Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kīlauea Volcano, Hawai‘i

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Abstract
Volcanoes represent one of the largest natural sources of metals to Earth’s surface. Emissions of these pollutants and/or nutrients have important implications for the biosphere. We compare gas and particulate chemistry, including metals, of the substantial magmatic (≥200 kt/day SO₂) and lava-seawater interaction (laze) plumes from the 2018 eruption of Kīlauea, Hawai‘i. The magmatic plume contains abundant volatile chalcophile metals (e.g. Se), whereas the laze is enriched in seawater components (e.g. Cl), yet Cu concentrations are 10⁵ times higher than seawater. High-temperature speciation modelling of magmatic gases at the lava-air interface emphasises chloride’s critical role in metal/metalloid complexation during degassing. In the laze, concentrations of moderately (Cu, Zn, Ag) to highly volatile (Bi, Cd) metals are elevated above seawater. These metals have an affinity for chloride and are derived from late-stage degassing of distal lavas, potentially facilitated...
by the HCl gas formed as seawater boils. Understanding these processes yields insights into the environmental impacts of volcanism in the present day and geological past. [163 words]
Introduction

Volcanoes have shaped the composition of Earth’s atmosphere over geological time, controlling Earth’s habitability through the outgassing of hydrogen-, carbon- and sulfur-bearing species\textsuperscript{1–3}. Volcanoes also supply significant fluxes of volatile trace elements, including metals and metalloids, in the gas phase or as non-silicate particulate matter (PM, also called aerosol)\textsuperscript{4–12}. Volcanogenic metal emissions have been sampled and studied at many volcanoes worldwide (e.g. \textsuperscript{6–13}), and early studies date back to the 1960s and 70s (e.g. \textsuperscript{14,15}). During periods of intense unrest or eruption, volcanic emission rates of metals such as cadmium (Cd), copper (Cu) and zinc (Zn) can be equal to or, in some cases, orders of magnitude greater than daily anthropogenic emissions from entire regions (e.g. the Mediterranean basin\textsuperscript{14}) or countries (Ilyinskaya et al. \textit{in review}), and volcanoes are one of the largest natural sources of many metals\textsuperscript{16}. Some trace metals present in volcanic plumes can act as nutrients for living organisms at low levels, yet at higher concentrations are categorised by environmental agencies as pollutants known to be harmful to health\textsuperscript{17,18}. Basaltic volcanoes typically release relatively ash-poor plumes into the troposphere\textsuperscript{9}, exposing populations both relatively nearby (e.g. Kīlauea, Hawai‘i, 1983–2018\textsuperscript{19}; Masaya, Nicaragua, 1993–present\textsuperscript{20}) and thousands of km downwind (e.g. Laki, Iceland\textsuperscript{21}) to sustained high levels of volcanogenic gases (e.g. SO\textsubscript{2}) and trace metal-bearing PM. Understanding volcanic metal emissions at volcanoes also provides important constraints on the environmental impact of large, prehistoric basaltic eruptions, including flood basalts\textsuperscript{22–24}. However, much remains to be discovered about metal abundance and speciation in volcanic gas and aerosol emissions.

Basaltic ocean island volcanoes, such as those found on the Island of Hawai‘i, can also produce an additional source of gas and PM emissions as lava flows reach coastlines and rapidly boil and evaporate seawater, with significant implications for the marine biosphere\textsuperscript{25}. Lava-seawater interactions, which produce acidic ‘laze’ plumes, have occurred
throughout Earth’s history, often associated with some of the most dramatic manifestations of volcanism (e.g. the eruption of ocean plateau basalts such as the Kerguelen and Ontong Java Plateaus). Fragments of silicate material can be generated during lava-seawater interactions through a fuel-coolant-type interaction as seawater invades lava tubes, as well as during collapse of lava deltas. A major component of laze plumes after water (~98–99 mol% of the gas phase) is hydrogen chloride (HCl) gas, and it has been suggested that HCl emission rates from laze plumes at Kīlauea volcano, Hawai’i are comparable to or may exceed that from coal-fired power plants in the United States. However, despite the hazards and potential impacts of lava ocean entry plumes on the biosphere, only a few detailed studies have been carried out and relatively little is known about their chemistry compared to magmatic plumes.

The 2018 eruption of Kīlauea – a basaltic shield volcano located in the south-east of the Island of Hawai’i (Figure 1A) – presented a rare opportunity to study the emissions of volatile trace metals in substantial magmatic and laze plumes. Before 30 April 2018, the eruptive activity at Kīlauea was relatively stable at two locations: a lava lake within the Halema’uma’u summit crater (active since 2008), and the Pu’u ‘Ō’ō cone and other vents in the East Rift Zone (ERZ), as part of the long-lived Pu’u ‘Ō’ō-Kupianaha eruption of Kīlauea (1983-2018). On 30 April 2020 the Pu’u ‘Ō’ō vent collapsed, and magma propagated down the lower East Rift Zone (LERZ) of Kīlauea. On 3 May 2018, the first of 24 fissures opened in the Leilani Estates subdivision on the LERZ, and by the end of May, activity had largely focused at a single vent known as Fissure 8 (19.4627 °N, 154.9091 °W, ~220 m a.s.l., Figure 1A). Lava flows from the 2018 LERZ eruption reached the coast on 23 May 2018, creating a laze plume (Figure 1C) as still-molten lava boiled and evaporated seawater. SO₂ emission rates recorded at Fissure 8 during the eruption were the highest since continuous SO₂ gas monitoring began at Kīlauea in 1979. Peak emission rates exceeding 200 kt/day were recorded from the LERZ in June and early July, exceeding Kīlauea’s 2014 to 2017 average SO₂ emission rate (combined summit and ERZ) of 5.1 ± 0.3 kt/day SO₂, by two orders of magnitude. Exposure to poor air quality (SO₂ and PM) during the 2018...
LERZ eruption surpassed that observed during the 1983–early 2018 eruption episodes at Kilaeua\textsuperscript{19,39}. Further, in terms of both eruption rates (50–500 m\textsuperscript{3}/s, dense rock equivalent)\textsuperscript{35,40} and erupted volume (\textasciitilde 1.5 km\textsuperscript{3} in 94 days)\textsuperscript{41}, the 2018 eruption was 1–2 orders of magnitude larger than any other in the preceding 180 years of activity on the LERZ\textsuperscript{41}. The lava effusion and SO\textsubscript{2} emissions from Fissure 8 declined dramatically on the 4\textsuperscript{th} August 2018\textsuperscript{35}.

During the 2018 LERZ eruption of Kilaeua we used both ground-based and Unoccupied Aircraft System (UAS) platforms (sample summary in Table S1; see also Methods, Figure S3 and S4) to quantify the major and trace element, including trace metals, compositions of gas and size-segregated PM (in µg/m\textsuperscript{3}) emitted in both the magmatic plume from the main active vent (Fissure 8, Figure 1B, data in Tables S8–S10) and the laze plume at the ocean entry (Figure 1C, data in Tables S12–S14). Here, we use emanation coefficients to quantify element volatility in the magmatic plume, and X/SO\textsubscript{2} ratios to demonstrate the consistency of Kilaeua’s volatile metal fingerprint across different eruptive periods (Table S11). We also use a Gibbs Energy Minimisation algorithm to model speciation during the oxidation and cooling of Kilaeua’s magmatic plume close to the lava-air interface, and we add to existing direct observations, experimental and modelling evidence (e.g.\textsuperscript{11,13,42–44}) of the importance of chloride as a control on trace metal degassing (Tables S20–S27). Our study of the laze plume reveals that late-stage degassing of distal lava flows at the ocean entry contains volatile metals that complex with chloride (e.g. Cu, Zn), while those that complex with sulfide (e.g. Se, As) are notably absent. We conclude that the chloride-rich environment of the ocean entry, as well as the changes in the volatile concentrations of degassing melts between the source vent and distal lava flows, promotes degassing of chloride complexes.
Results and discussion

Element volatility at Kīlauea Volcano

Measured concentrations of elements in the magmatic plume (Tables S8-10) can be used to calculate the relative volatility of each element during degassing (i.e. to what degree volatile trace elements degas from magmas). This volatility can be expressed using various measures, including enrichment factors and emanation coefficients. Here we use emanation coefficients to assess the volatility of each element (other measures are described in supplement section S5). Emanation coefficients describe the degree to which an element is degassed from its parent melt according to $\varepsilon = ([X]_i - [X]_f)/[X]_i$, where $[X]_i$ and $[X]_f$ are the initial undegassed and final degassed concentrations of element $X$ in the magma, respectively (originally defined by). Emanation coefficients can be estimated in a range of ways, including: 1) using enrichment factors and the assumed constant emanation coefficient of Pb from molten basalt and; 2) comparing undegassed and degassed melts (e.g. ). In this study, $[X]_i$ is calculated by adding the concentration of a degassed element in the magmatic plume (using X/S ratios measured at Fissure 8, corrected for air dilution) to a degassed matrix glass composition, i.e. $[X]_f$ (e.g. ; data sources in Table S15).

Methods. We use the calculated $\varepsilon$ values to group elements into volatile ($\varepsilon > 0.001\%$) and refractory elements ($\varepsilon < 0.001\%$; Figure 2A and B). For elements with a calculated $\varepsilon$ greater than zero, their order of increasing volatility is: $\varepsilon < 0.01\%$: Nd, Eu, Al, Ce, Ti, La, Ta, Ba, K, Cu; $\varepsilon > 0.1\%$: Zn, Ag, Sn, Pb; then at $\varepsilon > 1\%$: As, F, Bi; and $\varepsilon > 10\%$: In, Cd, Se, Cl, Re, Te, S.

Size-segregated concentrations of particles in the magmatic plume provide information on the mechanisms of particle formation, and can be used to corroborate $\varepsilon$ calculations. Previous work has ascribed broad formation processes to particle diameter ($D$) ranges: 1) $D < 0.1 \mu m$: the ‘nucleation’ mode, associated with cooling, oxidation and quenching of magmatic gases as they mix with the ambient atmosphere; 2) $0.1 \mu m < D < 2 \mu m$: the ‘accumulation’ mode, formed from the condensation of low volatility vapours and from
agglomeration (‘sticking together’) and growth of particles in the nucleation mode; 3) \( D > 2 \) \( \mu m \): the ‘coarse particle’ mode, composed largely of mechanically-generated particles (e.g. ash)\(^{48}\). In the magmatic plume emitted from Fissure 8, simultaneous gas and PM measurements (using filter packs, Methods) showed that PM accounted for < 0.01% of the total mass of S, Cl and F, i.e. these elements are present in the near-source plume almost entirely as gases (Figure 3). For the PM, S is concentrated in the smallest size fraction (~91% collected with diameter, \( D \leq 0.25 \mu m \); ~ 0.5% collected with \( D \geq 2.5 \mu m \); Figure 2B), while F is found predominantly (~57%) in the largest size fraction (\( D \geq 2.5 \mu m \)) and Cl concentrations are bimodal with the majority (~60%) found in \( D \leq 0.25 \mu m \), and ~27% found in \( D \geq 2.5 \mu m \). The presence of Cl, F and to a much lesser extent S, in the coarse fraction could represent adsorption of HCl, HF and SO\(_2\) gases onto ash in the plume\(^{49,50}\), however further investigation into this process at Kīlauea is beyond the scope of this study.

Volatile trace elements can be subdivided into a refractory ‘coarse particle’ fraction present as silicates (i.e. ash; Figure 2A) and a volatile fine fraction present as non-silicate PM (Figure 2B). Refractory elements (\( \epsilon < 0.001\% \), e.g. Ca, Ba, Al, P, Ti, Mn, Fe, Zr and the rare earth elements, REEs) in the magmatic plume are generally found in size fractions with \( D > 0.25 \mu m \); 10–100% of their concentration in PM is found within the \( D > 2.5 \mu m \). These elements are likely derived from ash generated during lava fountaining and fine fragmentation at the Fissure 8 vent. Weighted ash fractions (WAFs) calculated for these elements in the magmatic plume (ash correction in Methods, Table S11) support this conclusion: for all of the refractory elements in Figure 2A apart from Ti, La and Ba, >90% of their concentrations can be accounted for by ash (WAFs: Ti = 89%; La = 69%; Ba = 45%). In contrast, volatile elements (\( \epsilon > 0.001\% \), Cu, Zn, Ag, Sn, Pb, As, F, Bi, In, Cd, Se, Cl, Re, Te, S, in order of increasing volatility) are predominantly found at \( D < 0.25 \mu m \), consistent with typical diameters of the ‘nucleation mode’\(^{48}\), and have weighted ash fractions < 0.3%, except Cu (5%), Zn (2%), F (7%) and Cl (1%). The size-segregated concentrations of elements observed in Kīlauea’s 2018 magmatic plume match broadly with those made at Kīlauea’s
summit in 2008\textsuperscript{9} (i.e. refractory elements = coarse, volatiles = fine) however, concentrations
of volatile trace elements are more evenly distributed across the size bins in 2009 than in
2018 (discussed in supplement section \textbf{S10, Figure S18}).
Kīlauea’s trace metal compositional ‘fingerprint’

While volatile trace element fluxes at Kīlauea in 2018 are the highest recorded at the volcano (and at any intraplate volcano Figure 4B, Methods), the relative abundances of volatile trace elements measured at Kīlauea correspond closely between different eruptive periods. To eliminate differences between samples due to variable plume dilution, we compare the composition of Kīlauea’s 2018 magmatic plume composition to other volcanic plumes using trace element to SO$_2$ mass ratios (X/SO$_2$, Table S1 and Figure 4A). X/SO$_2$ ratios at Kīlauea in 2018 agree within an order of magnitude with previous measurements made at Kīlauea summit in 2008$^9$. Emanation coefficients calculated for Kīlauea in 2018 (Methods) also agree, to within an order of magnitude, with petrological estimates obtained through the comparison of variably degassed Kīlauean melt inclusions and matrix glasses$^{47}$ (Figure 5A). The order of element volatility at Kīlauea matches that derived from measurements made at Erta ‘Ale volcano, an intraplate basaltic volcano in Ethiopia$^{10}$ (Figure 5A). However, X/SO$_2$ ratios and emanation coefficients at Holuhraun, a hotspot-related, basaltic volcano, are 1–2 orders of magnitude lower than those measured at Kīlauea and Erta ‘Ale (Figure 4A; Figure 5A). This may be due to the low chlorine contents in the Holuhraun plume, reducing the availability of ligands$^{11}$ (total, gas + PM, S/Cl mass ratio at Holuhraun = 40–52$^{11}$; at Kīlauea = 27–29, this study; at Erta ‘Ale = 6-15$^{10}$).
Speciation of magmatic gases in Kīlauea’s magmatic plume

The speciation of volatile trace elements as they are emitted at the lava-air interface provides key initial conditions for the subsequent atmospheric transport, solubility, deposition and resulting hazard from these elements (Ilyinskaya et al. in review). Major elements – such as S, Cl, O and H (as well as, to a lesser extent, F and other halogens) – are the main ligand-forming elements for volatile trace metals in volcanic gas emissions (e.g. as sulfates \( \text{SO}_2^- \), sulfides \( \text{S}^2^- \), chlorides \( \text{Cl}^- \), fluorides \( \text{F}^- \), oxides \( \text{O}^{2-} \) and hydroxides \( \text{OH}^- \)\(^{10,43} \)).

The magmatic plume emitted from Fissure 8 was S-rich, with molar gas ratios for \( \text{SO}_2/\text{HCl} \) and \( \text{HCl}/\text{HF} \) of 30–32 and 2.4–2.8, respectively. These ratios are similar to those measured from previous persistent emissions at the Pu`u`Ō`ō vent in 2004–05 \( (\text{SO}_2/\text{HCl} \sim 23, \text{HCl}/\text{HF} \sim 1.4)^{51} \), and from the summit in 2008–09 \( (\text{SO}_2/\text{HCl} \sim 20–28, \text{HCl}/\text{HF} \sim 1.1–2.0)^9 \). The speciation of volatile trace elements at thermodynamic equilibrium during volcanic degassing has been modelled at several arc volcanoes (e.g. \(^{13,43}\) however models of trace element speciation at intraplate volcanoes are rarer. Factors that control the speciation of elements in volcanic gas emissions include the temperature at the point of degassing, the composition of the parent magma, the amount of atmospheric mixing before ‘quenching’ (i.e. the cooling of gases to a largely non-reactive state\(^{52}\)), and the volatility of the speciated or elemental forms they degas as from the parent magma\(^{43,53–55}\). We note that kinetic effects also play an important role in determining the speciation of emitted gases and particulates\(^{56}\), and these are not accounted for in the thermodynamic speciation model presented here. Speciation modelling in this study is relevant only to the high temperature mixture of atmospheric and magmatic gases generated close to the lava-air interface, where gases can be assumed to attain equilibrium rapidly, and kinetic effects are assumed to be negligible\(^{54,57}\). Mixing between a magmatic plume and the background atmosphere is typically described as a ratio \( V_a/V_m \), where \( V_a \) is the volume of air in the mixture, and \( V_m \) is the volume of undiluted magmatic plume in the mixture (mixing can also be described as a mol% of air in the mixture). Previous studies\(^{52,54}\) observed a compositional discontinuity (CD).
in plume chemistry corresponding to the near-complete oxidation of reduced gas species such as H$_2$S and S$_2$ (Figure 6A). Using a typical arc plume composition, Martin et al. observed a CD at ~ 5.7 mol% air ($V_A/V_M \sim 0.06$). For a Kilauea plume composition (Table S6), the CD occurs at ~ 15% air ($V_A/V_M \sim 0.16$, Figure S12), because of the higher concentration of reduced species in the Kilauea plume at the point of emission compared to arc volcanoes.

We modelled the equilibrium speciation of gas phases in the magmatic plume using the Gibbs Energy Minimisation module of HSC Chemistry (version 9.9.2, Outotec Research Oy, Finland; Methods). From an initial magmatic gas equilibrium temperature of 1145°C (based on the MgO content of 2018 Kilauea lavas, Methods), we model speciation during early mixing of magmatic gases with the atmosphere ($0 < (V_A/V_M) < 0.33$); atmosphere is added as a 78:21:1 mixture of N$_2$:O$_2$:Ar in increments of $V_A/V_M = 0.01$. To determine the temperature decrease during mixing, we use a simple model of temperature change during mixing of two gases of different temperatures – N$_2$, O$_2$ and Ar gases to represent the atmosphere at 25°C and H$_2$O vapour at 1145°C to represent the magmatic gases (following Ilyinskaya et al.; Methods). This generates a temperature decrease from 1145°C to 1016°C between $V_A/V_M = 0$ and $V_A/V_M = 0.33$.

Broadly, at the point of emission with no atmospheric mixing, $V_A/V_M = 0$, volatile trace elements can be grouped into those complexed as gases with S$^2$ (emanation coefficient, $\epsilon > 10\%$ – STe and SSe; $\epsilon > 1\%$ – BiS, AsS; $\epsilon > 0.01\%$ – PbS, SnS), those complexed with Cl$^-$ ($\epsilon > 10\%$ – InCl; $\epsilon > 0.01\%$ – AgCl, CuCl), and elemental gases ($\epsilon > 0.01\%$ – Cd, $\epsilon > 1\%$ – Bi, $\epsilon > 0.01\%$ – Ag, Zn, Cu; Figure 6B, Figure 9A). At $V_A/V_M = 0.33$ (or 25% air) and $T = 1016\degree$C, those elements with greatest affinity for S before the CD are now present predominantly as oxides, and those that were present in elemental forms now present as chlorides, hydroxides or oxides (Figure 6C). The speciation groupings observed at $V_A/V_M = 0$ highlights the critical role that the oxidation state of magmas (which will determine the availability of certain ligands, e.g. S$^2$), as well as their S and Cl contents, play in determining
degassing of volatile trace metals\textsuperscript{55}. The concentration of chloride complexes increases after the compositional discontinuity (Figure 6C), consistent with previous work\textsuperscript{54,57} that has shown that the oxidation of magmatic gases creates more reactive halide species, thus increasing the proportion of elements present as chlorides. Elements that do not complex with chloride (e.g. Se, Te, As) generally will not form chlorides unless the HCl gas content of the plume is increased between 100-1000 times ($V_A/V_M = 0$, $T = 1145^\circ$C, Figure S16; $V_A/V_M = 0.33$, $T = 1016^\circ$C, Figure 8). In the case of Se, even 1000 times the original HCl gas concentration does not cause Se to complex with chloride.

A number of previous studies have demonstrated or inferred the importance of chloride for trace metal degassing, from both natural sampling (at arcs\textsuperscript{13,43,55} and other hotspot volcanoes\textsuperscript{11}) and experimental work\textsuperscript{44}. Thermodynamic speciation modelling of the composition of magmatic gases released at arc volcanoes, which typically have a higher Cl content and more oxidised magmas than intraplate volcanoes, has shown that volatile trace metals and metalloids are speciated predominantly as chloride gases during high temperature degassing\textsuperscript{13,43}. For example, in the magmatic plume of Yasur, a basaltic volcano in the Vanuatu archipelago, at magmatic gas temperatures of 1100°C and no atmospheric mixing (i.e. $V_A/V_M = 0$) Pb is found mainly to be speciated as PbCl gas\textsuperscript{13}. This is in contrast to the Kīlauea plume modelled in this study, in which Pb is present predominantly as PbS gas at $V_A/V_M = 0$ and a temperature of 1145°C (modelling of the Kīlauea plume at 1100°C does not change the dominant speciation of Pb or Bi, i.e. the difference between Yasur and Kīlauea is not simply a temperature effect). Similarly, BiS gas is considerably less abundant in the Yasur plume compared to Kīlauea, with elemental Bi gas and BiCl gas dominant instead. Similar observations were made in thermodynamic models of the magmatic plume of Mount Augustine in Alaska\textsuperscript{43} (although some differences in this case may be due to improvements in the speciation models over time, through the introduction of new thermodynamic data).

Volcanic plumes in arc settings display characteristic differences in the relative abundances of volatile trace elements when compared to intraplate settings\textsuperscript{55}; $X/\text{SO}_2$ ratios
for some elements (e.g. In and Cu) are up to 2–3 orders of magnitude higher in arc plumes, while others (e.g. Te, Se, Sn) differ little between different tectonic settings (Figure 4A). These differences have been explained by more oxidized magmas, and higher concentrations of chlorine (mean arc SO$_2$/HCl $\sim$1.9$^{57}$, vs SO$_2$/HCl 30–32 at Kilauea, this study) and water at arc settings, which promote metal partitioning directly into aqueous/saline aqueous fluid$^{45}$. Speciation modelling in this study (Figure 6, Figure 8) supports these conclusions – it shows that the elements most enriched in arc emissions are present as chloride gases (e.g. InCl and CuCl, Figure 6B) at the point of emission (i.e. no mixing with air). In contrast, elements that behave similarly between volcanoes at different tectonic settings are emitted as sulfide gases at Kilauea (e.g. STe, SSe, SSn, Figure 6B).
The origin of the laze plume and late-stage degassing at the ocean entry

The composition of the laze plume, in terms of both volatile ligand-forming and trace elements, differs significantly from the magmatic plume. As has been shown in previous work\(^9\), the laze plume is relatively Cl-rich and S-poor, which mostly reflects the large contribution that boiled seawater makes to the laze plume. Total (gas and PM) molar ratios for S/Cl and Cl/F are 0.1 and 4.3, respectively (compared to \(~30–32\) and \(~2.4–2.8\), in the magmatic plume, Figure 3). In the laze plume, a larger fraction of S and Cl concentrations are measured in the PM (41–49\% S, 50–57\% Cl in PM), while the magmatic plume is gas-dominated at source for these elements (<0.3\% of S and Cl in PM). PM fractions for F are comparable between the laze plume (0–2\% in PM) and the magmatic plume (<1.2\% in PM) (Figure 3). S and Cl concentrations are distributed uniformly across the five size fractions (Figure 2D, Table S14), while F is concentrated in the largest size fraction (~75\% = \(D \geq 2.5\ \mu\text{m}\)), which may be linked to HF adsorption onto silicate particles\(^{49}\). Concentrations of volatile trace elements (\(\epsilon > 0.001\%\)) are generally lower in the laze plume than in the magmatic plume (with the notable exception of Cu, and to a lesser extent Ag, Table S8 and S12). As in the magmatic plume, volatile elements (\(\epsilon > 0.001\%\)) are found predominantly in the smallest size fraction: for all but Te, >40\% of the concentration of volatile elements (\(\epsilon > 0.001\%\)) is found in the \(D \leq 0.25\ \mu\text{m}\) fraction, consistent with particles formed by gas-to-particle conversion post-degassing\(^{48}\) (Figure 2D, Table S14). Note that Te concentrations are close to detection limits (Table S8) of the analysis (Methods). In contrast to the magmatic plume, the size distribution of particulates containing refractory elements (\(\epsilon < 0.001\%\)) in the laze plume is strongly bimodal, with many elements only measured above detection limits in the smallest (\(D \leq 0.25\ \mu\text{m}\)) and largest (\(D \geq 2.5\ \mu\text{m}\), consistent with a silicate source) size fractions (Figure 2C, Table S14).

To get a broad sense of trace metal emission rates from the laze plume in 2018 we follow the method of Edmonds and Gerlach\(^9\), who estimated the HCl emission rates in a laze plume associated with lava flows emanating from the Pu‘u ‘Ō‘ō vent (2004-05). We use
lava effusion rates at the main Fissure 8 vent\textsuperscript{40}, combined with assumptions about how much still-molten lava reaches the ocean entry, to estimate a Cl emission rate from seawater. The Cl emission rate is then combined with X/Cl ratios of trace elements measured in the laze plume to determine trace element emission rates (supplement section S9, Table S7). The uncertainties on these estimates are large. However, notably Cu emission rates from the ocean entry may be higher than those emitted at the main Fissure 8 vent (we estimate \( \sim 230 \text{–} 1600 \text{ kg Cu/day} \) for the laze plume, vs \( 116 \pm 29 \text{ kg/day} \) for Fissure 8), while other volatile metals may produce lower emission rates (laze plume: \( \sim 20 \text{–} 150 \text{ kg Zn/day} \); \( \sim 0.2 \text{–} 2 \text{ kg Ag/day} \); \( \sim 0.01 \text{–} 0.5 \text{ kg Bi/day} \)).

The similarity of the laze plume composition to seawater is assessed by comparing element/chlorine ratios (X/Cl) measured in the plume to X/Cl ratios in seawater (Figure 7). Note that that X/Cl ratios may be fractionated during the rapid evaporation of seawater, particularly for those elements that form salts that may be left behind\textsuperscript{29}. However, such fractionations are as yet unconstrained and so are not considered further here. For elements abundant in seawater (Ca, Mg, Na and K), the laze plume composition is close to an average global seawater composition\textsuperscript{59} (Table S16). However, for Al, Ti, Fe, the REEs and some volatile metals elements (Cd, Bi, Cu, Ag, Zn) the laze plume is enriched relative to average global seawater by \( \sim 2 \text{–} 6 \) orders of magnitude. Correcting the laze plume composition for a contribution from silicates (Methods), can account for elevated concentrations of refractory elements (Ti, Fe, Mn, REEs except La) in the laze plume (Figure 7). This silicate contribution may come from rapidly-quenched fragments of silicate glass generated by explosive hydro-magmatic fragmentation of lava as it interacts with seawater, or from congruent dissolution of basalt by seawater at the ocean entry (as proposed by \textsuperscript{32}). However, after the silicate correction La/Cl and Al/Cl in the laze plume remain \( 100 \) and \( 10000 \) times elevated above seawater ratios, respectively. La is the most volatile REE and therefore may be enriched in the laze plume because it is degassing from lava flows at the ocean entry (more detailed REE discussion in supplementary section S8). Al is intensely particle reactive throughout the water column (e.g.\textsuperscript{60}) and previous work using Al-spiked
seawater boiling experiments\textsuperscript{32} explained similar anomalous Al concentrations by adsorption of Al onto particles formed as seawater boils. If particles that have been subjected to Al adsorption were lofted into the laze plume this could provide an explanation for elevated concentrations of Al.

Silicate-corrected concentrations of Cd, Zn, Ag, Cu, Bi, Re are also elevated in the laze plume above seawater. Cu and Cd enrichments were also observed in a study of seawater close to Kīlauea’s ocean entry in July 2018\textsuperscript{31}. Due to the relatively high volatility of all these elements ($\varepsilon > 0.001\%$), it is likely that these elements are degassing from lava at the ocean entry\textsuperscript{32}. Critical factors that could explain the enhanced degassing of these elements include the oxidation state of the lavas/gases and the availability of ligand-forming elements, such as Cl and S. Basaltic melts have been shown to become more reduced during S degassing\textsuperscript{61}, therefore we would expect lava flow melts at the ocean entry to be more reduced that those emitted at the source vent. However, we note that Lerner et al.\textsuperscript{62} found that melts (matrix glass and melt inclusions) sampled from distal lava flows were more oxidised than those at the source, potentially due to atmospheric interaction during sub-aerial lava flow. Due to this uncertainty, we have investigated the effect of increasing/decreasing the Cl content at seven different initial HCl gas concentrations (0.001, 0.01, 0.1, 1, 10, 100 and 1000 times the initial concentration measured in the magmatic plume, Methods) on the speciation of trace elements in a gas mixture, at both comparatively reduced ($V_A/V_M = 0$) and oxidised ($V_A/V_M = 0.33$) conditions (Methods). The S/Cl ratio of the laze plume is comparable to the model run with ~100 times the amount of HCl gas in the magmatic plume (see data in Tables S8 and S12; and Figure 8).

Cu, Ag and Zn tend to complex predominantly with chloride, at both $V_A/V_M = 0$ and $V_A/V_M = 0.33$ (Figure 6), and their affinity for chloride increases markedly when the HCl gas content of the plume is increased ($V_A/V_M = 0$, $T = 1145^\circ$C, Figure S16; $V_A/V_M = 0.33$, $T = 1016^\circ$C, Figure 8). At $V_A/V_M = 0.33$, and at 100 times the initial HCl gas content, ~100% of Cu, Ag, Zn, Cd and Bi are present as chloride gases (Figure 8). At $V_A/V_M = 0$, Cu, Zn and
Ag are present almost exclusively as chloride gases, while only a small proportion of Bi and Cd are complexed with chloride. Re displays opposite speciation behaviour to Cd and Bi: Re is present as an chloride at $V_A/V_M = 0$ and as an oxide at $V_A/V_M = 0.33$. Without further investigation of the oxidation state of degassing melts at the ocean entry, these models are endmembers, whereas the true oxidation state of gases may lie somewhere in between. From the results of the speciation model, we would also expect other elements with strong chloride affinity to be elevated above seawater and silicate glass in the laze plume, such as Pb and In. These elements were not above detection limits in both filter pack samples (Methods); however, In was above detection limits in the size-segregated sampling (Figure 2D), and a small amount of Pb was detected in one of the UAS samples, as well as in a previous study of a laze plume at Kīlauea\textsuperscript{32}. The strong affinity of the degassed elements for chloride speciation, either at or above magmatic plume chloride concentrations, suggests that their degassing and/or detection at the ocean entry might be facilitated by the presence of elevated chloride.

The availability of Cl at the ocean entry is likely to be higher than that at Fissure 8 for two reasons. Firstly, fractional degassing of lavas between the source and the distal lava flows will decrease the S/Cl ratio of the remaining undegassed volatiles (by Rayleigh distillation)\textsuperscript{63}. For example, during the later stages of degassing of the 2014–15 Holuhraun eruption, S/Cl ratios in emissions were ~50 times lower than measured in the syn-eruptive plume. Secondly, the Cl-rich environment created at the ocean entry due to the boiling seawater to dryness, may facilitate the degassing of Cl-complexes. Our observations of the critical role of chloride from speciation modelling are supported by recent experimental work\textsuperscript{44}, which has shown that increasing the level of chloride available during degassing of a phonolitic melt can increase the amount of Cu hosted in the resulting sublimates, and that chloride sublimates can host significant amounts of Pb, Tl, As, Cu, Bi and Zn\textsuperscript{44}.

The absence of volatile elements that complex with sulfides on degassing (Se, Te and As, Figure 6B) is notable in the laze plume, and may suggest that either 1) processes at the ocean entry act to suppress the degassing of these elements, or 2) their concentrations in the
lava reaching the coast have been depleted by degassing as sulfides at the active vent (Fissure 8) and along the lava flows. This is supported by the observation that up to 90% of S in the melt is degassed at the vent\textsuperscript{62,64}.

The mechanisms by which 1) volatiles degas from rapidly-quenched lavas at the ocean entry, and 2) Cl from seawater enhances the degassing of elements with Cl-affinity, remain speculative. As lavas rapidly cool, quench and fragment during contact with seawater, gas trapped in bubbles within the lava may be released. This gas will then mix rapidly with pure boiled seawater components, including HCl gas. The high levels of Cl at the ocean entry may act to stabilise metal chlorides at the high temperatures of lava-seawater interaction.

**Synthesis**

The chemistry of volcanic plumes at basaltic intraplate volcanoes such as Kīlauea (and other hotspot volcanoes, e.g. Iceland) provide tantalising analogues for the gas and PM emissions during catastrophic volcanic events in Earth history such as flood basalt eruptions (forming LIPs). Scaled up to the erupted (and therefore degassed) volumes of LIPs, the composition of present-day plumes could be used to estimate the total emissions of volatile trace elements during flood basalt events. For example, the total SO\textsubscript{2} emitted during the eruption of the Deccan Traps LIP is estimated to be 3.5–6.5x10\textsuperscript{6} Mt\textsuperscript{65}. Using X/SO\textsubscript{2} ratios from Kīlauea in 2018, over the total 4 million year duration of the eruption, the Deccan Traps could have released long-term average daily emission rates of 5–100 kg Se/day and 7–13 kg Cu/day. However, given that the majority of the eruptive activity of the Deccan traps occurred over more concentrated eruptive periods within this time, daily emissions sustained over 10s–100s of years could be far greater than this long-term average\textsuperscript{66}.

Further, our results highlight the unique metal signature of lava-seawater interaction plumes, which would have been a common phenomenon during oceanic plateau basalt eruptions (e.g. Ontong-Java), and during continental flood basalt eruptions that reached
coastlines. Degassing of trace metals from late-stage lava flows at chlorine-rich ocean entries, whose melts are already enriched in Cl over S due to fractional degassing\textsuperscript{61,62}, produces a fundamentally different fingerprint of trace metals to magmatic plumes. During large basaltic eruptions, distal ocean entry environments are likely to have been important sites where volcanogenic metals (particularly Cu) are transferred from magmas into the environment, potentially hundreds of km\textsuperscript{67} from magmatic source vents.

[5354 words]
Figure captions

Figure 1. A: Map of the final extent of the 2018 LERZ eruption lava flows (red area, including extension of pre-LERZ coastline) and plume sampling locations during this study. Small red triangles represent the location of individual fissures active during the eruption. The yellow star marks the location of the Leilani Community Association, where UAS flights into the magmatic plume where launched. White triangles mark the locations from which UAS flights to sample the laze plume were launched. During the July-August 2018 campaign, we sampled the laze plume which was created near Isaac Hale Park. Inset map of Island of Hawai‘i with locations of Kīlauea summit (S), Pu‘u ‘Ō‘ō (P) and Fissure 8 (F8). Adapted from Neal et al.25. B: Aerial image (USGS) of Fissure 8 and the magmatic plume, taken on 24 July 2018 during a sampling flight, looking ~SE. UAS sampling of the magmatic plume was carried out ~300 m above the active vent. The cylindrical filter pack symbol (Figure S1) marks the approximate location of ground-based sampling. C: Aerial image (USGS) of the ocean entry and laze plume taken during a flight from Mackenzie State Recreation Area on 24 July 2018, looking ~NE. UAS sampling of the laze plume was carried out ~100 m above the ocean entry.

Figure 2. Size segregated concentrations (not ash corrected) of elements in particulate matter measured in the magmatic and laze plumes, in order of volatility. Note the different emanation coefficient scales on figures A and B. A: Refractory (ε < 0.001%) elements in the magmatic plume, with emanation coefficients (ε) calculated for the magmatic plume for the UAS and ground-based sample are also shown. B: Volatile (ε > 0.001%) elements in the magmatic plume, with emanation coefficients (ε). C: Refractory (ε < 0.001%) elements in the laze plume. D: Volatile (ε > 0.001%) elements in the laze plume. All elements were measured by ICP-MS or ICP-OES except where indicated; IC = ion chromatography. D = cut-off diameter as defined in methods. BDL = below detection limits (of either the instrument, or below filter blanks).
Figure 3. S, Cl, F, and N in the magmatic and laze plumes. Concentrations (mol/m$^3$) of S (measured as SO$_2^-$), Cl (measured as Cl$^-$), F (measured as F$^-$), and N (measured as NO$_3^-$) in the gas and PM phases of the magmatic (left, UAS and ground samples) and laze plumes (right, Isaac Hale Park and Mackenzie State Recreation Area samples). Percentages indicate the proportion of S, Cl, F, and N measured as gas and PM for each element. S/Cl and Cl/F ratios are total (gas + PM) molar ratios. Cl in PM at Fissure 8 is comparable to background levels measured in 2019 (Table S8, Ilyinskaya et al., in review).

Figure 4. Trace element emission rates and relative abundances in volcanic plumes. A: Trace element emissions rates for a selection of basaltic volcanoes normalised to emission rates in the Kīlauea 2008 eruptive plume$^9$. Kīlauea 2018 emission rates are calculated using an SO$_2$ emission rate of 39 ± 11 kt day$^{-1}$ as described in this work. Holuhraun 2015 data from$^{68}$. Etna 2001 data from$^7$. Erta Ale data from$^{10}$. B: Trace element concentrations, X, ratioed to SO$_2$ gas (SO$_2$) concentration to account for variable plume dilution, normalised to the X/SO$_2$ ratios in the Kīlauea 2008 eruptive plume$^9$. Arc volcanoes are shown as shaded regions, the bounds of which represent the error on the data, where errors are propagated from individual electron microprobe analyses of sulfur, which is typically 5%, and errors on X/SO$_2$, as described in$^{55}$. Etna 2001 data from$^7$. Stromboli 1993-97 data from$^6$. Masaya 2000-2001 data from$^8$. Ambrym 2007-08 data from$^{12}$. Elements are ordered by the average arc X/SO$_2$ ratio for the volcanoes shown. Kīlauea 2018 data are an average of non-saturated samples 8_1 and 8_5 and error bars are the standard deviation of these samples.

Figure 5. Emanation coefficients ($\varepsilon$) compared for a selection of volcanoes. A: Emanation coefficients at a selection of intraplate volcanoes, ordered to their magnitude in Kīlauea 2018 (average of ground and UAS samples). All emanation coefficients are calculated using X/SO$_2$ ratios as outlined in Methods, with the exception of Holuhraun, for
which the values are those given in the paper, calculated using $\varepsilon_{Pb}$. B: Emanation coefficients at a selection of arc settings. Data sources are as in Figure 4, in addition to a study of degassed and undegassed melts, and a compilation (Rubin) of $\varepsilon$ at a mixture of tectonic settings. Data for the figure can be found in Table S17 and a description of $\varepsilon$ calculations can be found in Methods. Error bars represent the emanation coefficients calculated for the maximum and minimum X/SO$_2$ ratio measured during each measurement campaign. Errors are not available for the Rubin compilation or the Holuhraun 2014-15 data.

Figure 6. Speciation of gases bearing a selection of trace elements in the Fissure 8 plume, modelled in the GEM module of HSC chemistry as detailed in the methods. A: The effect of atmospheric mixing (+ 78% N$_2$, 21% O$_2$, 1% Ar) on the speciation of major sulfur-bearing gases in the volcanic plume, with the compositional discontinuity at ~15% air. B: the speciation (gas phase only) of elements in the magmatic plume at 0% percent air ($V_A/V_M = 0$; no atmospheric mixing). C: the speciation after the compositional discontinuity, at 25% air ($V_A/V_M = 0.33$; the proportions of different species do not change significantly between 20-25% air). The model inputs can be found in Table S20 and the outputs can be found in Table S21.

Figure 7. Sources of elements in the laze plume. The laze plume composition presented as X/Cl ratios in the plume compared to X/Cl ratios in average global seawater (SW). Compositions corrected for a basaltic ‘ash’/silicate glass contribution are also shown as star symbols (when elements do not change position after the correction they are shown as stars only). The solid blue line represents a 1:1 correspondence between the X/Cl ratios of the laze plume and the seawater. Dashed diagonal black lines represent orders of magnitude enrichments in laze plume above the seawater X/Cl ratio. Elements are coloured by emanation coefficient.
Figure 8. The effect of increasing/decreasing the chlorine content of the oxidised magmatic plume on speciation. Elements are shown in order of decreasing volatility from top to bottom. From left to right, the input concentration (mol) of HCl(g) in the starting model is increased by an order of magnitude per column, and each column represents a discrete step of the model. The model uses the same input composition as in Figure 6 (Table S20) and data outputs from the altered HCl(g) models can be found in Table S21-27. Results are shown at $V_A/V_M = 0.33$ or 25% mixing with ambient atmosphere. Results at $V_A/V_M = 0$ or 0% air are shown in Figure S16.

Figure 9. Summary of processes occurring in A: the magmatic plume and B: the laze plume.

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Author contributions

EM, PW, EJL, EI and RCWW were the fieldwork team with local assistance from CK, TE, DS, and PAN. TCW and AJSM collected SO$_2$ flux data, with assistance from EJL and TP. EM carried out the majority of the lab work, along with EJL, EI and PW. EM created figures and wrote the manuscript with assistance from all authors.

Competing interests

No competing interests to declare.

Materials and correspondence

All correspondence should be directed to EM. All data used can be found in the supplementary information and an online database (tbd).
Methods

Multi-GAS sampling

During the ground-based measurements of the magmatic plume emitted from Fissure 8, local wind conditions and thermal upwelling of the plume over the vent meant that the plume was only directed down (or ‘grounded’) towards our instruments periodically. To account for this, a mobile multi-component Gas Analyser System (Multi-GAS\textsuperscript{69,70}) was used to simultaneously measure concentrations of CO\textsubscript{2}, SO\textsubscript{2} and H\textsubscript{2}S, as well as pressure, temperature and relative humidity. Air was sampled through a 1.0 μm particle filter exposed to ambient air, at a flow rate of 1.0 l/min. SO\textsubscript{2} and H\textsubscript{2}S electrochemical sensors (T3ST/F-TD2G-1A and T3H-TC4E-1A, both City Technology) were calibrated for 0–200 and 0–50 ppmv, respectively, with an accuracy of ± 2% and a resolution of 0.1 ppmv. A non-dispersive infrared (NDIR) spectrometer (Gascard EDI030102NG, Edinburgh Instruments) was calibrated for 0–3000 ppmv CO\textsubscript{2} with an accuracy of ± 1.5% and a resolution of 1 ppmv. Pressure, temperature, and relative humidity (RH) were also measured at 1 Hz (KVM3/5 Galltec-Mela T/Rh sensor). The multi-GAS was calibrated at the University of Palermo prior to and following the field campaign; no sensor drift was identified. CO\textsubscript{2}/SO\textsubscript{2} molar ratios were calculated using Ratiocalc\textsuperscript{71} (supplement section S2). Multi-GAS SO\textsubscript{2} concentrations were used to determine the time in plume (and therefore the volume of plume sampled) for ground-based sampling, which gives a time-averaged concentration. The SO\textsubscript{2} concentration at which the instruments were inferred to be exposed to the grounding magmatic plume (rather than local fumarolic emissions) was set at 1 ppm SO\textsubscript{2}, which corresponds to the concentration baseline between SO\textsubscript{2} peaks (Figure S6B). Further information, supplementary figures and data are given in supplement section S2 and Table S17.

Filter pack and cascade impactor sampling

Filter packs were used to collect simultaneous samples of gas and bulk particulate material (PM) in both the magmatic (Fissure 8) and the laze plumes (Figure S1). We
followed a well-established technique previously used in multiple volcanological studies (e.g. 9,73). The filter packs contained one particle filter (Whatman™ WTP PTFE (polytetrafluoroethylene) 47 mm diameter, pore size 1.0 μm) followed by 3-4 alkali-impregnated gas filters (Whatman™ Quantitative Filter Papers, Ashless, Grade 41, 55 mm diameter). Gas filters were washed, impregnated with a 5% K₂CO₃ + 1% glycerol mixture and dried in a clean lab environment prior to use in the field. This base treatment of the gas filters captures acidic gases (e.g., SO₂, HF and HCl) by conversion to their weakly basic counter-anions (e.g., SO₄²⁻, F⁻ and Cl⁻). PTFE filters were not pre-washed. Airflow through the filter pack was generated using an external 12 V pump (Charles Austin Capex) running at ~20 l/min, if ground-based, and using an SKC Leland Legacy pump running at ~9 l/min if UAS-based (specific flow rates in Table S1). The flow rate was measured at the start and end of each sampling period. The uncertainty introduced by variations in the flow rate, and by the accuracy of the flow meter are 10%. Immediately after sampling, the filter pack was closed by Parafilm to prevent particle loss and contamination. Filters were later transferred into individual polypropylene bags (2 layers) using metal-free tweezers and gloves.

Cascade impactors consist of a series of stages between apertures of decreasing diameter. Larger particles are aerodynamically deposited on earlier collection stages, while finer particles are only deposited after passing through later narrower apertures, once they achieve a sufficiently high flow velocity to impinge on a collection stage. The cutoff diameter is conventionally reported as Dₚ₅₀ — the particle diameter retained with 50% efficiency on the given stage, and is dependent on Stokes number parameters. The Sioutas cascade impactor (SKC Inc., Figure S2) was used to collect size-segregated particles in five size bins. Cutoff diameters are 2.5, 1.0, 0.50, and 0.25 μm, with all particles smaller than 0.25 μm collected on the final ‘after-stage’. A flow rate of 9 l/min was maintained for PM collection by a Leland Legacy (SKC Inc.) dual diaphragm pump and PTFE filters were used on each stage of the impactor (Zefluor™, 25 mm diameter, 0.5 μm), including the after-stage (SKC Inc., 37 mm diameter, 2.0 μm).
A UAS (Unoccupied Aircraft System, DJI Matrice 600 Pro, Figure S3), owned and operated by the United States Geological Survey (USGS), was used to sample the Fissure 8 and laze plumes, ~300 m and ~100 m above the ground, respectively. The filter pack and cascade impactor were flown on separate flights due to the payload capacity of the UAS. However, instruments were flown in succession to obtain samples under as similar conditions as possible. Two sampling flights were launched from the Leilani Community Association (19.4660° N, 154.9156° W, 230 m a.s.l.) and flown into the Fissure 8 plume, one each for the filter pack and cascade impactor. For all UAS flights, an approximate ‘in-plume’ duration was estimated using visual identification of the plume in footage acquired by the UAS-mounted camera during flight. It should also be noted that rotor turbulence (or thermal updrafts) may affect the ingestion of airborne PM during UAS sampling (e.g. by altering the ‘true’ particle size distribution), compared to traditional ground-based sampling, and this effect is not yet unconstrained. Even if these effects are subtle, due to the low concentrations of some of the elements considered, they might cause significant differences in measured values.

Aerial measurements were also complemented by ground-based sampling near to Fissure 8. The Fissure 8 plume was sampled by placing the sampling equipment in a specially designed drop-and-run backpack frame (Figure S4) with the instruments attached ~50 cm off the ground to minimize contamination from windblown silicate material in the tephra field. The drop-and-run frame was designed to minimize the time spent setting up the equipment near the active volcanic vent. Ground-based sampling was made near the south-western edge of Fissure 8 by walking in through the evacuated section of Leilani Estates (Kupono Street) where the plume grounded periodically (approximate location shown in Figure 1). Two filter packs were run simultaneously (Table S1) alongside a multi-GAS. Only filter pack samples where flow rates were measured successfully at the start and end of sampling are presented here. Some filter packs showed evidence of saturation of the gas filters (more detail in supplement, section S1.4) – only data from the PM collected on the first filter are presented in this case (Table S8).
The laze plume was sampled using solely aerial techniques, as the plume was lofting over the sea and therefore inaccessible to ground-based sampling. The UAS was flown from Isaac Hale Park (19.4595, -154.8423, 7 m a.s.l.), and Mackenzie State Recreation Area, both on the southeast coast. At Mackenzie State Recreation Area, one filter pack flight was undertaken. At Isaac Hale Park, one filter pack sampling flight was undertaken, followed by three consecutive cascade impactor sampling flights. The same impactor was flown on each flight to ensure a total exposure time sufficient to collect concentrations above detection limits for trace elements. Lava flows by the coast were still degassing during the flights, so some contribution from those emissions cannot be ruled out. Further details of sampling can be found in supplementary section S1.

Sample extraction and analysis

All filter extractions were carried out in a class-10000 clean lab environment at the University of Cambridge. PM on PTFE filters was first extracted in Milli-Q (MQ) water + propan-2-ol (to reduce the hydrophobicity of the PTFE filters), shaken and left for 24 hours. After centrifugation, the water-soluble supernatant was extracted for analysis by IC and solution ICP-MS and/or ICP-OES (inductively coupled plasma - mass spectrometry and - optical emission spectroscopy, respectively). The remaining solution and filters were transferred to acid-cleaned PFA (perfluoroalkoxy) vials and refluxed at 120°C for three hours with concentrated distilled nitric acid (HNO₃) + hydrofluoric acid (HF), followed by concentrated distilled HNO₃ that was subsequently diluted with MQ to a 5% HNO₃ solution for analysis. Solutions were dried down in between reflux stages at 90°C in a class-100 laminar flow cabinet. Volatile species collected on gas filters were extracted in MQ water + H₂O₂ (used to oxidise), shaken and left for 24 hours (following⁷⁷,⁷⁸). Solution was then extracted for pH and IC measurements. SO₂, HCl, HF and HNO₃ collected on the gas filters were measured (as SO₄²⁻, Cl⁻, F⁻ and NO₃⁻ respectively) by ion chromatography at the University of Leeds (on Thermo Dionex ion chromatograph system). These major anions were also measured by IC on the PTFE PM filters. Major and trace elements were measured
in extraction solutions by ICP-MS (Thermo iCAP Qc ICP-MS) and/or ICP-OES (Thermo iCAP 7400). All major elements were measured by ICP-MS, with the exception of Mg, Ca, K, Ba, Sr, Al, P, Na, S, Fe, which were measured by ICP-OES. For filter pack measurements, Ba, Sr, Be, B, V, Cr, Co, Ni, Mo, Cs, Lu, U were measured but were below detection limits of the ICP-MS and/or ICP-OES instruments. For cascade impactor measurements, these elements were also below detection limits, in addition to Li, K, Sc, and Ta. The presence of more elements below detection limits for impactor measurements reflects the fact that these instruments segregate PM by size onto five separate filters, whereas filter packs deposit all particulate material on a single filter. All elements and species are at least one order of magnitude above background levels measured in 2019 in the Leilani Estates, except for Sc, Ta, and Tb; these elements have not been considered further (Table S8). Chloride measured in the PM at Fissure 8 is also below background levels measured in 2019. Propagated errors are provided alongside data in the supplement and error propagation is detailed in supplement section S7. Errors for all elements measured by ICP-MS or ICP-OES, as well as Cl⁻ and SO₄²⁻ by ion chromatography were ± 10–18%. Errors for NO₃⁻ and F⁻ were around ~25%. Blank filters were also measured, with concentrations negligible (with the exception of W and P) compared to in-plume samples (Table S19).

**SO₂ and multi-element fluxes**

SO₂ emission rates of the magmatic plume from Fissure 8 were measured on 31 July 2018 (the same day as ground-based filter-pack sampling) using a PiSpec instrument, a low-cost, 3D-printed UV spectrometer⁷⁹,⁸⁰ (Table S4). Typical traverse-mode differential optical absorption spectroscopy (DOAS) retrievals were employed⁸¹, traversing beneath the plume on state highway Route 130 (Figure 1A) with the PiSpec looking upwards. A total of 4 traverses were performed, between 15:20 and 16:40 local time. Due to extremely high column densities of SO₂ (at times exceeding 10,000 ppm.m) the spectrometer retrievals were corrected for non-linearity following⁸²,⁸³, using a modelled PiSpec response to account for the saturation effect. Relatively long wavelength fitting windows, typically 322-332 nm,
were used, to exploit weaker absorption bands where the saturation effect is less
pronounced; due to the wide range column densities found during traverses, each spectrum
was processed manually with an optimised fitting window. Wind speed was taken from the
National Oceanic and Atmospheric Administration (NOAA) Global Data Assimilation System
(GDAS), which provides 1° latitudinal/longitudinal resolution. The speed was estimated to be
6.5 m s\(^{-1}\) during the times of the traverses.

Trace element fluxes cannot be measured directly, and are estimated based on the
measured X/SO\(_2\) ratio in the plume and the independently measured SO\(_2\) emission rate, as:

\[
\text{emission rate of } X = X/SO_2 \times SO_2 \text{ emission rate}
\]

The weighted mean of SO\(_2\) emission rates measured during our fieldwork is 39 ± 11
kt/day (where the error is the standard deviation of three measurements and the full range is
27–54 kt/day, Table S4). Another study found higher SO\(_2\) emission rates of 71 ± 31 kt/day
on the same day of sampling\(^{37}\) – this may be related to differences in data processing
methodologies. Earlier in the eruption, during June and early July 2018, a higher emission
rate of 200 kt/day SO\(_2\) was reported\(^{84}\). If X/SO\(_2\) ratios remain constant with changing SO\(_2\)
emission rate, the metals emission rates earlier in the eruption may have been up to four
times higher than those presented here.

**Silicate (ash) correction**

To determine the concentration of elements in the non-silicate aerosol phase, the
contribution from a silicate (ash) component must be removed. Here, for our ash
compositions, we used the same composition as the \(X_{\text{degassed}}\) term use for calculation of
emanation coefficients above (data in Table S15).

For the ash correction, we consider the concentration of element A on the filter to be
derived from two volcanic components, silicate ash and non-silicate aerosol:

\[
[A]_{\text{filter}} = [A]_{\text{ash}} \times X_{\text{ash}} + [A]_{\text{aerosol}} \times (1 - X_{\text{ash}})
\]
Where $X_{ash}$ is the proportion of element A on the filter that is present in the ash phase. If A is a lithophile/refractory element (e.g. REEs, Sc Th or some combination of lithophiles), we assume that the concentration of this element in the aerosol phase is zero ($[A]_{aerosol} = 0$), allowing the equation to be simplified to:

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

In the ash corrections performed in this study, we use a combination of major and trace refractory elements to calculate the ash correction: Fe, Al, Ti, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb (other combinations of refractory elements are compared in Figure S8). Light REEs La and Ce were excluded from the correction as they displayed evidence of volatile behaviour (Figure 2). The higher concentrations of major elements (compared to REEs) in silicate material, allow smaller ash contributions to be resolved, and are thus more sensitive to the small amounts of ash in the Fissure 8 or laze plumes. Weighted ash fractions (WAF) can then be calculated for each sample:

$$WAF = 100 \times \frac{X_{ash} \times [A]_{ash}}{[A]_{filter}}$$

A consensus approach to quantifying ash contributions to volcanogenic PM is lacking in the volcanic plume sampling literature. Regardless of how ash-poor a plume appears during the sampling period, small amounts of ash can have a disproportionately large effect on the concentrations measured on the filter, and therefore the fluxes and measures of volatility calculated from the data, due to the high concentrations of many elements in silicate material. For example, a contribution of only 0.001% ash by weight to the concentration on the particulate filter, would result in a measured ash-derived concentration of 85 ppm Fe and 71 ppm Al.

**Measures of volatility**

We calculate emanation coefficients ($\varepsilon_x$) using the ratio of element concentration to sulfur ($X/S$) in the volcanic plume, combined with an estimate of total S degassed during subaerial eruption:
where $X_{aerosol}$ is the concentration of element $X$ measured on particulate filters (corrected for silicates, as above); $S_{total}$ is the total S measured on filter pack particulate and gas filters and $X_{degassed}$ is the concentration of element $X$ measured in a degassed melt (i.e. matrix glass). Ideally, $X_{degassed}$ would be measured in a degassed melt that is closely temporally related to the melt from which the measured plume emissions are degassed. However, this is often not possible as it requires sampling in hazardous or inaccessible environments (e.g. active lava flows or recent tephra falls). Here, where data availability and quality allowed for the elements of interest, $X_{degassed}$ is an average composition of basaltic matrix glass from two 2018 samples (one overflow sample, one lava channel sample) collected close to the time and location at which the magmatic plume was sampled (Wieser et al., in prep). The elements in these matrix glass samples were measured by electron microprobe and LA-ICP-MS (laser ablation – ICP-MS). Where elements were not measured in the 2018 samples, either a 1971 summit composition or preferred BHVO values were used (Table S15 contains more detail).

Ideally, $S_{degassed}$ is the concentration of S (in ppm) degassed from the melt from which the measured emissions are released, measured by comparing degassed and undegassed glass compositions. However, this data is not yet available for the Fissure 8 lavas. Recent work suggests that the during the 1971 summit eruption as much as ~1200-1300 ppm of S was degassed, with degassed amounts of up to ~1465 ppm possible in the most primitive eruptions of Kīlauea. Therefore to cover the full range of possible $S_{degassed}$ values, we use a $S_{degassed}$ value of 1250 ± 300 ppm to calculate $\epsilon_x$.

### Equilibrium chemistry modelling

The Gibbs free energy minimisation (GEM) module of HSC Chemistry (version 9.9.2, Outotec Research Oy, Finland) was used to model gas and condensed speciation in the
Fissure 8 plume. The GEM module solves a series of mass balance and mass action relations. Detailed descriptions are provided in previous works\cite{54,57,85}. Model inputs are major and trace species gas concentrations (kmol), pressure, temperature and the phases expected in the plume. Using the method from Helz and Thornber\cite{86}, the MgO content (6.50 ± 0.13 wt%, Wieser et al., in prep) of Fissure 8 lavas give an equilibrium temperature of the magmatic gases emitted at the time of plume sampling of ~1145 ± 1.6 °C. Further cooling of gases may occur during adiabatic expansion of bubbles. Oppehnerimer et al\cite{87} demonstrated that the cooling associated depends on the size of the bubbles, with bubbles of radius 2 m producing a cooling of ~100°C. Based of footage of degassing taken during sampling, we assess that this is a reasonable upper limit for bubble size during degassing at Fissure 8. Therefore an additional lower uncertainty of 100°C is considered but did not have a significant effect on the dominant speciation of volatile trace elements. We determine the temperature of the gas mixture at the range of mixing ratios considered (0 < (V_A/V_M) < 0.33) using a simple fluid mixing model, defined as follows:

$$T_{\text{mixture}} (°C) = \frac{(T_1 \times m_1 \times c_1) + (T_2 \times m_2 \times c_2) + \ldots + (T_n \times m_n \times c_n)}{(m_1 + c_1) + (m_2 + c_2) + \ldots + (m_n + c_n)},$$

where $T_{\text{mixture}}$ is the temperature of the mixture of magmatic gases; $T_n$ is the input temperature of the gases (i.e. 25°C for air; 1145°C for magmatic gas); $m_n$ is the mass of gas (in kg) present in the mixture; and $c_n$ is the specific heat of the gas (in kJ/(kg*K)) at the relevant $T_n$. Specific heat values for atmospheric N\(_2\), O\(_2\) and Ar gases at 25°C are 1.0, 0.9 and 0.5 kJ/(kg*K), respectively; the specific heat for magmatic H\(_2\)O vapour at 1145°C is 2.5 kJ/(kg*K)). The mixing model produces an approximately linear relationship between temperature (from 1145 to 1016°C) and $V_A/V_M$ (0 to 0.33; Figure S14), which is then used to parameterise the HSC Chemistry GEM model. We note that adiabatic decompression of vapour bubbles in magma as they degas at the surface may have some cooling effect, however this is not incorporated in the simple model presented here. Input concentrations of major gas species (e.g. H\(_2\)O, CO\(_2\), SO\(_2\), H\(_2\)S etc.) are from Gerlach\cite{88}, and trace metal concentrations are from the filter pack samples presented in this study. While a more recent
gas composition for major species would be favourable, the speciation model is very sensitive to the concentrations of reduced species and this dataset provides the most complete composition of the Kilauea plume and allows comparison with previous work\(^54\). The data presented in Gerlach\(^88\) display a similar CO\(_2\)/SO\(_2\) ratio (~0.3) to that measured by the multi-Gas in this study (supplement section S2) and others\(^89\). An approximate HBr concentration for the plume was calculated using a HBr/SO\(_2\) ratio from Mather et al.\(^9\). Trace metal data were corrected for the dilution that occurs over the distance between emission at source and sampling location by multiplication of element ratios to total sulfur as follows:

\[
X_{\text{source}} \ (\text{mol}) = \left( \frac{X_{FP}}{S_T} \right) \cdot S_{\text{source}} \cdot X_{\text{source}}
\]

is the concentration of the element of interest at the point of emission, \(S_T\) is the total sulfur concentration (mol) measured on all filters of the filter pack, \(X_{FP}\) is the ash-corrected concentration (mol) of element \(X\) measured on the particle filter of our filter packs and \(S_{\text{source}}\) is the concentration (mol) of S in the plume at the point of emission. In this case \(S_{\text{source}}\) is the total sulfur concentration (measured as SO\(_2\), H\(_2\)S, S\(_2\) and COS gases) as determined by Gerlach\(^88\). Organic compounds are excluded from the calculation because they are unstable at high temperatures\(^54\). An assumption of the modelling is that the elemental composition of the plume is not fractionated between the point of emission at the lava-air interface and the point of sampling, which we consider reasonable given that the travel time for gases and particulates to reach the sampling instruments – either on the ground or to the UAS – is likely to be on the order of a few minutes or less. The oxidation of the magmatic plume was also modelled at 0.001, 0.01, 0.1, 10, 100, and 1000 times the actual measured initial HCl gas concentration to assess the effect of changing Cl concentrations in the plume on speciation. All input conditions, including the simple temperature model, were the same as in the main model (Table S20).
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