sulfate) and the shaded area shows upper and lower estimates with assumed densities of 1.1 (smoke) and 2.3 g/cm^3 , (glass), respectively. Other assumptions are outlined in Section 5.2.4.

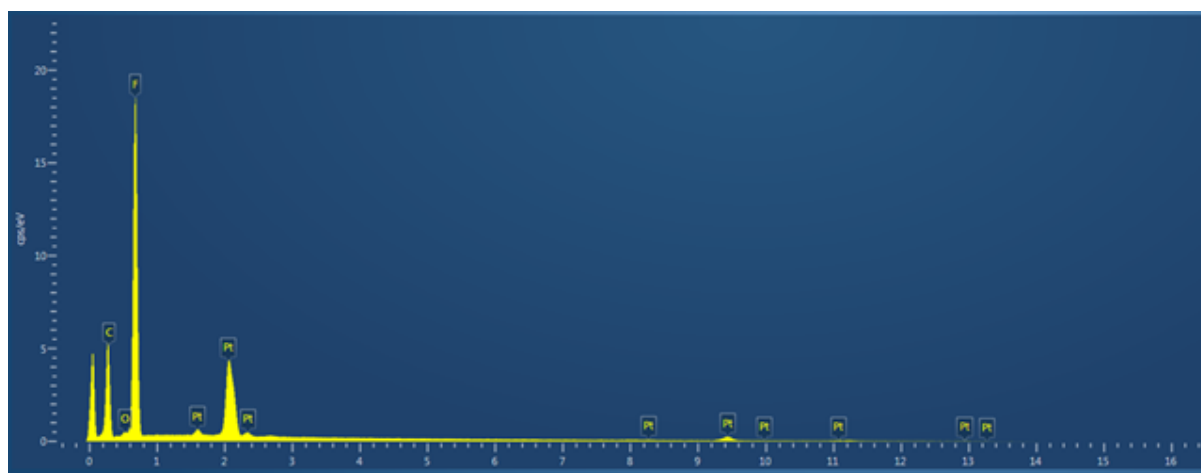


Figure C.4: Point Analysis EDS Spectra for a blank unused PTFE filter containing C, O, and F. Pt peaks are due to Pt coating of the sample.

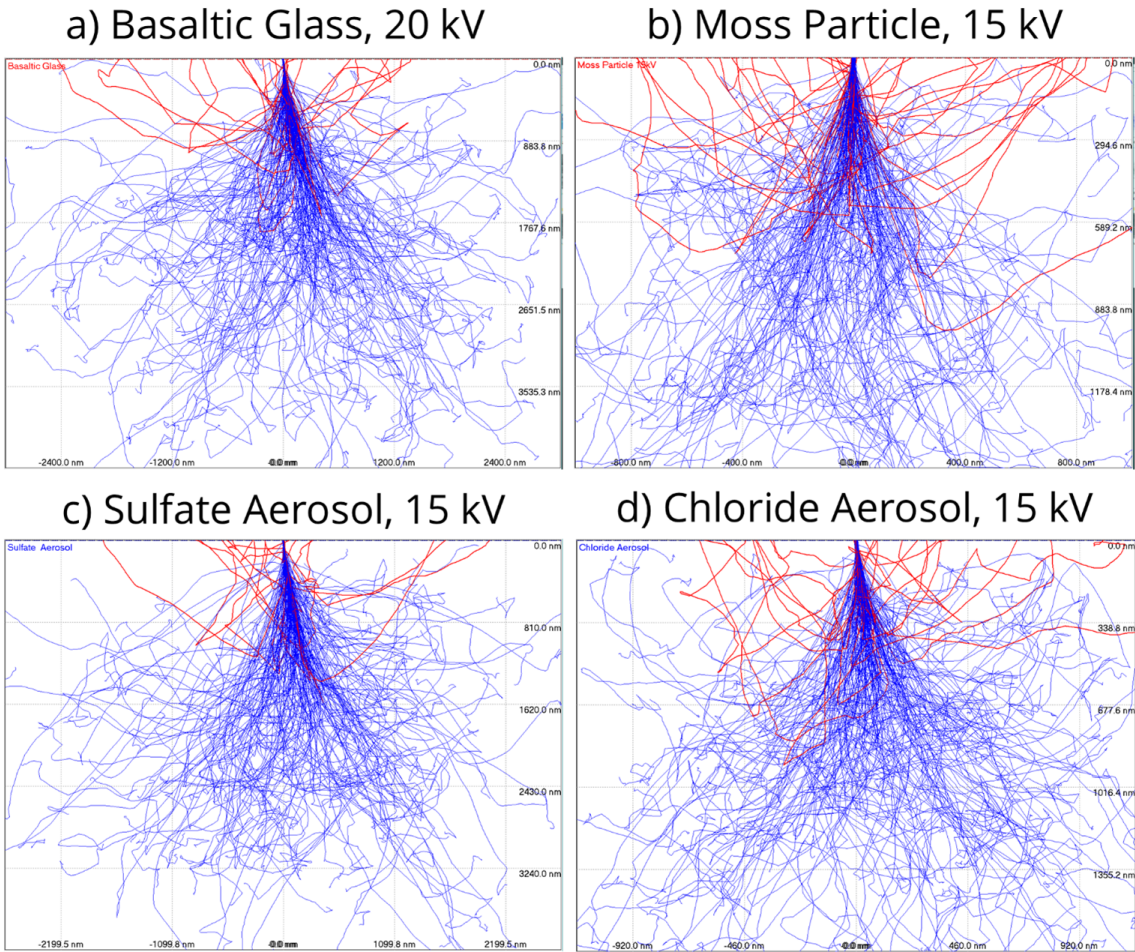


Figure C.5: Interaction volumes calculated using the CASINO software (Hovington et al., 2006) for a) basaltic glass, b) organic moss particle, c) sulfate aerosol, and d) chloride aerosol.

Colour Code	Concentration Range		Description
	PM2.5	PM10	
Dark Green	0-10	0-25	Little to no air pollution. Probably no health effects
Light Green ⁴	10-15	25-50	Some air pollution. Highly sensitive individuals and individuals with asthma or other underlying conditions may experience symptoms
Yellow	15-25	50-75	Some air pollution. Sensitive individuals and individuals with asthma or other underlying conditions may experience symptoms
Orange	25-50	75-100	High levels of air pollution. People with serious heart and/or lung disease should avoid being outdoors. Strenuous work or outdoor exercise should be avoided
Red	50+	100+	Exceeding the formal upper limit, informally classified as “Very high levels of air pollution”

Table C.2: PM Air Quality 1 hr Exposure Thresholds from the Icelandic Environment Agency (Icelandic Environment Agency, 2025).

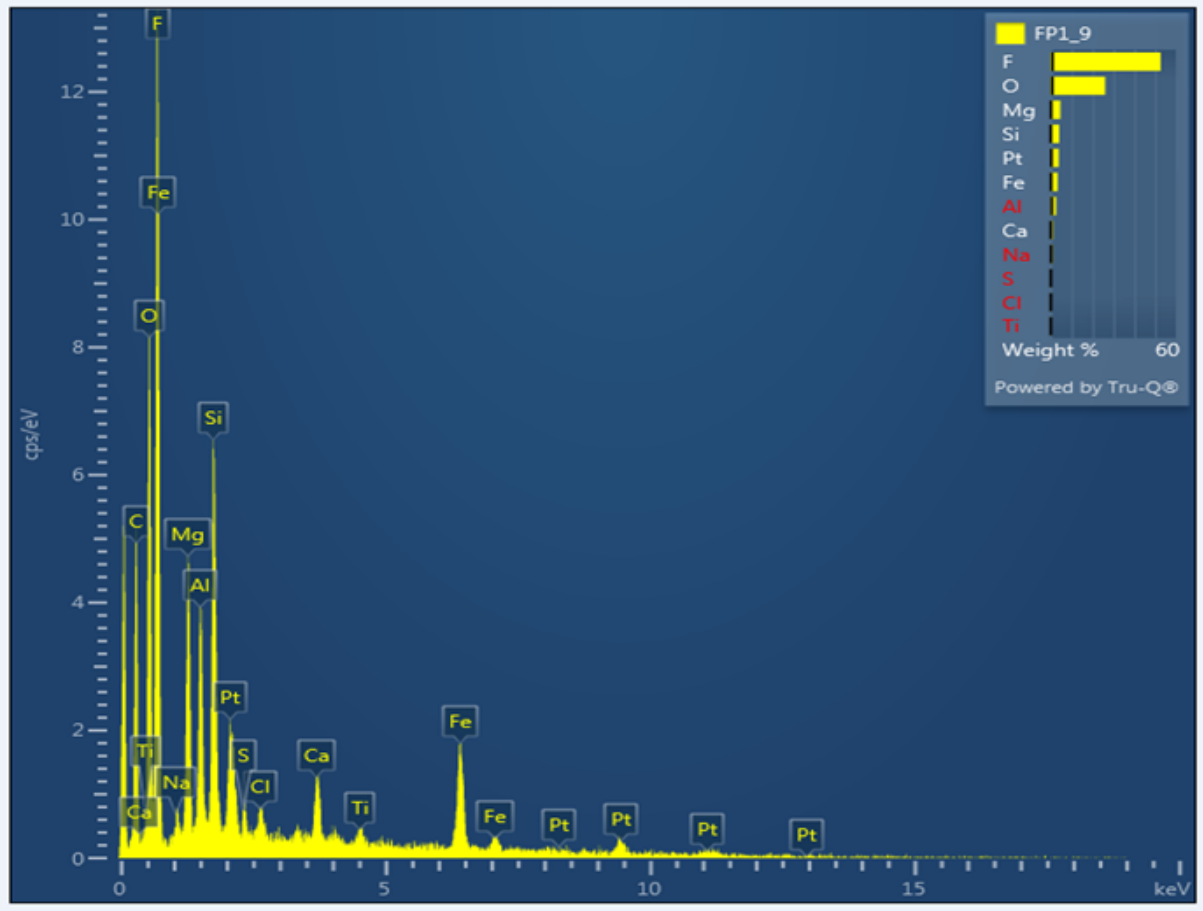


Figure C.6: Point Analysis EDS Spectra for the Augite crystal shown in Figure 5.3b of the main text.

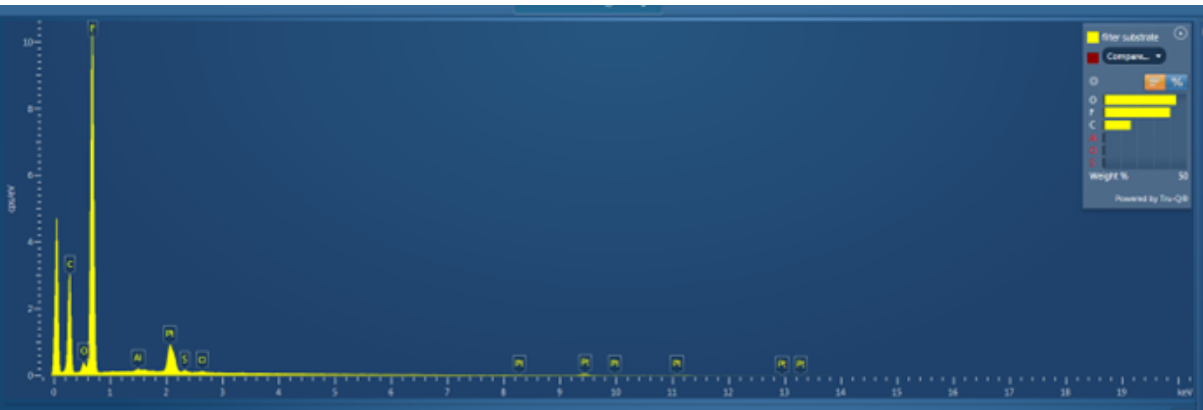


Figure C.7: Point Analysis EDS Spectra for the background of filter sample LHFP1. Minor peaks in S and Cl.

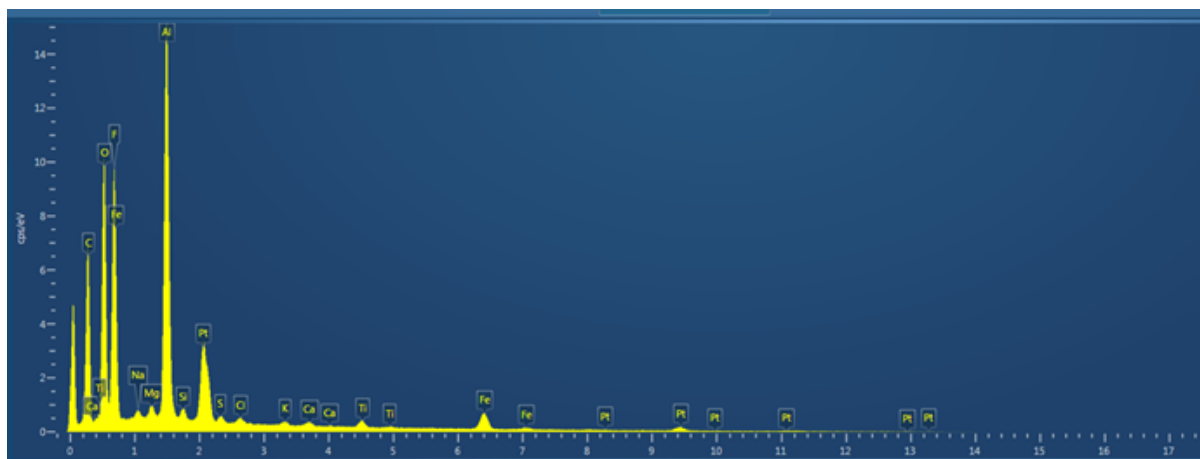


Figure C.8: Point Analysis EDS Spectra for an organic fibrous moss particle at 15 kV. Minor peaks in S and Cl. Due to the larger interaction volume and porosity of the particle the x-rays also interacted with the background filter producing peaks in F, C, and O.

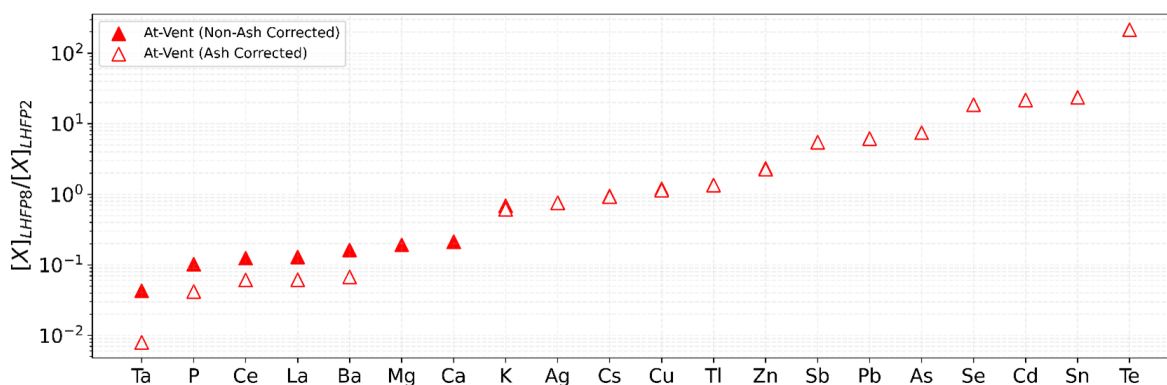


Figure C.9: Trace Element Concentrations in At-Vent sample LHFP8 normalized to concentrations in lava outgassing sample LHFP2. Solid red triangles show non-ash corrected at-vent concentrations and red outlined triangles show ash corrected concentrations for comparison. The most affected elements, and thus those hosted predominantly in the primary silicate aerosol phase are Ta, P, Ce, La, and Ba as well as Mg and Ca (which are assumed to be hosted entirely in the ash fraction and thus corrected to zero). Differences in relative element enrichments between lava flow and vent samples are also consistent with previous observations, where the vent is relatively more enriched in Se and Te, which have an affinity for S, compared to elements which tend to form chlorides such as Cu, Pb, and Ag (Mason et al., 2021, Wainman et al., 2024). This relative difference between vent and downflow trace element concentrations is a consequence of fractionation between halogens and sulfur degassing downflow as the lava cools and ages where most sulfur-complexing elements are emitted directly at the vent, whilst chloride degassing continues further downflow (Wainman et al., 2024, Toutain et al., 1990). The ash correction calculation is outlined below and major and trace element data from matrix glass included in the electronic supplement Sheets C8 and C9.