Trace element emissions during the 2018 Kīlauea Lower East Rift Zone eruption

Emily Mason*[1], *Penny Wieser*[1], *Emma Liu*[2], *Marie Edmonds*[1], *Evgenia Ilyinskaya*[3], *Rachel C W Whitty*[3], *Tamsin Mather*[4], *Tamar Elias*[5], *Patricia Amanda Nadeau*[5], *Christoph Kern*[6,7], *David J Schneider*[8] *and Clive Oppenheimer*[9]

This study presents the trace element composition and speciation of emissions from the **magmatic plume** (B, right) and **lava-seawater interaction plume** ('laze', C, left) associated with the 2018 eruption of Kīlauea volcano, with a particular focus on the **trace metal and metalloid degassing**.

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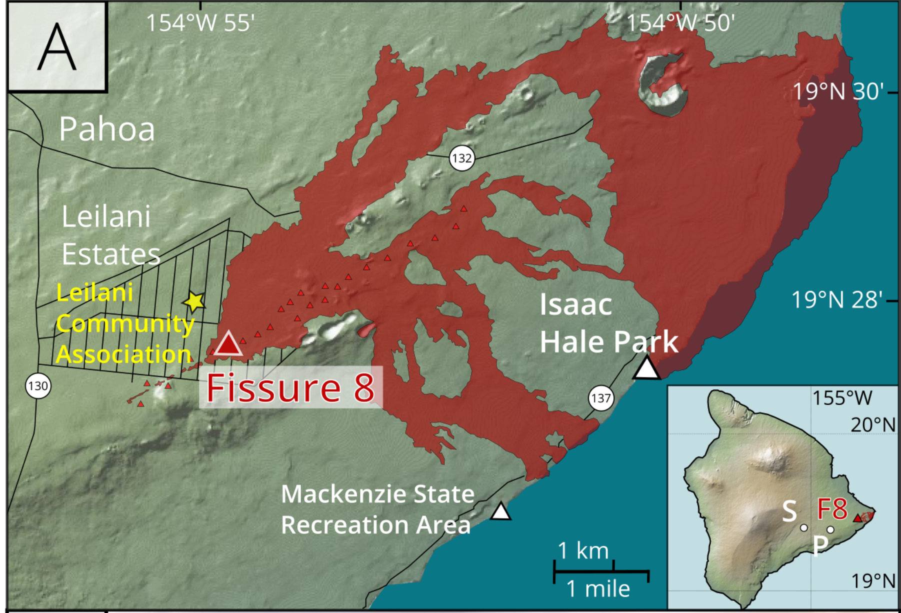

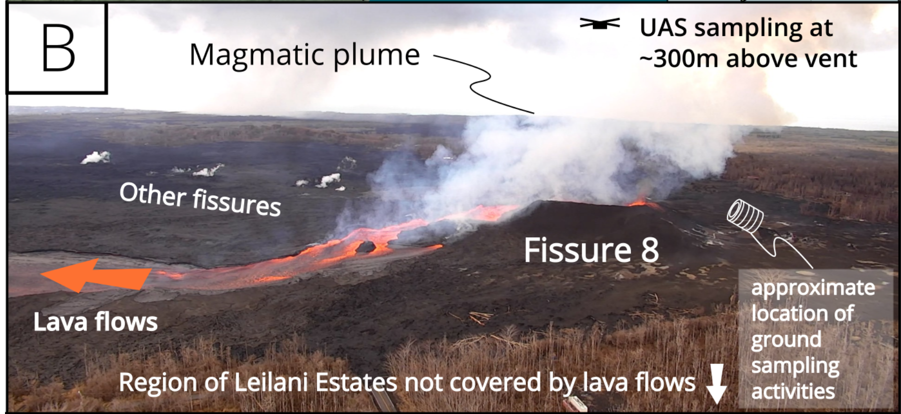

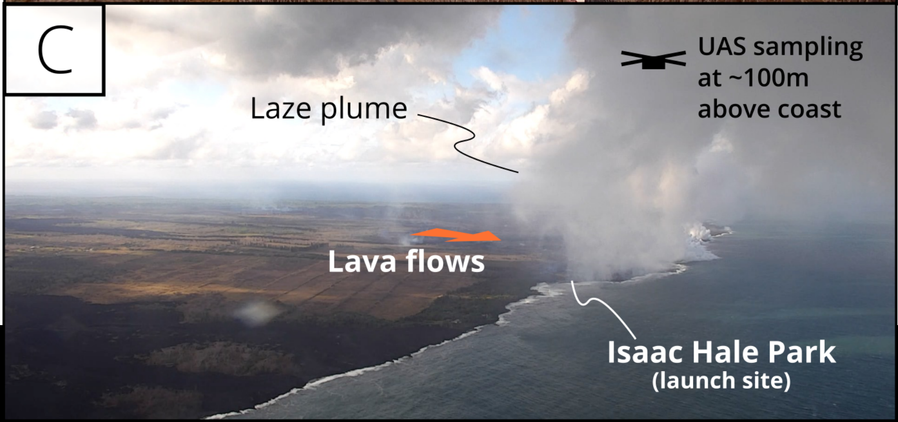

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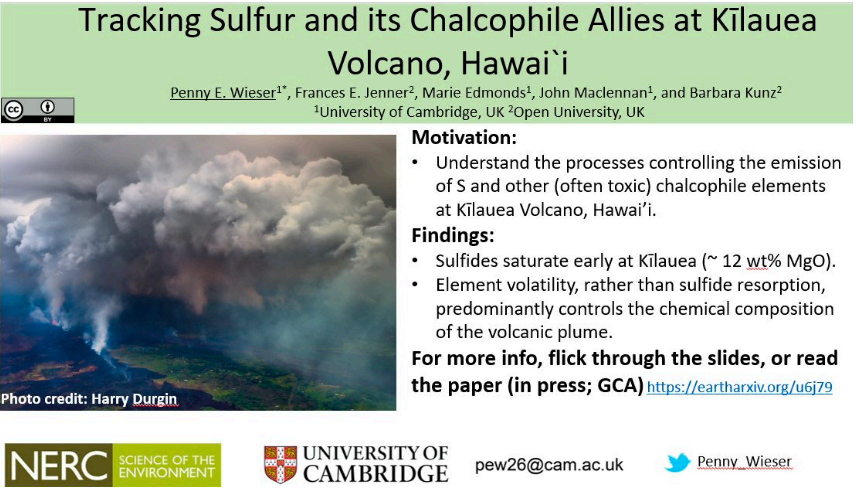

Tracking Sulfur and its Chalcophile Allies at Kīlauea Volcano, Hawai`i

Penny E. Wieser[1*], Frances E. Jenner[2], Marie Edmonds[1], John Maclennan[1], and Barbara Kunz[2]
[1]University of Cambridge, UK [2]Open University, UK

Motivation:

- Understand the processes controlling the emission of S and other (often toxic) chalcophile elements at Kīlauea Volcano, Hawai'i.

Findings:

- Sulfides saturate early at Kīlauea (~ 12 wt% MgO).
- Element volatility, rather than sulfide resorption, predominantly controls the chemical composition of the volcanic plume.

For more info, flick through the slides, or read the paper (in press; GCA) https://eartharxiv.org/u6j79

Photo credit: Harry Durgin

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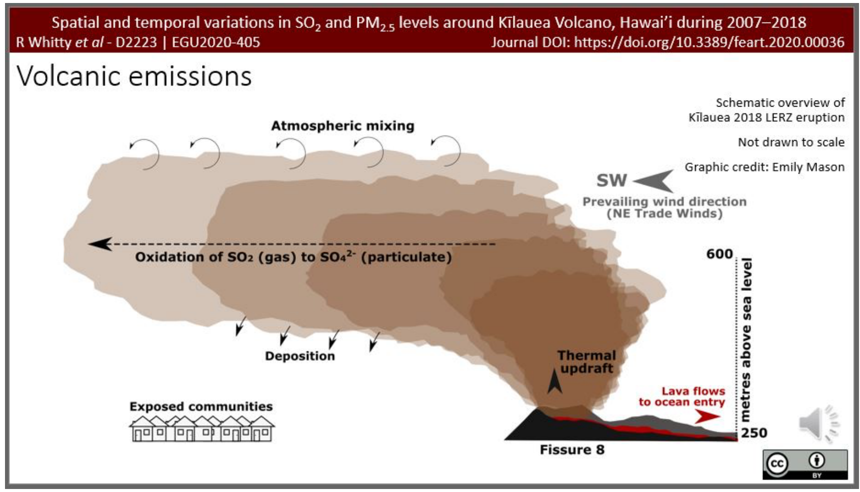
Evgenia Ilyinskaya *et al.*

Self limiting atmospheric lifetime of environmentally reactive elements in volcanic plumes

EGU2020-19656
| ITS2.13/AS4.29/CL4.43/GMPV10.2
Wed, 06 May, 10:45–12:30 | D2242



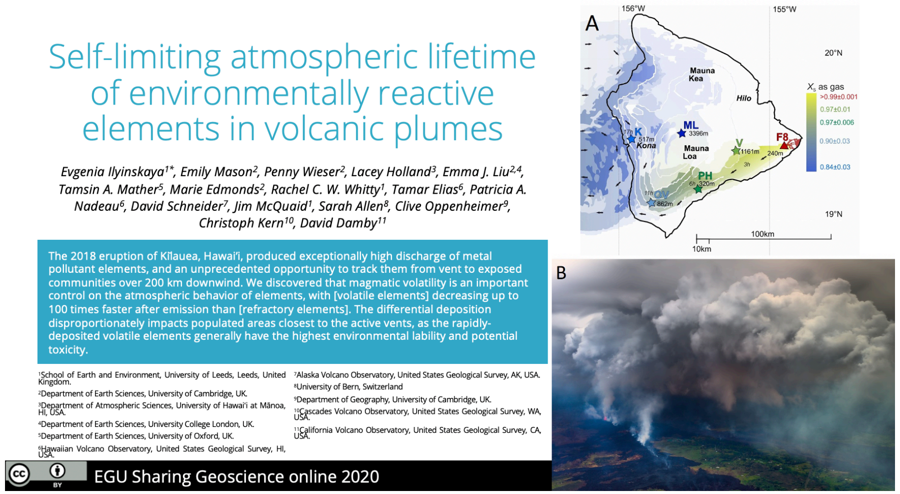
Spatial and temporal variations in SO_2 and $PM_{2.5}$ levels around Kīlauea Volcano, Hawai'i during 2007–2018
R Whitty *et al* - D2223 | EGU2020-405 Journal DOI: https://doi.org/10.3389/feart.2020.00036

Volcanic emissions

Penny Wieser *et al.*

Tracking sulfur and its allies at Kīlauea volcano Hawai'i

EGU2020-355 | GMPV8.3/NH2.7
Tue, 05 May, 14:00–15:45 | D1553



Self-limiting atmospheric lifetime of environmentally reactive elements in volcanic plumes

Evgenia Ilyinskaya[1], Emily Mason[2], Penny Wieser[2], Lacey Holland[3], Emma J. Liu[2,4], Tamsin A. Mather[5], Marie Edmonds[2], Rachel C. W. Whitty[1], Tamar Elias[6], Patricia A. Nadeau[6], David Schneider[7], Jim McQuaid[1], Sarah Allen[8], Clive Oppenheimer[9], Christoph Kern[10], David Damby[11]*

The 2018 eruption of Kīlauea, Hawai'i, produced exceptionally high discharge of metal pollutant elements, and an unprecedented opportunity to track them from vent to exposed communities over 200 km downwind. We discovered that magmatic volatility is an important control on the atmospheric behavior of elements, with [volatile elements] decreasing up to 100 times faster after emission than [refractory elements]. The differential deposition disproportionately impacts populated areas closest to the active vents, as the rapidly-deposited volatile elements generally have the highest environmental lability and potential toxicity.

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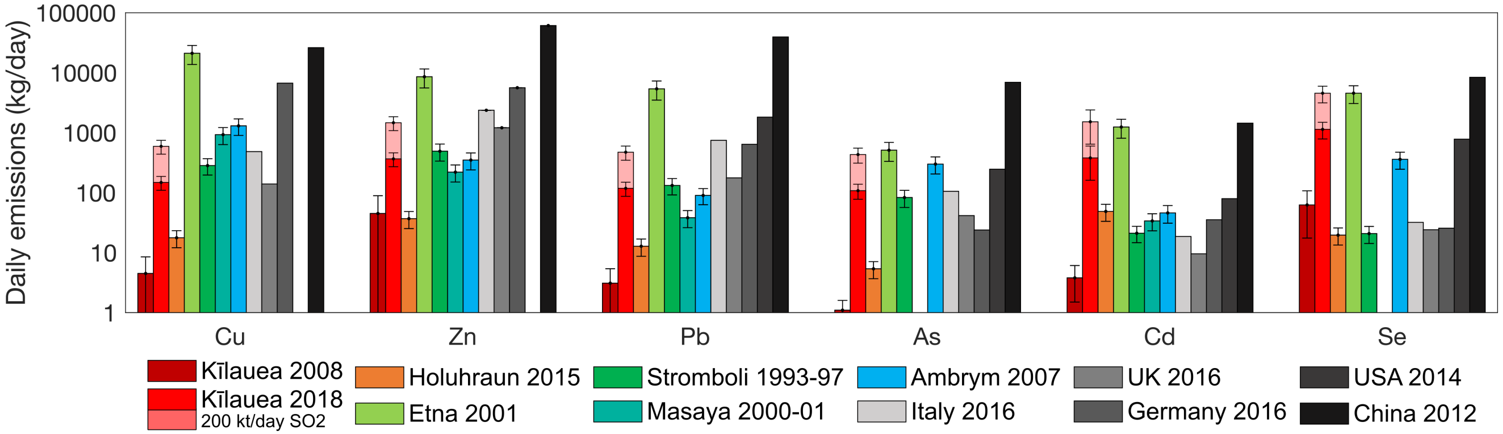
Rachel Whitty *et al.*

Spatial and temporal variations in ambient SO2 and PM2.5 levels influenced by Kīlauea Volcano, Hawai'i, 2007 - 2018

EGU2020-405
| ITS2.13/AS4.29/CL4.43/GMPV10.2
Wed, 06 May, 08:30–10:15 | D2223

Why study volatile trace element emissions from volcanoes?

1. Volcanoes can emit significant fluxes of trace metals, comparable to some anthropogenic sources: **daily emissions from individual volcanoes** = **daily anthropogenic emissions from entire countries**



Data sources: Volcanoes - Edmonds *et al.* 2018 and references therein; National emissions (based on fuel sold) – European Environment Agency, Tian *et al.* (2015) and United States Environmental Protection Agency. Figure from Ilyinskaya, Mason et al. (*in revision*)

2. Volatile trace elements sourced from volcanoes can acts as **nutrients**, **pollutants** and **biological catalysts**. For example **selenium**, present in selenoproteins, is an essential component of major metabolic pathways (Brown and Arthur, 2001) and has been implicated in processes affecting cancer risk (Rayman, 2005). However, at high levels selenium toxicosis (selenosis) causes symptoms such as hair loss and reductions in livestock productivity (Aitken, 2001).

…however, the data needed to develop guidelines for exposure to and hazard from metal pollutants during volcanic eruptions are currently lacking.

Kīlauea displays a consistent fingerprint of volatile trace elements

Kīlauea displays a (ash-corrected, see extra slides) fingerprint or pattern of trace metals consistent with:

- Previous measurements at **Kīlauea summit in 2008/09** (Mather et al., 2012)
- Other **rift and hotspot volcanoes**

This consistent fingerprint could be used to:

- predict emissions of nutrient/toxic pollutant metals from future eruptions
- identify types of eruptive activity in geological records (e.g. sediments and ice cores)

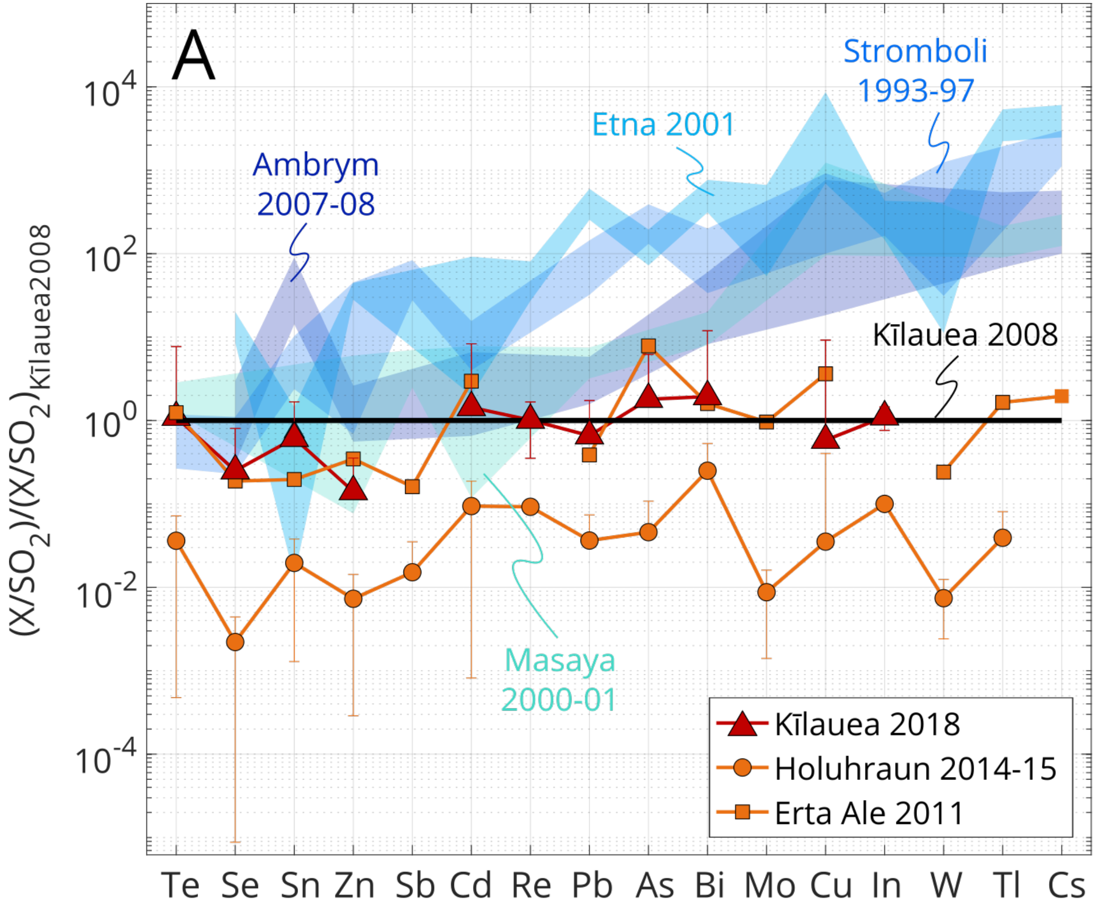
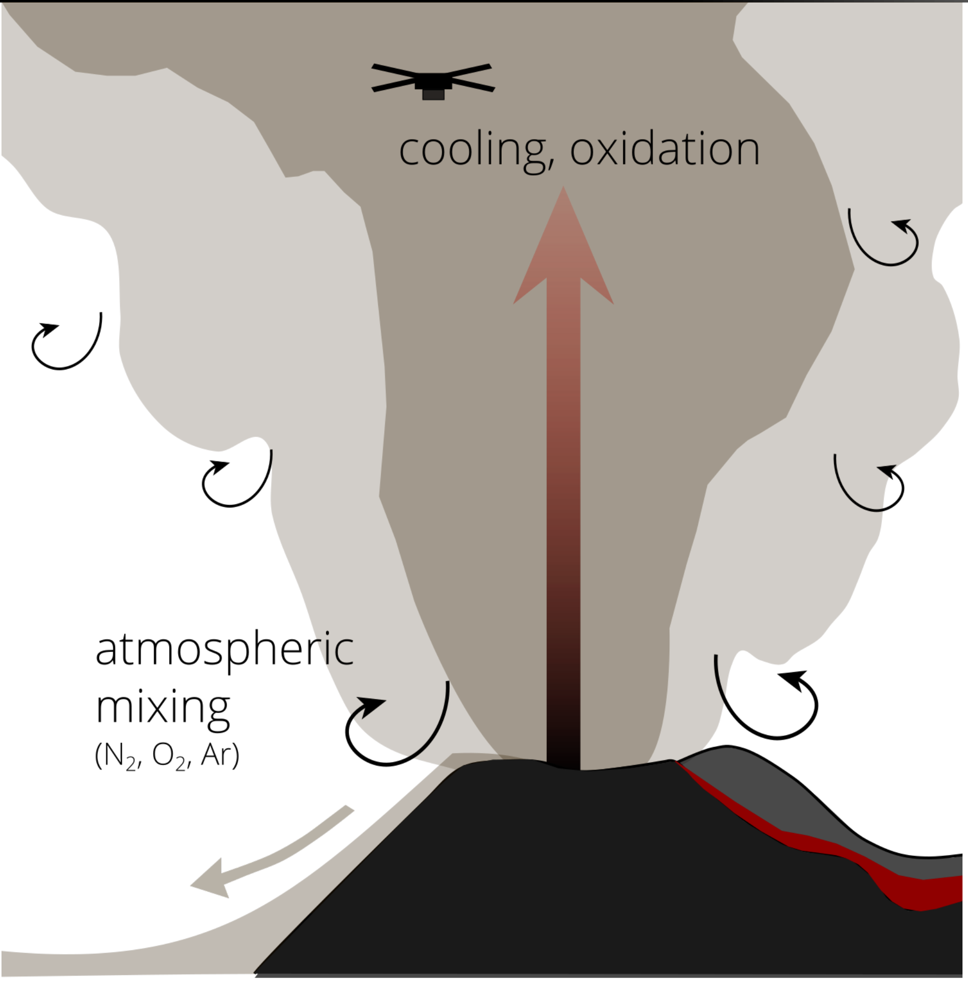
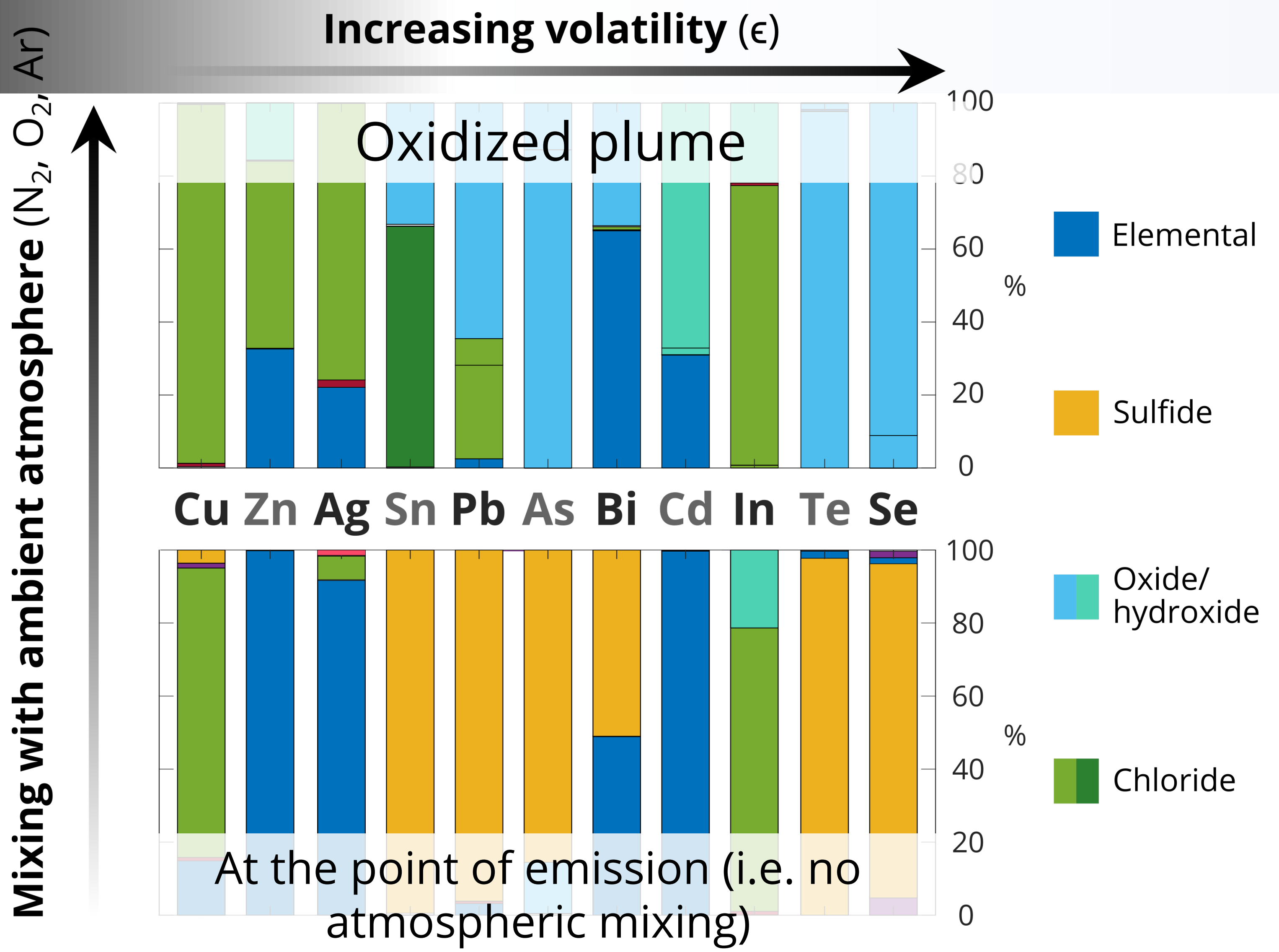


Figure: from Mason *et al.*, (*pre-submission*). Data sources: Arcs – Edmonds et al. (2018 and references therein); Holuhraun 2015 – Gauthier et al. (2016); Kīlauea 2008 – Mather et al. (2012); Kīlauea 2018 – this study. All **normalized to Kilauea 2008**.

Speciation of volatile trace elements during oxidation of the plume

See more detailed/extra slides for more detail on this figure





Figures from Mason et al., (pre-submission).

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How similar is the laze plume to seawater, when corrected for silicate contribution?

The laze plume composition **is comparable to SW** for:

- **Major elements in SW**, e.g. Na, Mg, Ca etc.

Correcting the laze plume composition for a **contribution from volcanic glass** accounts for:

- Elevated REE and Ti, Mn, and Fe concentrations

Volatile metals remain elevated:

- Cu, Zn, Ag (all speciate with Cl at either magmatic [Cl]); Bi, Cd, Re – speciate with Cl when the [intial HCl(g)] is increased
- sourced from **degassing at the ocean entry**.

Se, As, Te are **notably absent** despite highly volatile nature – removed during lava flow degassing? Or are these sulfur-loving elements suppressed due to low S availability?

Could *degassing in presence of elevated Cl^- and/or H_2O* enhance concentrations of elements with Cl-affinity ()se extra slides for speciation evidence of this affinity?

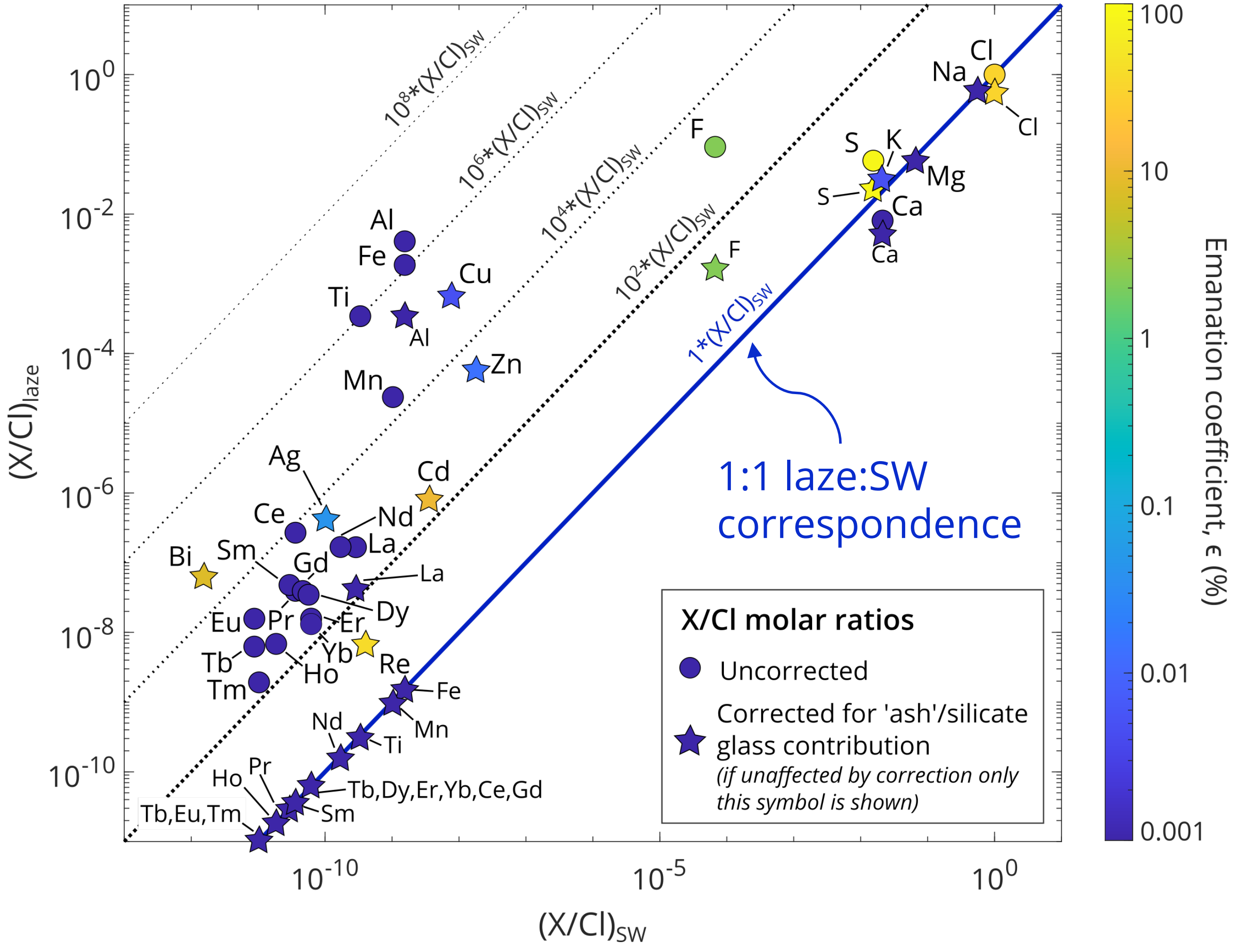
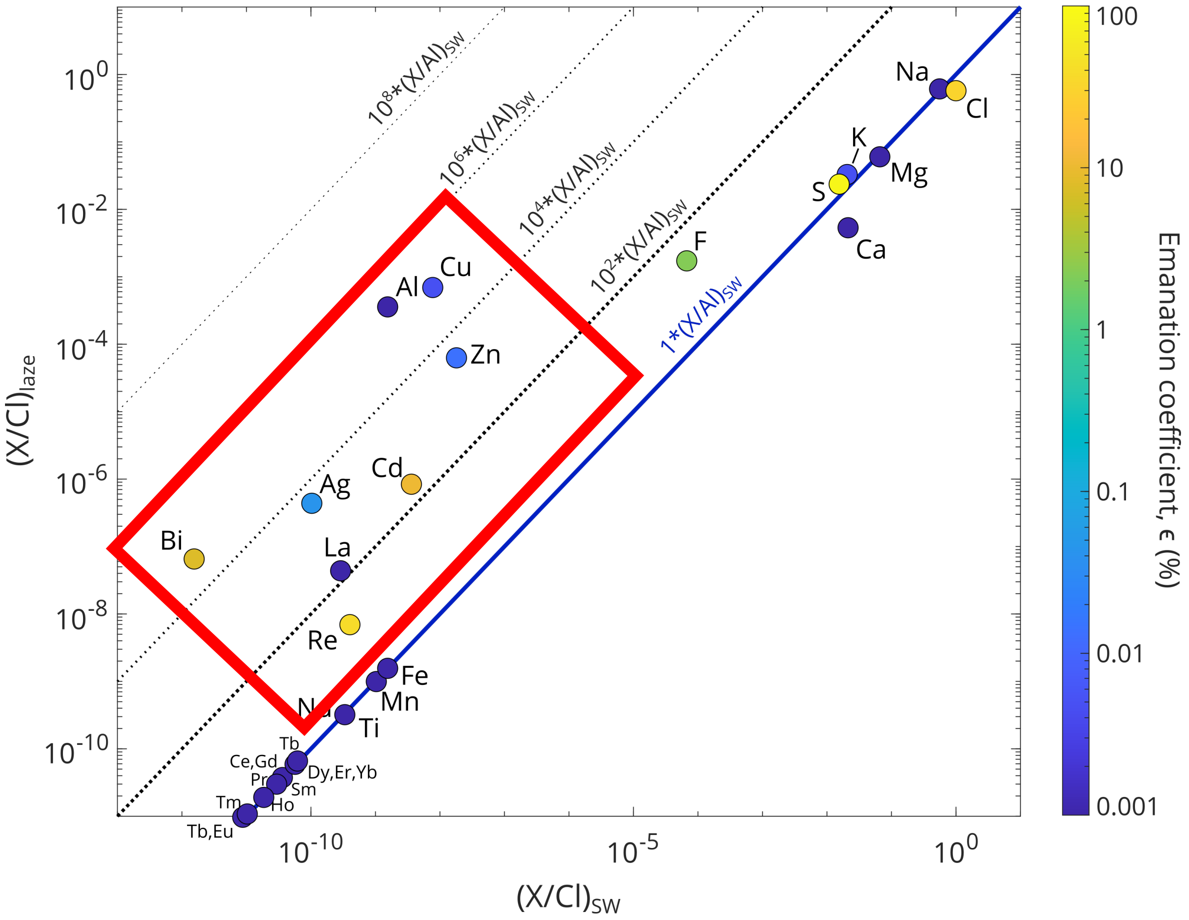
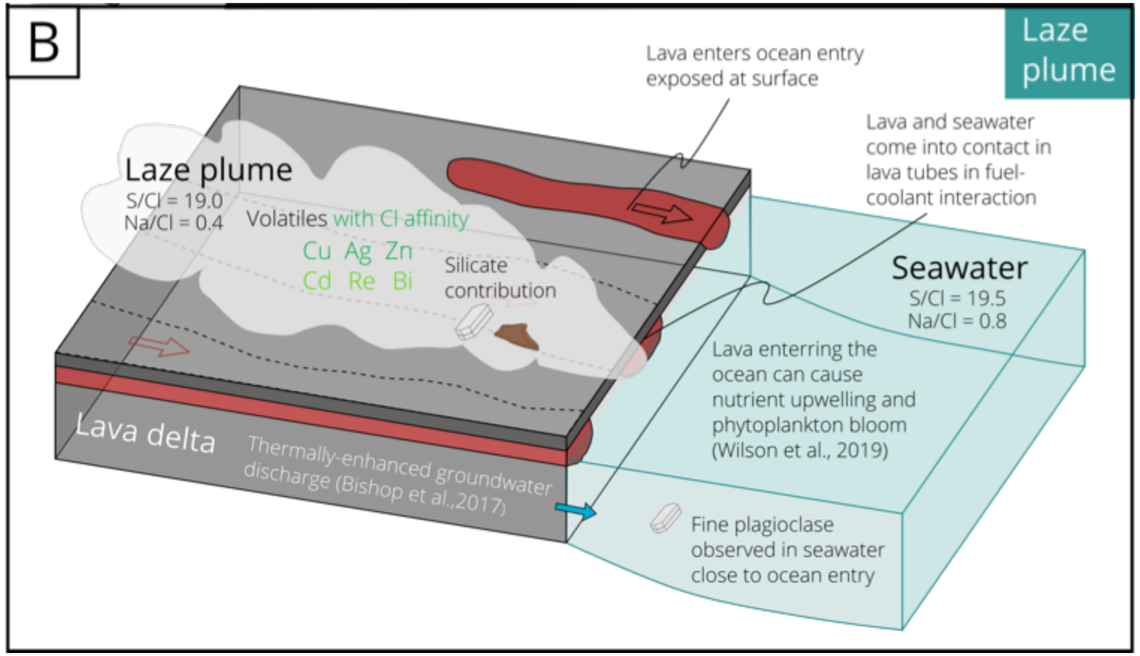


Figure from Mason et al., (pre-submission). Global seawater composition from: https://www.mbari.org/summary-table-of-mean-ocean-concentrations-and-residence-times/.These results agree well with Resing and Sansone (2001).

…and these are the volatile elements in the laze plume that are elevated above both seawater and basalt compositions

Figures from Mason et al., (pre-submission).





Is enhanced degassing of these elements facilitated by the presence of excess chloride, sourced from seawater?

- Kīlauea emits a **consistent fingerprint** of volatile trace elements – this could pre used for **forecasting** purposes and identifying volcanic signatures in **geological records.**
- Speciation models can be used as **initial conditions in atmospheric transport models**
- The laze plume composition represents **seawater enriched by degassing of volatiles + dissolution of basalt** but some elements with Cl^- affinity (Cu, Ag, Zn, Cd, Bi, Re) may be sourced from late-stage degassing, **enhanced in the presence of elevated Cl^-**?

Thank you

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More detailed slides

The eruption of Kīlauea in 2018 produced two very different plumes of gas and particles

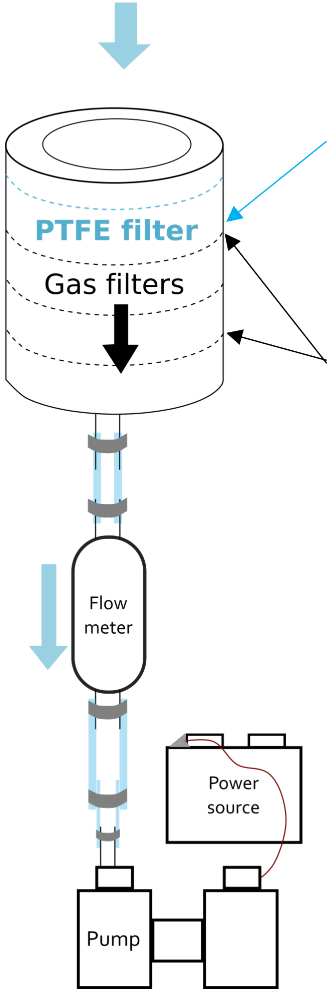

Photo: Emily Mason

Magmatic plume emitted from the Fissure 8 vent: *degassing from a magma (gases and particulate matter) + silicate ash*


Photo: Harry Durgin

Lava-seawater interaction (laze) plume emitted at ocean entry: *lava boils and evaporates seawater + late stage degassing + silicate fragments from hydro-volcanic explosions*

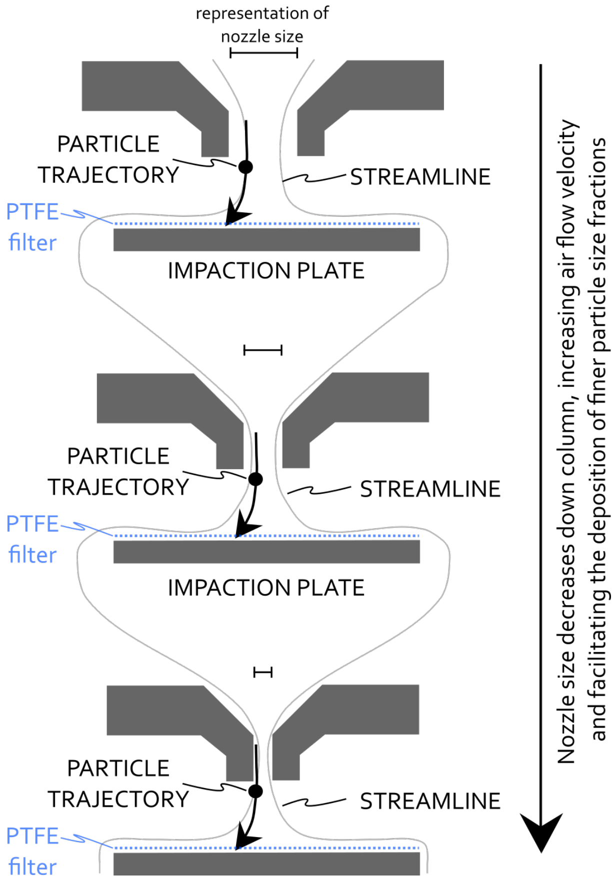
Sampling and analysis



Inductively coupled plasma mass spectrometry

Ion chromatography

Filter packs were used to simultaneously gas and particulate matter in the magmatic and laze plumes



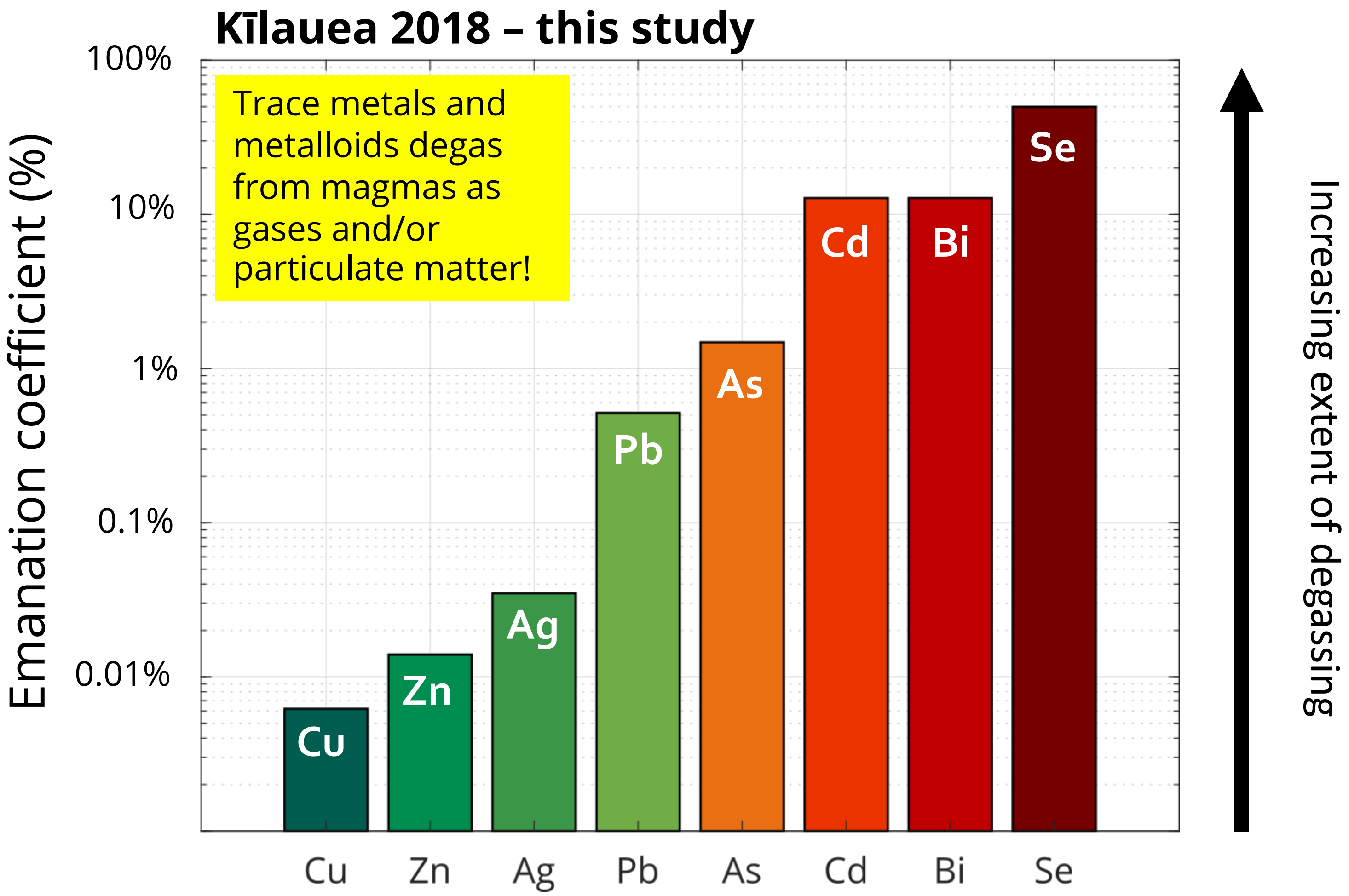
Figures from Mason et al., (pre-submission).

Cascade impactors were used to sample size-segregated particulate matter

Both instruments were used for **ground-based** sampling and **aerial sampling** using a Unoccupied Aerial Vehicle

Samples analysed for major anions (SO_4^{2-}, Cl^-, NO_3^-, F^-) by **ion chromatography**
Samples analysed for further major and trace elements by **ICP-MS and/or ICP-OES**

We describe the extent to which an element degasses from a magma using emanation coefficients



Emanation coefficients

$$\epsilon = \frac{c_i - c_f}{c_i}$$

Initial concentration

Final concentration

Measure of how extensively an element degasses from magma

(originally defined by Lambert (1985) and Gill (1985))

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But other methods are available…

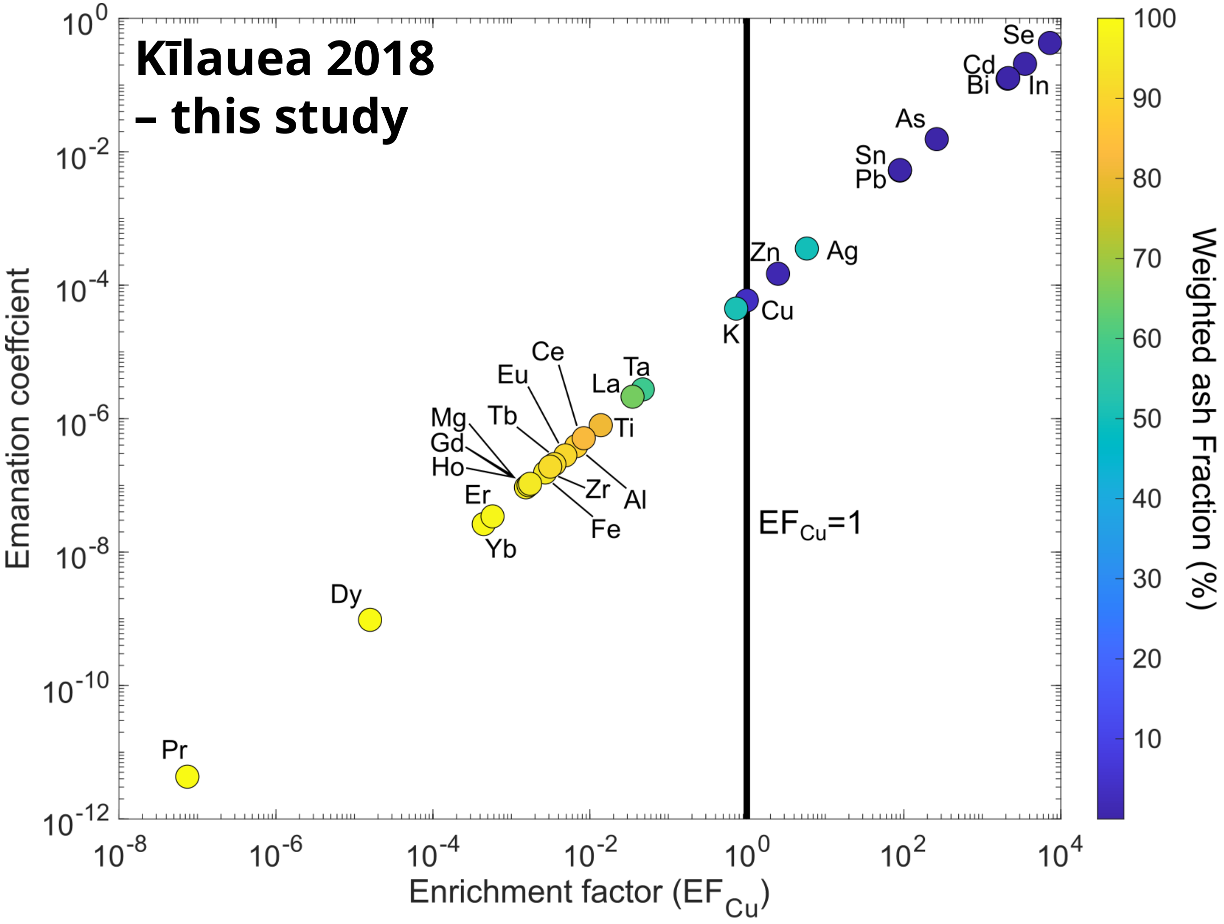
Weighted ash fractions describe the percentage of an element's concentration tat can be accounted for by a contribution from ash of a known composition (see extra slides). We have also used this to 'remove' the ash component from our data and therefore just look at the elements at the concentrations at which they were degassed from magma (as gases or non-silicate particulate matter)

Enrichment factors describe the extent to which an element in the degassed plume is enriched/depleted compared to the magma from which is was emitted:

$$EF_X = \frac{([X]/[Y_{ref}])_{plume}}{([X]/[Y_{ref}])_{magma}}$$

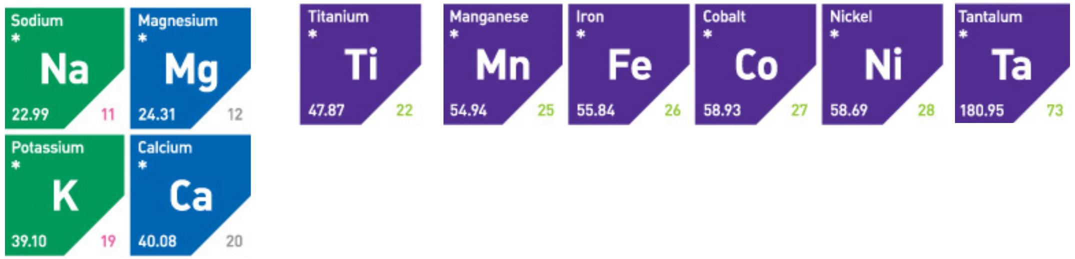
Where X is the element of interest and Y is a (typically lithophile/refractory) element.
We decided not to used these as our main method of describing volatility as use of EFs in the literature varies widely, which makes it difficult to compare different datasets.

Figures from Mason et al., (pre-submission).



Volatile vs. refractory elements

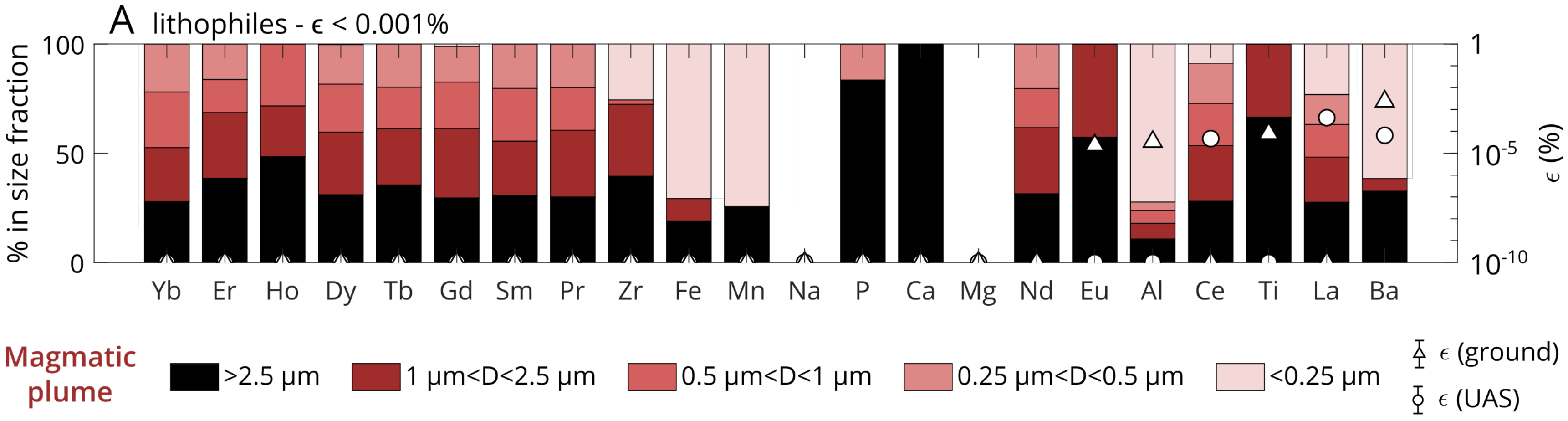
Refractory lithophiles



+REEs

- Found in **volcanic ash, glass** etc.
- Low emanation coefficients, i.e. they **do not degas** much/at all from the magma. They are instead hosted in silicate material emitted from the volcano, i.e. ash, and are found in **coarse** size fractions (black on the figure below)

- We define the lithophile/refractory elements as those that have an emanation coefficient (ϵ) of <0.001%, i.e. less than 0.001% of the concentration of that element in undegassed magma is degassed from the magma



Figures from Mason et al., (pre-submission).

Volatile vs. refractory elements

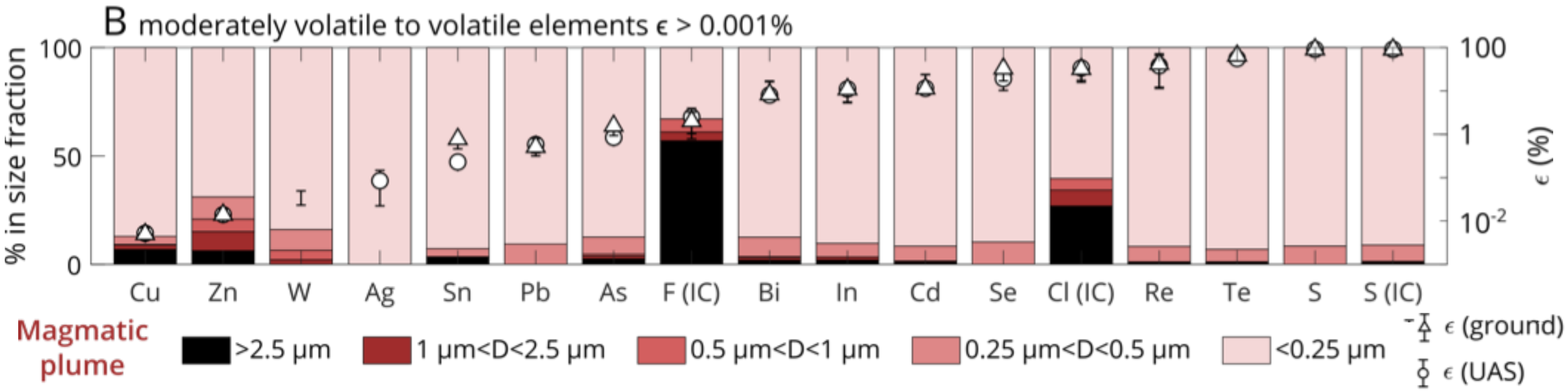
Volatile Nutrients/Pollutants

- They are found in the **fine size fractions**, consistent with the **nucleation** mode (formed from gas to particle condensation after degassing) or the **accumulation** mode (formed by agglomeration and growth of particles in the nucleation mode, as defined by Whitby, 1978)

- Small amounts can be crucial nutrients to **human, animal, and plant health**
- Larger amounts can be **toxic**

Common ligand-forming elements

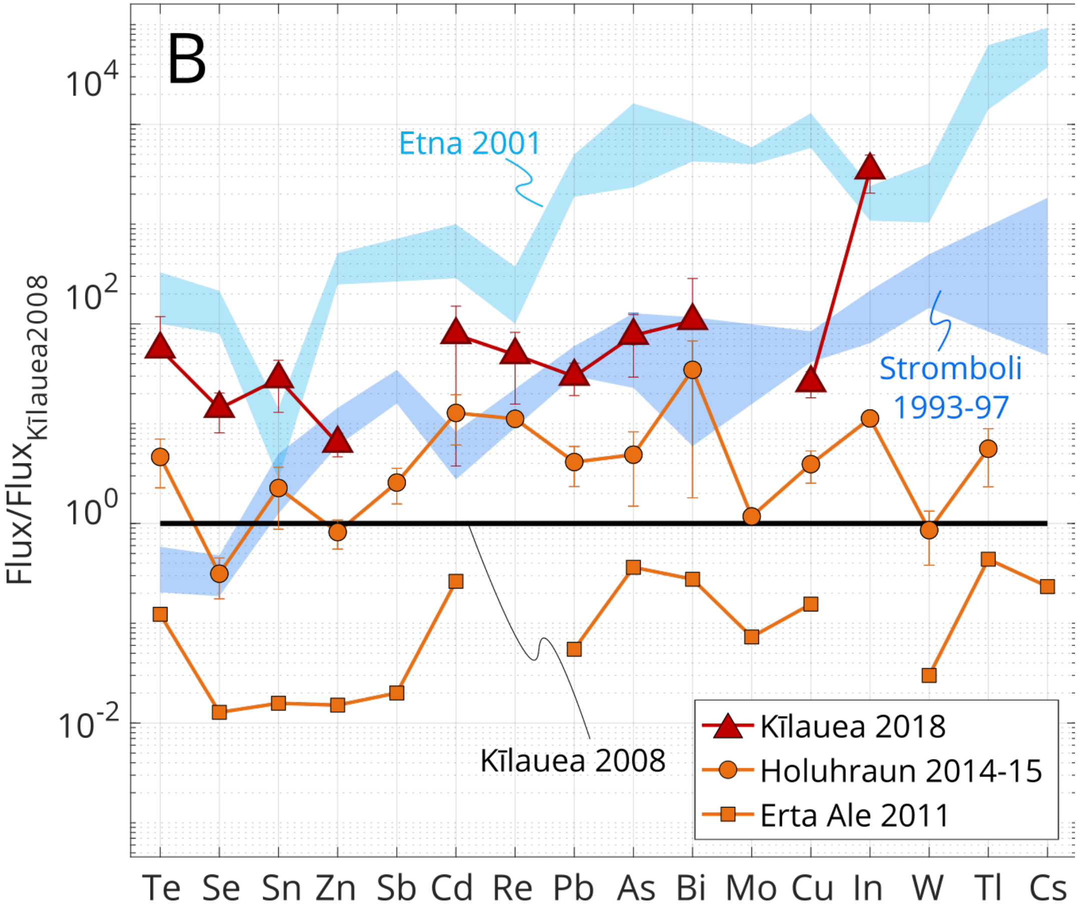
- We define the volatile elements as those that have an emanation coefficient (ϵ) of >0.001%, i.e. more than 0.001% of the concentration of that element in undegassed magma is degassed from the magma



Figures from Mason et al., (pre-submission).

Trace element fluxes – ash corrected (see extra slides)

- Fluxes of trace metals from Kīlauea in 2018 are:
  - the **highest measured for any hotspot or rift volcano**
  - **Comparable to Mount Etna** (for some elements), which has the highest recorded fluxes for any volcano



Data sources: Etna 2001 - Aiuppa et al. (2003); Holuhraun 2015 – Gauthier et al. (2016); Kīlauea 2008 – Mather et al. (2012); global flux estimate – Hinkley et al. (1999); Kīlauea 2018 – this study

How are volatile trace elements speciated in volcanic plumes?

- Previous studies have shown that trace metals complex with ligands in the gas phase (e.g. Zelenski *et al.*, 2013, Symonds *et al.,* 1992).
- Major elements in magmatic plumes such as S, Cl, O and H (and more minor elements such as F and other halides) represent the **main ligand-forming elements** for volatile trace metals in volcanic plumes.
- These ligands act as **electron donors** and complex with metals in the form of negative or neutrally charged ions or molecules such as sulfates, sulfides, chlorides , fluorides, oxides and hydroxides.

Depending on composition, fO_2, P, T etc.

Elemental gases

Sulfide gases

Chloride gases

Oxide gases

Hydride gases

Hydroxide gases

Fluoride gases

Bromide gases

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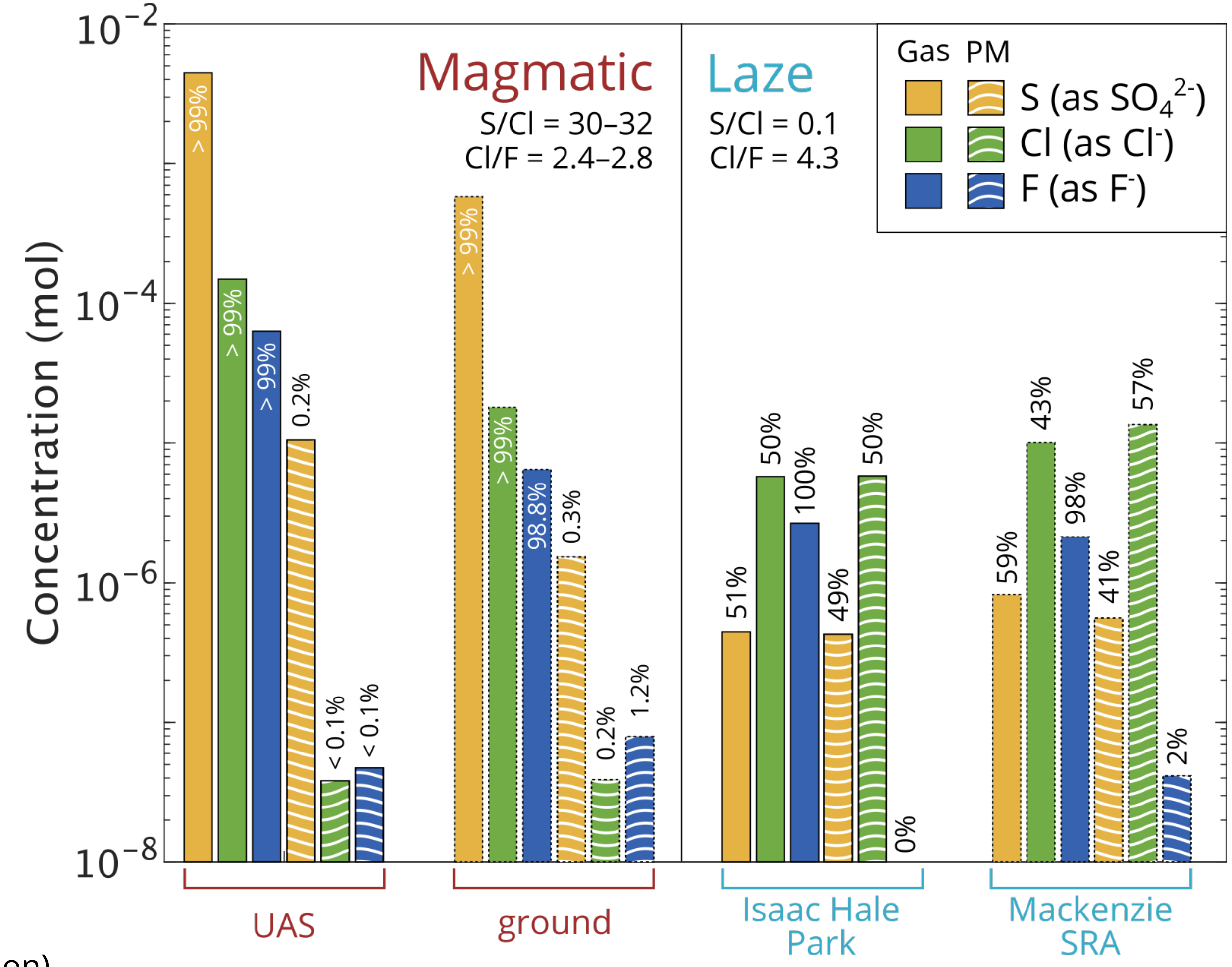
Common ligand-forming elements in the magmatic and laze plumes for Kīlauea 2018

Magmatic plume

- **<0.1%** particulate matter
- Dominated by **sulfur** in both the **gas** and **particulate** phase

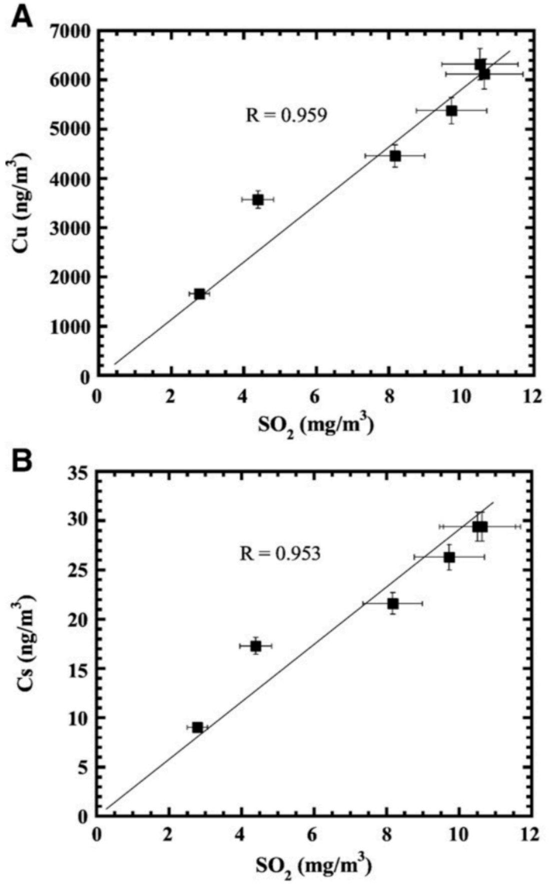


Laze plume

- **~50%** particulate matter
- Dominated by **chlorine**, lower in sulfur

Figures from Mason et al., (pre-submission).

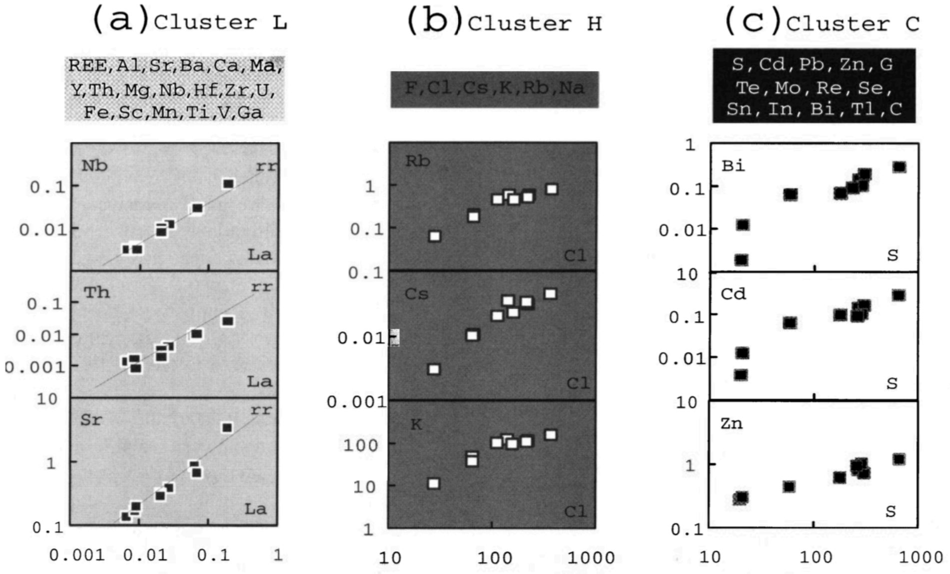
How do we determine the speciation of volatile trace elements in high temperature gases?



Correlation coefficients: Moune et al., 2010

Previous studies of volcanic emissions have taken different approaches to determine or infer speciation.

- **thermodynamic models**, e.g. HSC chemistry – Mandon et al., (2019), Martin, Mather and Pyle (2006), Gerlach (2004); and GASWORKS/SOLVGAS (Symonds, Reed and Rose, 1992);

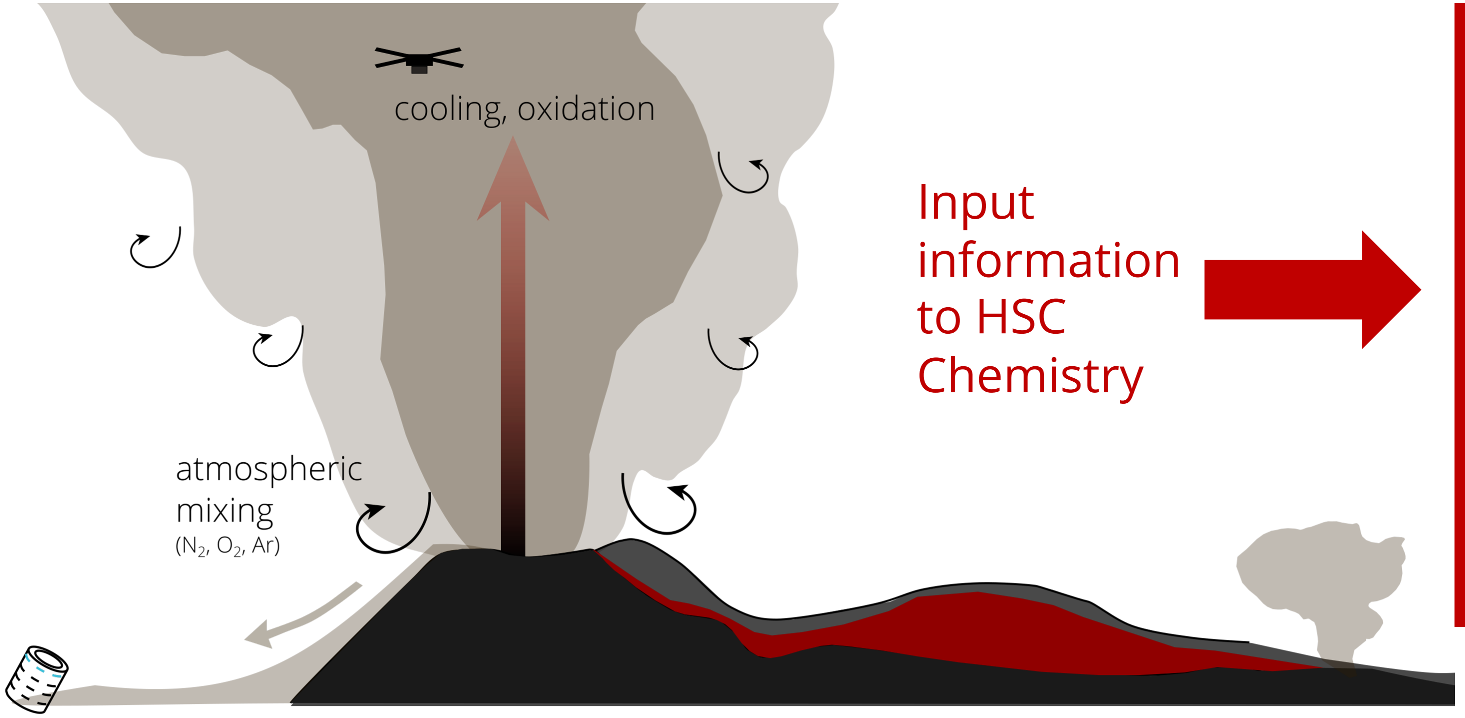


Cluster analysis: Aiuppa *et al.*, 2003

- **cluster analysis** (Aiuppa *et al.*, 2003);
- comparison of **correlation coefficients** between trace elements and different ligands (Moune *et al.*, 2010);
- and studies of **mineral species in sublimates** (Zelenski *et al.*, 2013).

In this study we used HSC Chemistry to model the speciation in the high temperature magmatic plume emitted from Fissure 8

We modelled the oxidation (i.e. mixing with ambient atmosphere) of the magmatic plume at a constant temperature and pressure. HSC then solves a series of mass-balance and mass-action relations to determine the equilibrium speciation of elements in the gas mixture.



Fissure 8

Input information to HSC Chemistry →

1 atm

1145°C
(no cooling)

Major gas inputs
(our data + literature data)

Trace element inputs – ASH CORRECTED
(our data)

Possible phases

HSC chemistry Outotec

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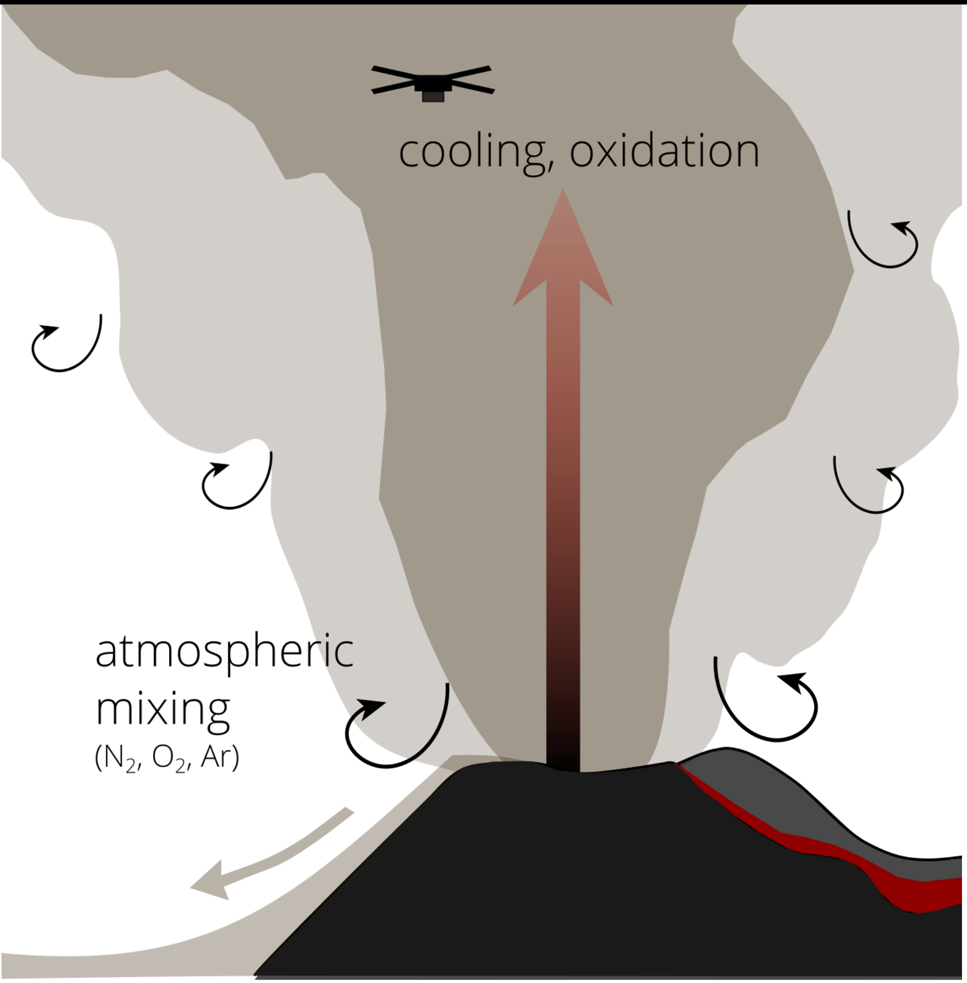
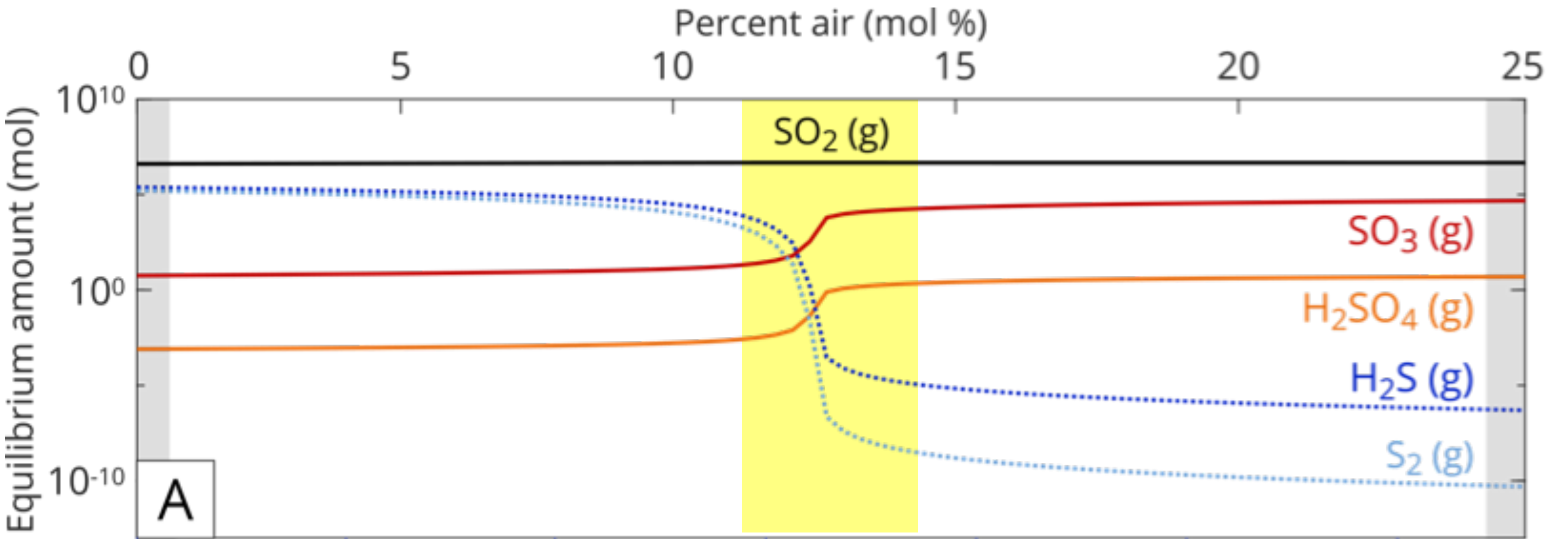
Speciation during oxidation at constant T – the compositional discontinuity



Figures from Mason et al., (pre-submission).

Progressive **mixing** with ambient atmosphere (N_2, O_2, Ar)



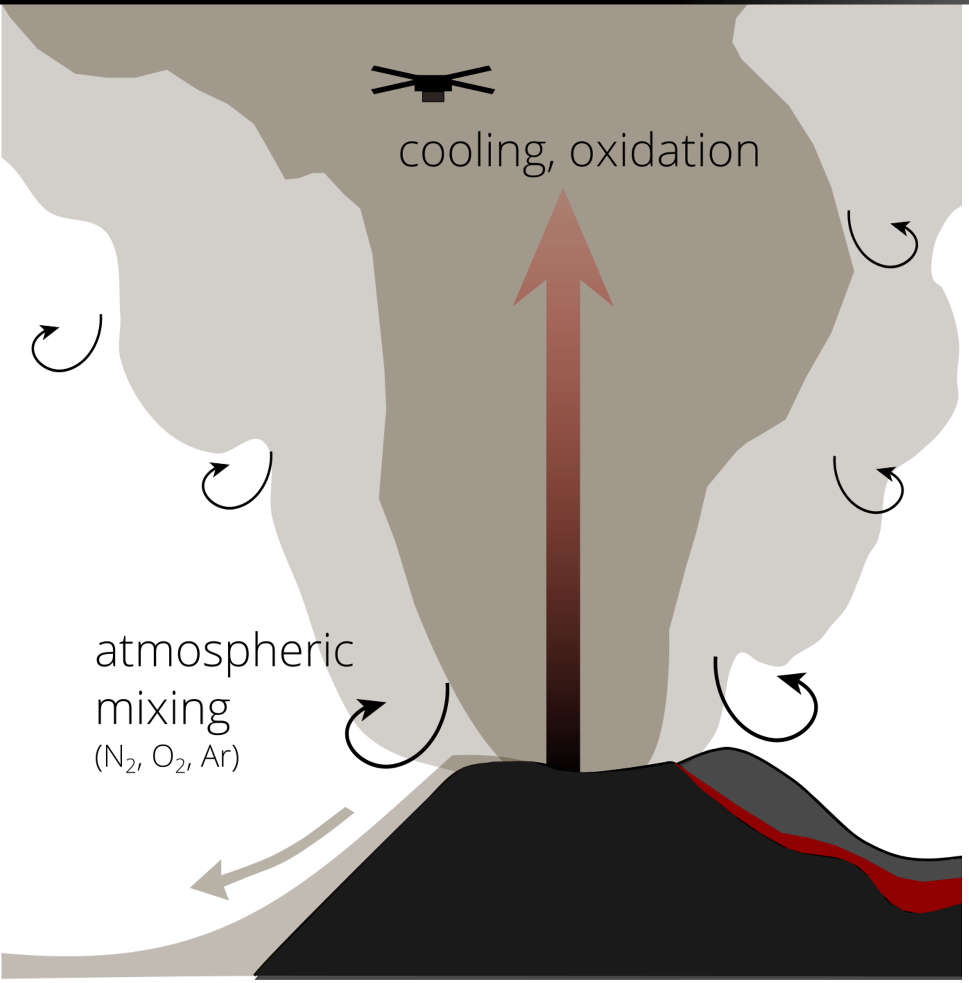
Compositional discontinuity = complete oxidation of reduced species in plume

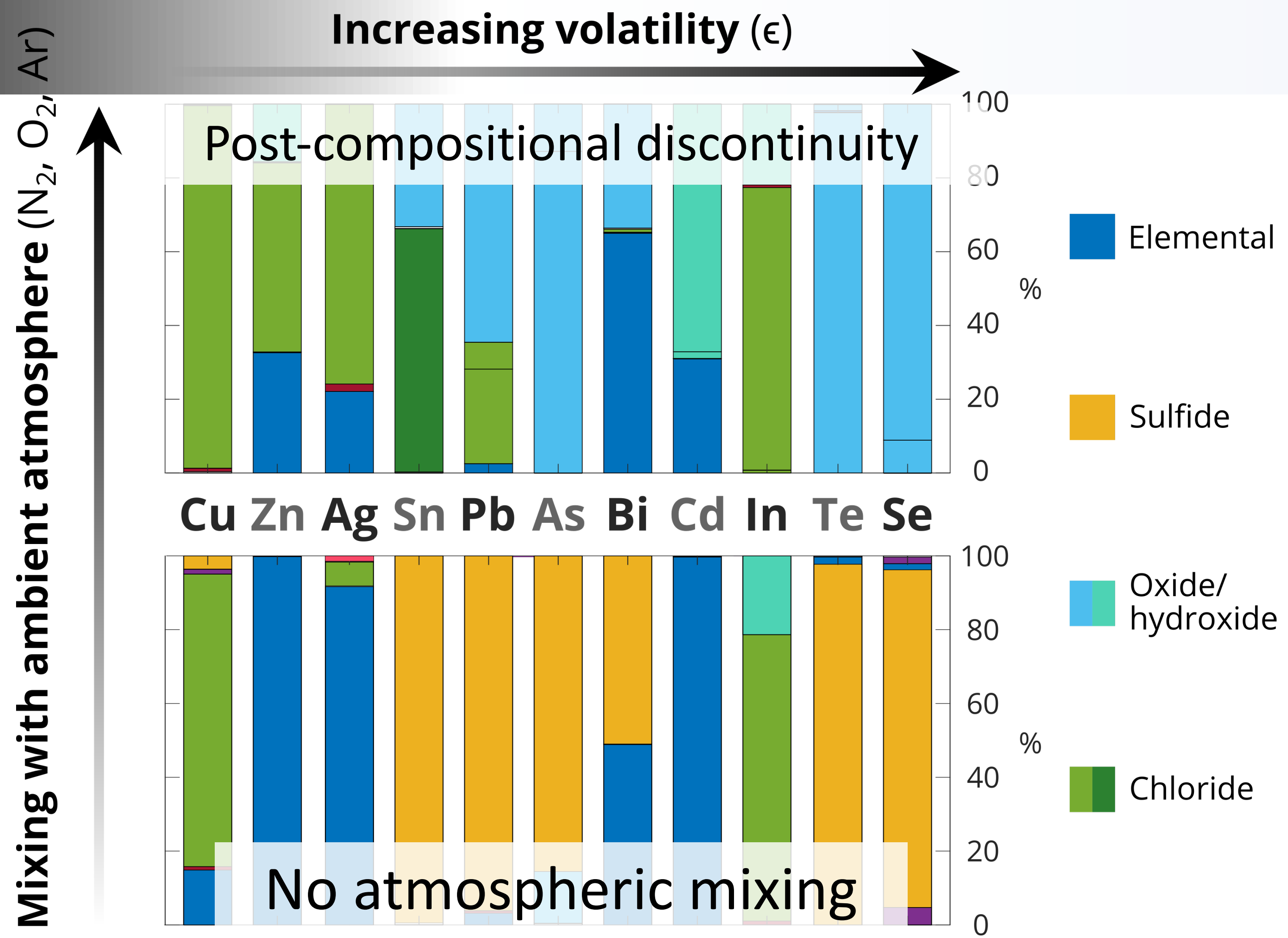
Plot data: this study. Compositional discontinuity observed by Gerlach and Nordlie (1975); Martin et al. (2006)

HSC chemistry
Outotec

Speciation of volatile trace elements

See extra slides for more detail on this figure





Figures from Mason et al., (pre-submission).

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Increasing the amount of Cl in the plume causes certain elements to be present more predominantly as chlorides: particularly, Cd, Bi, Re, Ag, Zn and Cu….

Figure from Mason et al., (pre-submission).

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- Kīlauea emits a **consistent fingerprint** of volatile trace elements – this could pre used for **forecasting** purposes and identifying volcanic signatures in **geological records.**
- Speciation models can be used as **initial conditions in atmospheric transport models**
- Size fractions allow us to put elements into **broad source categories** (i.e. ash and non-silicate aerosol)
- The laze plume composition represents **seawater enriched by degassing of volatiles + dissolution of basalt** but some elements with Cl^- affinity (Cu, Ag, Zn, Cd, Bi, Re) may be sourced from late-stage degassing, **enhanced in the presence of elevated Cl^-**?

Thank you

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Extra slides

Ash corrections

Ash proportion

$$= [A]_{aerosol}/[A]_{glass}$$

Where A is the reference element

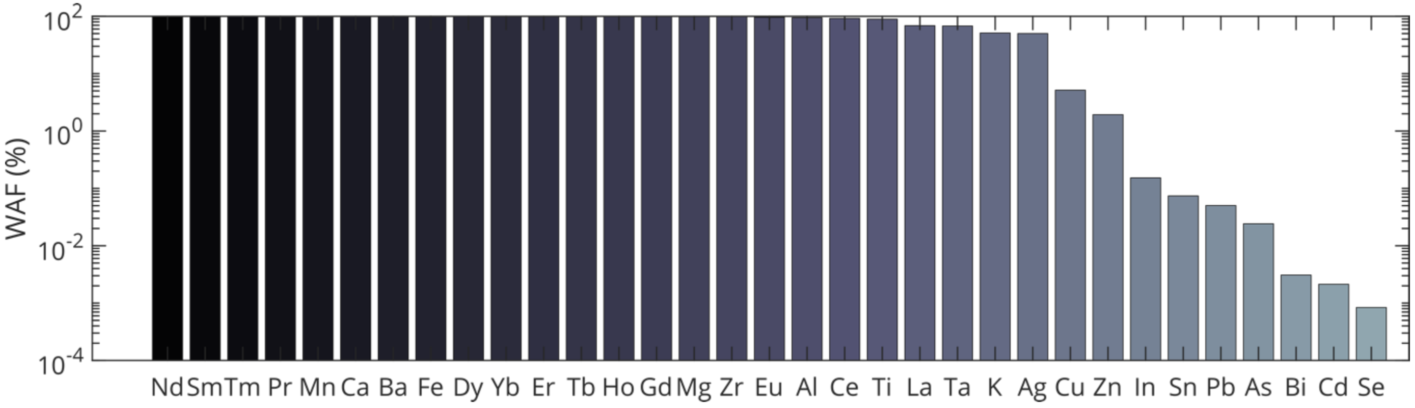
Here: all REEs (except La and Ce +Fe, Ti, Al) – thick black dashed line, below)

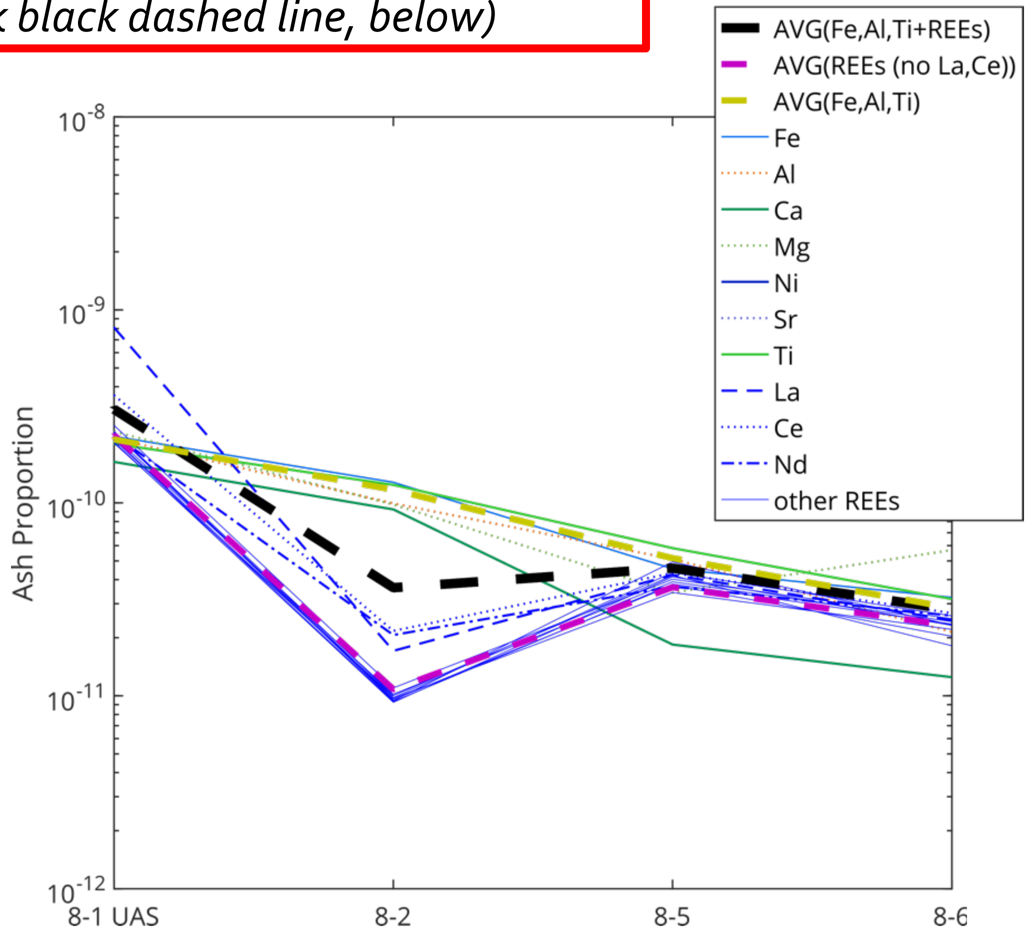
$$[A]_{filter} = [A]_{ash} * X_{ash} + [A]_{aerosol} * (1 - X_{ash})$$

Using lithophile reference element(s), assume $[A]_{aerosol} = 0$, so:

$\longrightarrow X_{ash} = [A]_{filter}/[A]_{ash}$

Weighted ash fraction (%): $WAF = 100 * \left(X_{ash} * [A]_{glass}\right)/[A]_{aerosol}$





More detailed figure for speciation

No atmospheric mixing

Post-compositional discontinuity