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

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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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Related presentations at EGU this year

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Tracking sulfur and its chalcophile allies at Kīlauea volcano, Hawai’i
EGU2020-355 | GMPV8.3/NH2.7
Tue, 05 May, 14:00–15:45 | D1553

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

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
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**

2. Volatile trace elements sourced from volcanoes can act as **nutrients, pollumants 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 Kīlauea 2008.
Speciation of volatile trace elements during oxidation of the plume

At the point of emission (i.e. no atmospheric mixing)

Oxidized plume

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

Figures from Mason et al., (pre-submission).
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 H2O enhance concentrations of elements with Cl-affinity ()see extra slides for speciation evidence of this affinity?

...and these are the volatile elements in the laze plume that are elevated above both seawater and basalt compositions. 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 be 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**
More detailed slides
The eruption of Kīlauea in 2018 produced two very different plumes of gas and particles

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

**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

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

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

\[
\epsilon = \frac{c_i - c_f}{c_i}
\]

Measure of how extensively an element degasses from magma

(Originally defined by Lambert (1985) and Gill (1985))
But other methods are available...

Weighted ash fractions describe the percentage of an element's concentration that 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 it 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 use 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.
Volatile vs. refractory elements

Refractory lithophiles

• 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 ($\epsilon$) 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)

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

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

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
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

![Bar chart showing concentration in mol for magmatic plume](image)

**Laze plume**

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

![Bar chart showing concentration in mol for laze plume](image)

Figures from Mason et al., (pre-submission).
How do we determine the speciation of volatile trace elements in high temperature gases?

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);

- 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.
Speciation during oxidation at constant T – the compositional discontinuity

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

Progressive mixing with ambient atmosphere (N\textsubscript{2}, O\textsubscript{2}, Ar)

Compositional discontinuity = complete oxidation of reduced species in plume

Figures from Mason et al., (pre-submission).
Speciation of volatile trace elements

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

See extra slides for more detail on this figure.
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).
• 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
Extra slides
Ash corrections

\[ [A]_{\text{filter}} = [A]_{\text{ash}} \times X_{\text{ash}} + [A]_{\text{aerosol}} \times (1 - X_{\text{ash}}) \]

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

\[ \rightarrow X_{\text{ash}} = \frac{[A]_{\text{filter}}}{[A]_{\text{ash}}} \]

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

**Ash proportion**

\[ = [A]_{\text{aerosol}} / [A]_{\text{glass}} \]

*Where A is the reference element*

*Here: all REEs (except La and Ce +Fe, Ti, Al) – thick black dashed line, below*
More detailed figure for speciation

No atmospheric mixing

Post-compositional discontinuity