

Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

1st Oct 20

Dear Ms Mason,

Please allow me to apologise for the delay in sending a decision on your manuscript titled "Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kīlauea Volcano, Hawai'i". It has now been seen by 3 reviewers, and I include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in *Communications Earth & Environment*, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

In addition, please ensure that the revised manuscript addresses the following editorial thresholds:

****Provide compelling evidence for a substantial enrichment in chloride complexing metals in the laze plume relative to the magmatic plume during the 2018 eruption of Kīlauea****

****Fully discuss the uncertainties associated with your calculations of HCl and SO₂ flux including the limitations and caveats these may place on your interpretations****

****Streamline and focus the paper to bring out your main findings on the variation in composition between the magmatic and laze plume as well as the implications for estimates of trace metal transfer to the environment throughout geologic time****

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter) and the completed checklist:

[link redacted]

**** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first ****

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be

happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Joe Aslin

Associate Editor,
Communications Earth & Environment
<https://www.nature.com/commsenv/>
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statements-data-citations.pdf"><http://www.nature.com/authors/policies/data/data-availability-statements-data-citations.pdf>.

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Please refer to our data policies at <http://www.nature.com/authors/policies/availability.html>.

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

This paper is a well-written documentation of lava-seawater interaction, degassing and resultant metal emissions from both the gas and 'laze' (seawater vapor + particle haze) components of the 2018 eruption of Kilauea. The strengths of the paper are it is well-written and organized. The study is data-rich and an extremely comprehensive documentation of all variables affecting metal-loading from what was a crisis-eruption at the time in 2018. Of particular note are the partitions of different element families among different size classes of particles. I cannot find much if any flaws in the data collection, presentation or interpretations.

Descriptions of and the use of the measurements require several assumptions in further calculations (enrichment factor or emanation coefficients) and in modelling. These important facets of the study required nearly twice the length of the paper as Supplemental Material. An example of the complexity is shown in Figure 6 and 8 – which can take a long look to pick through and understand even FOR a practiced reader in this research area. The point is some of the material and many facets

of the study, were underplayed or raced through for space reasons.

Overall, and most importantly, as a reader one struggles to find much new or novel in what was actually observed. At the end of the day, many observations here on laze, metal emissions or the modelling of volcanic degassing mostly corroborate the previous work, as was cited throughout the study, including previous 2003 and 2008 Kilauea eruptions. For example, I note there are several other studies cited on metals in laze, even by one of the co-authors, so one doesn't really see a new or novel story here. There are also other previous studies on metal behaviour and/or enrichment in laze, also cited here. Lastly, the modelling of volcanic gases herein has also been done before, as noted by the referenced work by Mandon, Wahrenberger, Hemley and Seward. The outcome here for gas resultant from seawater interactions was not particularly different. None of this is to dismiss the importance of the study, but the novelty or uniqueness of it did not ring out in several of the observations.

I applaud the many measurements and they are surely worthy of publication. At the end, the reader struggles to go beyond more than the following: (1) a large eruption of lava reached seawater and created laze, (2) the laze shows enrichment in Cl, and (3) the laze is enriched in Cu, an element known to complex with Cl. Many points (1) to (3) have been recognized previously. In this way, no case for any greater impact of the study or of 'laze' is made. Whether laze itself is more than a transient signal to metal loading over earth history was not really addressed or developed here more than a back-of-the-envelope calculation applied to a sub-aerial eruption (Deccan Traps) that questionably never interacted with seawater. In addition, metal loading estimates from volcanoes also exist in the literature. My point is not to downplay any of the excellent work that went into this study, more about its impact and novelty, which I think is the emphasis of a paper in *Communications Earth & Environment*. If the Cl and Cu in laze has a big impact on metal loading or environmental degradation, that point was not really demonstrated in this study. The excellent, further documentation of the 2018 eruption shown here truly belongs in a volcanological journal, where it can be fleshed out and not hidden in Supplemental that goes unread by most non-experts.

Reviewer #2 (Remarks to the Author):

Review of "Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kīlauea Volcano, Hawai'i, submitted by Mason and co-workers for publication in *Communications Earth & Environment*

The manuscript reports on measurements of concentrations and fluxes of trace metals in the atmosphere caused by the 2018 eruption of Kilauea volcano.

The authors conducted their sampling using filter packs and cascade impactor both located on the ground and on an unmanned aerial vehicle (UAV). Using this strategy they were able to measure separately the plume emanating from the magmatic degassing (lava fountains) and from the ocean entry.

This is definitely a quite interesting piece of research, which has implications as diverse as the environmental impact of lava flow reaching the sea, the trace geochemistry signature of flood basalts and massive shallow water volcanism in the ancient Earth. It is only the second time such a detailed trace metal geochemistry study is conducted for such a massive eruption, and the first time it is conducted in lava-seawater interaction plume. The methodology of gas and aerosol sampling and analysis is at state-of-art level. Thermodynamic modelling looks solid (although it is not my area

of specialty) and the manuscript is well-written.

However, the study presents several shortcomings that need to be addressed before publication

1°) The quantification of the HCl flux from the ocean entry, which is one of the cornerstones of this research, needs to be improved. The estimation method of the HCl emission rate based on the basalt effusion rate is pure hand waving, because it is currently not known what percentage of seawater is effectively heated to ebullition when a lava flow enters the sea. There are many other ways to dissipate the thermal energy of the lava when it enters the sea: among them fragmentation and heating seawater to sub-boiling temperature. The original article of Edmonds et al., argues that 1 to 10 % of the thermal energy is effectively used to boil sea water, so it points out that this method of estimation is affected by one order of magnitude of uncertainty and is not directly scalable to larger flows.

2°) Similarly, the authors should try to improve the accuracy of the SO₂ flux reported in the study. The authors state that the measurements were conducted with the PySpec 3D-printed spectrometers. Wilkes et al. (2028) reported that their PySpec spectrometers are affected by a higher straylight than most of the commercial spectrometers. At the extreme concentration reported by the authors, straylight is a tremendous source of error that is added to the atmospheric scattering effects reported by Kern et al (2012). All these errors generally produce an underestimation of the SO₂ column densities and emission rate. I would suggest that the authors consider using satellite data (OMI or TROPOMI), whose measurements of SCD downwind of the plume, once they undergo a sufficient dilution, are less subject to errors (e.g. Beirle et al., 2014).

3°) In absence of geochemical analysis of the concentrations of the several trace metals in the melt at different stages (melt inclusions, channel lava and lava having interacted with sea water), many processes suggested by the author to explain the trends in their data remain speculative. I annotated the pdf document to highlight points where rock geochemistry could be an utterly useful complement to the gas/particle geochemistry reported here. In particular it could:

1) Elucidate whether the apparent depletion in chalcophile elements in the haze plume compared to the magmatic plume is due to one of the two hypotheses proposed by the authors, or to another unconsidered process (such as dilution of the magmatic signature by an oceanic signature and S-depletion in the melt)

2) Identify unambiguously the processes responsible for the distinct geochemical signature of the haze plume. I suggest that the author consider a leaching/evaporation process as being responsible for it rather than some kind of degassing from the lava.

Further, more specific, comments are written directly on the PDF.

These comments are meant to improve and consolidate this research work before its publication and not to reject it. I do support the publication of this high-quality research in this journal after these moderate revisions/additions are done.

Reviewer #3 (Remarks to the Author):

The manuscript by Mason et al. entitled "Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kilauea Volcano, Hawaii" reports a thorough chemical investigation of the

emissions of volatile trace metals in magmatic and laze plumes during the 2018 eruption of Kilauea. The manuscript is well written and well illustrated. The amount of work the authors have put in this study is significant and the study is interesting. Very little is known about the chemistry of laze compared to magmatic plumes. Their case study provides an analogue for the gas and PM emissions during catastrophic volcanic events in Earth history such as flood basalt eruptions, which bring constraints on their environmental impacts. The synthesis is well thought out and well constructed. I am happy to recommend its publication after some minor to moderate modifications.

General comment:

A lot of the details regarding methods and such are pushed into the supplement (34 pages in total with 18 figures + 7 tables + two excel files). It is thus sometimes hard to follow the main thread of the paper because I needed to constantly check the supplement files, there's no dataset table in the main ms for instance. I suggest adding some of this information in the main text.

However, considering the ms as a whole (the main text and the supplements) it's already a very long paper with a lot of information, and I feel that one can easily lose track of the main points. I would suggest to delete or shorten some sections of the ms: sections that (i) do not bring important information/results for the conclusions such as the REE behaviour (S8) and/or (ii) are already well described in previous papers (such as S1.1 and the S5, Fig. S5, Table S5 about the volatility and choice between enrichment factors and emanation coefficient). S1.4 and Table S2 could be also explained more concisely for instance. The whole ms could be thus shortened and re-organised to aid communication of the most important findings.

Minor comments:

The way the emanation coefficients are calculated needs more explanation in the main text and/or methods (better define C_i and C_f).

The figures are well done. The summary of processes (Fig. 9) is important and well illustrated. However, in order to focus on the comparison between magmatic and laze plumes, some data are missing (S/Cl for magmatic plume, indication of the speciation of trace elements in the laze plume for instance).

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

3
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15 Geography.

16 **Abstract**

17 Volcanoes represent one of the largest natural sources of metals to Earth's surface.
18 Emissions of these pollutants and/or nutrients have important implications for the biosphere.
19 We compare gas and particulate chemistry, including metals, of the substantial magmatic
20 (≥ 200 kt/day SO₂) and lava-seawater interaction (laze) plumes from the 2018 eruption of
21 Kīlauea, Hawai'i. The magmatic plume contains abundant volatile chalcophile metals (e.g.
22 Se), whereas the laze is enriched in seawater components (e.g. Cl), yet Cu concentrations
23 are 10⁵ times higher than seawater. High-temperature speciation modelling of magmatic
24 gases at the lava-air interface emphasises chloride's critical role in metal/metalloid
25 complexation during degassing. In the laze, concentrations of moderately (Cu, Zn, Ag) to
26 highly volatile (Bi, Cd) metals are elevated above seawater. These metals have an affinity
27 for chloride and are derived from late-stage degassing of distal lavas, potentially facilitated

28 by the HCl gas formed as seawater boils. Understanding these processes yields insights into
29 the environmental impacts of volcanism in the present day and geological past.
30 [163 words]

31 Introduction

32

33 Volcanoes have shaped the composition of Earth's atmosphere over geological time,
34 controlling Earth's habitability through the outgassing of hydrogen-, carbon- and sulfur-
35 bearing species¹⁻³. Volcanoes also supply significant fluxes of volatile trace elements,
36 including metals and metalloids, in the gas phase or as non-silicate particulate matter (PM,
37 also called aerosol)⁴⁻¹². Volcanogenic metal emissions have been sampled and studied at
38 many volcanoes worldwide (e.g. ⁶⁻¹³), and early studies date back to the 1960s and 70s (e.g.
39 ^{14,15}). During periods of intense unrest or eruption, volcanic emission rates of metals such as
40 cadmium (Cd), copper (Cu) and zinc (Zn) can be equal to or, in some cases, orders of
41 magnitude greater than daily anthropogenic emissions from entire regions (e.g. the
42 Mediterranean basin¹⁴) or countries (Ilyinskaya et al. *in review*), and volcanoes are one of
43 the largest natural sources of many metals¹⁶. Some trace metals present in volcanic plumes
44 can act as nutrients for living organisms at low levels, yet at higher concentrations are
45 categorised by environmental agencies as pollutants known to be harmful to health^{17,18}.
46 Basaltic volcanoes typically release relatively ash-poor plumes into the troposphere⁹,
47 exposing populations both relatively nearby (e.g. Kīlauea, Hawai'i, 1983–2018¹⁹; Masaya,
48 Nicaragua, 1993–present²⁰) and thousands of km downwind (e.g. Laki, Iceland²¹) to
49 sustained high levels of volcanogenic gases (e.g. SO₂) and trace metal-bearing PM.
50 Understanding volcanic metal emissions at volcanoes also provides important constraints on
51 the environmental impact of large, prehistoric basaltic eruptions, including flood basalts²²⁻²⁴.
52 However, much remains to be discovered about metal abundance and speciation in volcanic
53 gas and aerosol emissions.

54 Basaltic ocean island volcanoes, such as those found on the Island of Hawai'i, can
55 also produce an additional source of gas and PM emissions as lava flows reach coastlines
56 and rapidly boil and evaporate seawater, with significant implications for the marine
57 biosphere²⁵. Lava-seawater interactions, which produce acidic 'laze' plumes, have occurred

58 throughout Earth's history, often associated with some of the most dramatic manifestations
59 of volcanism (e.g. the eruption of ocean plateau basalts such as the Kerguelen and Ontong
60 Java Plateaus²⁶). Fragments of silicate material can be generated during lava-seawater
61 interactions through a fuel-coolant-type interaction²⁷ as seawater invades lava tubes, as well
62 as during collapse of lava deltas²⁸. A major component of laze plumes after water (~98–99
63 mol% of the gas phase) is hydrogen chloride (HCl) gas^{29,30}, and it has been suggested that
64 HCl emission rates from laze plumes at Kīlauea volcano, Hawai'i are comparable to or may
65 exceed that from coal-fired power plants in the United States²⁹. However, despite the
66 hazards and potential impacts of lava ocean entry plumes on the biosphere, only a few
67 detailed studies have been carried out (e.g. ^{31–33}) and relatively little is known about their
68 chemistry compared to magmatic plumes.

69 The 2018 eruption of Kīlauea – a basaltic shield volcano located in the south-east of
70 the Island of Hawai'i (**Figure 1A**) – presented a rare opportunity to study the emissions of
71 volatile trace metals in substantial magmatic and laze plumes. Before 30 April 2018, the
72 eruptive activity at Kīlauea was relatively stable at two locations: a lava lake within the
73 Halema'uma'u summit crater (active since 2008), and the Pu'u 'Ō'ō cone and other vents in
74 the East Rift Zone (ERZ), as part of the long-lived Pu'u 'Ō'ō-Kupianaha eruption of Kīlauea
75 (1983-2018)³⁴. On 30 April 2020 the Pu'u 'Ō'ō vent collapsed, and magma propagated down
76 the lower East Rift Zone (LERZ) of Kīlauea³⁵. On 3 May 2018, the first of 24 fissures opened
77 in the Leilani Estates subdivision on the LERZ³⁵, and by the end of May, activity had largely
78 focused at a single vent known as Fissure 8 (19.4627 °N, 154.9091 °W, ~220 m a.s.l.,
79 **Figure 1A**). Lava flows from the 2018 LERZ eruption reached the coast on 23 May 2018,
80 creating a laze plume (**Figure 1C**) as still-molten lava boiled and evaporated seawater³⁵.
81 SO₂ emission rates recorded at Fissure 8 during the eruption were the highest since
82 continuous SO₂ gas monitoring began at Kīlauea in 1979³⁶. Peak emission rates exceeding
83 200 kt/day were recorded from the LERZ in June and early July³⁷, exceeding Kīlauea's 2014
84 to 2017 average SO₂ emission rate (combined summit and ERZ³⁸) of 5.1 ± 0.3 kt/day SO₂,
85 by two orders of magnitude. Exposure to poor air quality (SO₂ and PM) during the 2018

86 LERZ eruption surpassed that observed during the 1983–early 2018 eruption episodes at
87 Kīlauea^{19,39}. Further, in terms of both eruption rates (50–500 m³/s, dense rock
88 equivalent)^{35,40} and erupted volume (~1.5 km³ in 94 days)⁴¹, the 2018 eruption was 1–2
89 orders of magnitude larger than any other in the preceding 180 years of activity on the
90 LERZ⁴¹. The lava effusion and SO₂ emissions from Fissure 8 declined dramatically on the 4th
91 August 2018³⁵.

92 During the 2018 LERZ eruption of Kīlauea we used both ground-based and
93 Unoccupied Aircraft System (UAS) platforms (sample summary in **Table S1**; see also
94 **Methods, Figure S3 and S4**) to quantify the major and trace element, including trace
95 metals, compositions of gas and size-segregated PM (in μg/m³) emitted in both the
96 magmatic plume from the main active vent (Fissure 8, **Figure 1B**, data in **Tables S8–S10**)
97 and the laze plume at the ocean entry (**Figure 1C**, data in **Tables S12–S14**). Here, we use
98 emanation coefficients to quantify element volatility in the magmatic plume, and X/SO₂ ratios
99 to demonstrate the consistency of Kīlauea’s volatile metal fingerprint across different
100 eruptive periods (**Table S11**). We also use a Gibbs Energy Minimisation algorithm to model
101 speciation during the oxidation and cooling of Kīlauea’s magmatic plume close to the lava-air
102 interface, and we add to existing direct observations, experimental and modelling evidence
103 (e.g.^{11,13,42–44}) of the importance of chloride as a control on trace metal degassing (**Tables**
104 **S20–S27**). Our study of the laze plume reveals that late-stage degassing of distal lava flows
105 at the ocean entry contains volatile metals that complex with chloride (e.g. Cu, Zn), while
106 those that complex with sulfide (e.g. Se, As) are notably absent. We conclude that the
107 chloride-rich environment of the ocean entry, as well as the changes in the volatile
108 concentrations of degassing melts between the source vent and distal lava flows, promotes
109 degassing of chloride complexes.

110

111 Results and discussion

112 Element volatility at Kīlauea Volcano

113

114 Measured concentrations of elements in the magmatic plume (**Tables S8-10**) can be
115 used to calculate the relative volatility of each element during degassing (i.e. to what degree
116 volatile trace elements degas from magmas⁴²). This volatility can be expressed using
117 various measures, including enrichment factors and emanation coefficients. Here we use
118 emanation coefficients to assess the volatility of each element (other measures are
119 described in supplement section **S5**). Emanation coefficients describe the degree to which
120 an element is degassed from its parent melt according to $\varepsilon = ([X]_i - [X]_f)/[X]_i$, where $[X]_i$
121 and $[X]_f$ are the initial undegassed and final degassed concentrations of element X in the
122 magma, respectively (originally defined by⁴⁵). Emanation coefficients can be estimated in a
123 range of ways, including: 1) using enrichment factors and the assumed constant emanation
124 coefficient of Pb from molten basalt⁴⁶ and; 2) comparing undegassed and degassed melts
125 (e.g. ⁴⁷). In this study, $[X]_i$ is calculated by adding the concentration of a degassed element
126 in the magmatic plume (using X/S ratios measured at Fissure 8, corrected for air dilution) to
127 a degassed matrix glass composition, i.e. $[X]_f$ (e.g. ⁴²; data sources in **Table S15**,
128 **Methods**). We use the calculated ε values to group elements into volatile ($\varepsilon > 0.001\%$) and
129 refractory elements ($\varepsilon < 0.001\%$; **Figure 2A and B**). For elements with a calculated ε
130 greater than zero, their order of increasing volatility is: $\varepsilon < 0.01\%$ Nd, Eu, Al, Ce, Ti, La, Ta,
131 Ba, K, Cu; $\varepsilon > 0.1\%$: Zn, Ag, Sn, Pb; then at $\varepsilon > 1\%$: As, F, Bi; and $\varepsilon > 10\%$ In, Cd, Se, Cl,
132 Re, Te, S.

133 Size-segregated concentrations of particles in the magmatic plume provide information
134 on the mechanisms of particle formation, and can be used to corroborate ε calculations.
135 Previous work has ascribed broad formation processes to particle diameter (D) ranges: 1) D
136 $< 0.1 \mu\text{m}$: the 'nucleation' mode, associated with cooling, oxidation and quenching of
137 magmatic gases as they mix with the ambient atmosphere; 2) $0.1 \mu\text{m} < D < 2 \mu\text{m}$: the
138 'accumulation' mode, formed from the condensation of low volatility vapours and from

139 agglomeration ('sticking together') and growth of particles in the nucleation mode; 3) $D > 2$
140 μm : the 'coarse particle' mode, composed largely of mechanically-generated particles (e.g.
141 ash)⁴⁸. In the magmatic plume emitted from Fissure 8, simultaneous gas and PM
142 measurements (using filter packs, **Methods**) showed that PM accounted for $< 0.01\%$ of the
143 total mass of S, Cl and F, i.e. these elements are present in the near-source plume almost
144 entirely as gases (**Figure 3**). For the PM, S is concentrated in the smallest size fraction (\sim
145 91% collected with diameter, $D \leq 0.25 \mu\text{m}$; $\sim 0.5\%$ collected with $D \geq 2.5 \mu\text{m}$; **Figure 2B**),
146 while F is found predominantly ($\sim 57\%$) in the largest size fraction ($D \geq 2.5 \mu\text{m}$) and Cl
147 concentrations are bimodal with the majority ($\sim 60\%$) found in $D \leq 0.25 \mu\text{m}$, and $\sim 27\%$
148 found in $D \geq 2.5 \mu\text{m}$. The presence of Cl, F and to a much lesser extent S, in the coarse
149 fraction could represent adsorption of HCl, HF and SO_2 gases onto ash in the plume^{49,50},
150 however further investigation into this process at Kīlauea is beyond the scope of this study.
151 Volatile trace elements can be subdivided into a refractory 'coarse particle' fraction present
152 as silicates (i.e. ash; **Figure 2A**) and a volatile fine fraction present as non-silicate PM
153 (**Figure 2B**). Refractory elements ($\epsilon < 0.001\%$, e.g. Ca, Ba, Al, P, Ti, Mn, Fe, Zr and the rare
154 earth elements, REEs) in the magmatic plume are generally found in size fractions with $D >$
155 $0.25 \mu\text{m}$; $10\text{--}100\%$ of their concentration in PM is found within the $D > 2.5 \mu\text{m}$. These
156 elements are likely derived from ash generated during lava fountaining and fine
157 fragmentation at the Fissure 8 vent. Weighted ash fractions (WAFs) calculated for these
158 elements in the magmatic plume (ash correction in **Methods**, **Table S11**) support this
159 conclusion: for all of the refractory elements in **Figure 2A** apart from Ti, La and Ba, $> 90\%$ of
160 their concentrations can be accounted for by ash (WAFs: Ti = 89% ; La = 69% ; Ba = 45%). In
161 contrast, volatile elements ($\epsilon > 0.001\%$, Cu, Zn, Ag, Sn, Pb, As, F, Bi, In, Cd, Se, Cl, Re, Te,
162 S, in order of increasing volatility) are predominantly found at $D < 0.25 \mu\text{m}$, consistent with
163 typical diameters of the 'nucleation mode'⁴⁸, and have weighted ash fractions $< 0.3\%$, except
164 Cu (5%), Zn (2%), F (7%) and Cl (1%). The size-segregated concentrations of elements
165 observed in Kīlauea's 2018 magmatic plume match broadly with those made at Kīlauea's

166 summit in 2008⁹ (i.e. refractory elements = coarse, volatiles = fine) however, concentrations
167 of volatile trace elements are more evenly distributed across the size bins in 2009 than in
168 2018 (discussed in supplement section **S10**, **Figure S18**).

169

170 **Kīlauea’s trace metal compositional ‘fingerprint’**
171

172 While volatile trace element fluxes at Kīlauea in 2018 are the highest recorded at the
173 volcano (and at any intraplate volcano **Figure 4B, Methods**), the relative abundances of
174 volatile trace elements measured at Kīlauea correspond closely between different eruptive
175 periods. To eliminate differences between samples due to variable plume dilution, we
176 compare the composition of Kīlauea’s 2018 magmatic plume composition to other volcanic
177 plumes using trace element to SO₂ mass ratios (X/SO₂, **Table S11** and **Figure 4A**). X/SO₂
178 ratios at Kīlauea in 2018 agree within an order of magnitude with previous measurements
179 made at Kīlauea summit in 2008⁹. Emanation coefficients calculated for Kīlauea in 2018
180 (**Methods**) also agree, to within an order of magnitude, with petrological estimates obtained
181 through the comparison of variably degassed Kīlauean melt inclusions and matrix glasses⁴⁷
182 (**Figure 5A**). The order of element volatility at Kīlauea matches that derived from
183 measurements made at Erta ‘Ale volcano, an intraplate basaltic volcano in Ethiopia¹⁰(**Figure**
184 **5A**). However, X/SO₂ ratios and emanation coefficients at Holuhraun, a hotspot-related,
185 basaltic volcano, are 1–2 orders of magnitude lower than those measured at Kīlauea and
186 Erta ‘Ale (**Figure 4A; Figure 5A**). This may be due to the low chlorine contents in the
187 Holuhraun plume, reducing the availability of ligands¹¹ (total, gas + PM, S/Cl mass ratio at
188 Holuhraun = 40–52¹¹; at Kīlauea = 27–29, this study; at Erta ‘Ale = 6–15¹⁰).

189 Speciation of magmatic gases in Kīlauea's magmatic plume

190
191 The speciation of volatile trace elements as they are emitted at the lava-air interface
192 provides key initial conditions for the subsequent atmospheric transport, solubility, deposition
193 and resulting hazard from these elements (Ilyinskaya et al. *in review*). Major elements –
194 such as S, Cl, O and H (as well as, to a lesser extent, F and other halogens) – are the main
195 ligand-forming elements for volatile trace metals in volcanic gas emissions (e.g. as sulfates
196 (SO_4^{2-}), sulfides (S^{2-}), chlorides (Cl^-), fluorides (F^-), oxides (O^{2-}) and hydroxides (OH^-)^{10,43}.
197 The magmatic plume emitted from Fissure 8 was S-rich, with molar gas ratios for SO_2/HCl
198 and HCl/HF of 30–32 and 2.4–2.8, respectively. These ratios are similar to those measured
199 from previous persistent emissions at the Pu'u'Ō'ō vent in 2004–05 ($\text{SO}_2/\text{HCl} \sim 23$, and
200 $\text{HCl}/\text{HF} \sim 1.4$)⁵¹, and from the summit in 2008–09 ($\text{SO}_2/\text{HCl} \sim 20$ –28, and $\text{HCl}/\text{HF} \sim 1.1$ –2.0)⁹.

201 The speciation of volatile trace elements at thermodynamic equilibrium during
202 volcanic degassing has been modelled at several arc volcanoes (e.g. ^{13,43}) however models
203 of trace element speciation at intraplate volcanoes are rarer. Factors that control the
204 speciation of elements in volcanic gas emissions include the temperature at the point of
205 degassing, the composition of the parent magma, the amount of atmospheric mixing before
206 'quenching' (i.e. the cooling of gases to a largely non-reactive state⁵²), and the volatility of
207 the speciated or elemental forms they degas as from the parent magma^{43,53–55}. We note that
208 kinetic effects also play an important role in determining the speciation of emitted gases and
209 particulates⁵⁶, and these are not accounted for in the thermodynamic speciation model
210 presented here. Speciation modelling in this study is relevant only to the high temperature
211 mixture of atmospheric and magmatic gases generated close to the lava-air interface, where
212 gases can be assumed to attain equilibrium rapidly, and kinetic effects are assumed to be
213 negligible^{54,57}. Mixing between a magmatic plume and the background atmosphere is
214 typically described as a ratio V_A/V_M , where V_A is the volume of air in the mixture, and V_M is
215 the volume of undiluted magmatic plume in the mixture (mixing can also be described as a
216 mol% of air in the mixture). Previous studies^{52,54} observed a compositional discontinuity (CD)

217 in plume chemistry corresponding to the near-complete oxidation of reduced gas species
218 such as H₂S and S₂ (**Figure 6A**). Using a typical arc plume composition, Martin *et al.*⁵⁴
219 observed a CD at ~ 5.7 mol% air ($V_A/V_M \sim 0.06$). For a Kīlauea plume composition (**Table**
220 **S6**), the CD occurs at ~ 15% air ($V_A/V_M \sim 0.16$, **Figure S12**), because of the higher
221 concentration of reduced species in the Kīlauea plume at the point of emission compared to
222 arc volcanoes.

223 We modelled the equilibrium speciation of gas phases in the magmatic plume using
224 the Gibbs Energy Minimisation module of HSC Chemistry (version 9.9.2, Outotec Research
225 Oy, Finland; **Methods**). From an initial magmatic gas equilibrium temperature of 1145°C
226 (based on the MgO content of 2018 Kīlauea lavas, **Methods**), we model speciation during
227 early mixing of magmatic gases with the atmosphere ($0 < (V_A/V_M) < 0.33$); atmosphere is
228 added as a 78:21:1 mixture of N₂:O₂:Ar in increments of $V_A/V_M = 0.01$. To determine the
229 temperature decrease during mixing, we use a simple model of temperature change during
230 mixing of two gases of different temperatures – N₂, O₂ and Ar gases to represent the
231 atmosphere at 25°C and H₂O vapour at 1145°C to represent the magmatic gases (following
232 Ilyinskaya *et al.*⁵⁸; **Methods**). This generates a temperature decrease from 1145°C to
233 1016°C between $V_A/V_M = 0$ and $V_A/V_M = 0.33$.

234 Broadly, at the point of emission with no atmospheric mixing, $V_A/V_M = 0$, volatile trace
235 elements can be grouped into those complexed as gases with S²⁻ (emanation coefficient, $\epsilon >$
236 10% – S₂Te and S₂Se; $\epsilon > 1\%$ – BiS, AsS; $\epsilon > 0.01\%$ – PbS, SnS), those complexed with Cl⁻
237 ($\epsilon > 10\%$ – InCl; $\epsilon > 0.01\%$ – AgCl, CuCl), and elemental gases ($\epsilon > 0.01\%$ – Cd, $\epsilon > 1\%$ –
238 Bi, $\epsilon > 0.01\%$ – Ag, Zn, Cu; **Figure 6B**, **Figure 9A**). At $V_A/V_M = 0.33$ (or 25% air) and T =
239 1016°C, those elements with greatest affinity for S before the CD are now present
240 predominantly as oxides, and those that were present in elemental forms now present as
241 chlorides, hydroxides or oxides (**Figure 6C**). The speciation groupings observed at $V_A/V_M =$
242 0 highlights the critical role that the oxidation state of magmas (which will determine the
243 availability of certain ligands, e.g. S²⁻), as well as their S and Cl contents, play in determining

244 degassing of volatile trace metals⁵⁵. The concentration of chloride complexes increases after
245 the compositional discontinuity (**Figure 6C**), consistent with previous work^{54,57} that has
246 shown that the oxidation of magmatic gases creates more reactive halide species, thus
247 increasing the proportion of elements present as chlorides. Elements that do not complex
248 with chloride (e.g. Se, Te, As) generally will not form chlorides unless the HCl gas content of
249 the plume is increased between 100-1000 times ($V_A/V_M = 0$, $T = 1145^\circ\text{C}$, **Figure S16**; V_A/V_M
250 $= 0.33$, $T = 1016^\circ\text{C}$, **Figure 8**). In the case of Se, even 1000 times the original HCl gas
251 concentration does not cause Se to complex with chloride.

252 A number of previous studies have demonstrated or inferred the importance of
253 chloride for trace metal degassing, from both natural sampling (at arcs^{13,43,55} and other
254 hotspot volcanoes¹¹) and experimental work⁴⁴. Thermodynamic speciation modelling of the
255 composition of magmatic gases released at arc volcanoes, which typically have a higher Cl
256 content and more oxidised magmas than intraplate volcanoes, has shown that volatile trace
257 metals and metalloids are speciated predominantly as chloride gases during high
258 temperature degassing^{13,43}. For example, in the magmatic plume of Yasur, a basaltic
259 volcano in the Vanuatu archipelago, at magmatic gas temperatures of 1100°C and no
260 atmospheric mixing (i.e. $V_A/V_M = 0$) Pb is found mainly to be speciated as PbCl gas¹³. This is
261 in contrast to the Kīlauea plume modelled in this study, in which Pb is present predominantly
262 as PbS gas at $V_A/V_M = 0$ and a temperature of 1145°C (modelling of the Kīlauea plume at
263 1100°C does not change the dominant speciation of Pb or Bi, i.e. the difference between
264 Yasur and Kīlauea is not simply a temperature effect). Similarly, BiS gas is considerably less
265 abundant in the Yasur plume compared to Kīlauea, with elemental Bi gas and BiCl gas
266 dominant instead. Similar observations were made in thermodynamic models of the
267 magmatic plume of Mount Augustine in Alaska⁴³ (although some differences in this case
268 may be due to improvements in the speciation models over time, through the introduction of
269 new thermodynamic data).

270 Volcanic plumes in arc settings display characteristic differences in the relative
271 abundances of volatile trace elements when compared to intraplate settings⁵⁵; X/SO₂ ratios

272 for some elements (e.g. In and Cu) are up to 2–3 orders of magnitude higher in arc plumes,
273 while others (e.g. Te, Se, Sn) differ little between different tectonic settings (**Figure 4A**).
274 These differences have been explained by more oxidized magmas, and higher
275 concentrations of chlorine (mean arc $\text{SO}_2/\text{HCl} \sim 1.9^{57}$, vs SO_2/HCl 30–32 at Kīlauea, this
276 study) and water at arc settings, which promote metal partitioning directly into
277 aqueous/saline aqueous fluid⁵⁵. Speciation modelling in this study (**Figure 6, Figure 8**)
278 supports these conclusions – it shows that the elements most enriched in arc emissions are
279 present as chloride gases (e.g. InCl and CuCl, **Figure 6B**) at the point of emission (i.e. no
280 mixing with air). In contrast, elements that behave similarly between volcanoes at different
281 tectonic settings are emitted as sulfide gases at Kīlauea (e.g. S₂Te, S₂Se, S₂Sn, **Figure 6B**).
282

283 The origin of the laze plume and late-stage degassing at the ocean entry

284
285 The composition of the laze plume, in terms of both volatile ligand-forming and trace
286 elements, differs significantly from the magmatic plume. As has been shown in previous
287 work²⁹, the laze plume is relatively Cl-rich and S-poor, which mostly reflects the large
288 contribution that boiled seawater makes to the laze plume. Total (gas and PM) molar ratios
289 for S/Cl and Cl/F are 0.1 and 4.3, respectively (compared to ~30–32 and ~2.4–2.8, in the
290 magmatic plume, **Figure 3**). In the laze plume, a larger fraction of S and Cl concentrations
291 are measured in the PM (41–49% S, 50–57% Cl in PM), while the magmatic plume is gas-
292 dominated at source for these elements (<0.3% of S and Cl in PM). PM fractions for F are
293 comparable between the laze plume (0–2% in PM) and the magmatic plume (<1.2% in PM)
294 (**Figure 3**). S and Cl concentrations are distributed uniformly across the five size fractions
295 (**Figure 2D, Table S14**), while F is concentrated in the largest size fraction (~75% = $D \geq 2.5$
296 μm), which may be linked to HF adsorption onto silicate particles⁴⁹. Concentrations of
297 volatile trace elements ($\epsilon > 0.001\%$) are generally lower in the laze plume than in the
298 magmatic plume (with the notable exception of Cu, and to a lesser extent Ag, **Table S8** and
299 **S12**). As in the magmatic plume, volatile elements ($\epsilon > 0.001\%$) are found predominantly in
300 the smallest size fraction: for all but Te, >40% of the concentration of volatile elements ($\epsilon >$
301 0.001%) is found in the $D \leq 0.25 \mu\text{m}$ fraction, consistent with particles formed by gas-to-
302 particle conversion post-degassing⁴⁸ (**Figure 2D, Table S14**). Note that Te concentrations
303 are close to detection limits (**Table S8**) of the analysis (**Methods**). In contrast to the
304 magmatic plume, the size distribution of particulates containing refractory elements ($\epsilon <$
305 0.001%) in the laze plume is strongly bimodal, with many elements only measured above
306 detection limits in the smallest ($D \leq 0.25 \mu\text{m}$) and largest ($D \geq 2.5 \mu\text{m}$, consistent with a
307 silicate source) size fractions (**Figure 2C, Table S14**).

308 To get a broad sense of trace metal emission rates from the laze plume in 2018 we
309 follow the method of Edmonds and Gerlach²⁹, who estimated the HCl emission rates in a
310 laze plume associated with lava flows emanating from the Pu'u 'Ō'ō vent (2004-05). We use

311 lava effusion rates at the main Fissure 8 vent⁴⁰, combined with assumptions about how
312 much still-molten lava reaches the ocean entry, to estimate a Cl emission rate from
313 seawater. The Cl emission rate is then combined with X/Cl ratios of trace elements
314 measured in the laze plume to determine trace element emission rates (supplement section
315 **S9, Table S7**). The uncertainties on these estimates are large. However, notably Cu
316 emission rates from the ocean entry may be higher than those emitted at the main Fissure 8
317 vent (we estimate ~230–1600 kg Cu/day for the laze plume, vs 116 ± 29 kg/day for Fissure
318 8), while other volatile metals may produce lower emission rates (laze plume: ~20–150 kg
319 Zn/day; ~0.5–3.5 kg Cd/day; ~0.2–2 kg Ag/day; ~0.01–0.5 kg Bi/day).

320 The similarity of the laze plume composition to seawater is assessed by comparing
321 element/chlorine ratios (X/Cl) measured in the plume to X/Cl ratios in seawater (**Figure 7**).
322 Note that that X/Cl ratios may be fractionated during the rapid evaporation of seawater,
323 particularly for those elements that form salts that may be left behind²⁹. However, such
324 fractionations are as yet unconstrained and so are not considered further here. For elements
325 abundant in seawater (Ca, Mg, Na and K), the laze plume composition is close to an
326 average global seawater composition⁵⁹ (**Table S16**). However, for Al, Ti, Fe, the REEs and
327 some volatile metals elements (Cd, Bi, Cu, Ag, Zn) the laze plume is enriched relative to
328 average global seawater by 3–6 orders of magnitude. Correcting the laze plume composition
329 for a contribution from silicates (**Methods**), can account for elevated concentrations of
330 refractory elements (Ti, Fe, Mn, REEs except La) in the laze plume (**Figure 7**). This silicate
331 contribution may come from rapidly-quenched fragments of silicate glass generated by
332 explosive hydro-magmatic fragmentation of lava as it interacts with seawater, or from
333 congruent dissolution of basalt by seawater at the ocean entry (as proposed by ³²).
334 However, after the silicate correction La/Cl and Al/Cl in the laze plume remain 100 and
335 10000 times elevated above seawater ratios, respectively. La is the most volatile REE and
336 therefore may be enriched in the laze plume because it is degassing from lava flows at the
337 ocean entry (more detailed REE discussion in supplementary section **S8**). Al is intensely
338 particle reactive throughout the water column (e.g.⁶⁰) and previous work using Al-spiked

339 seawater boiling experiments³² explained similar anomalous Al concentrations by adsorption
340 of Al onto particles formed as seawater boils. If particles that have been subjected to Al
341 adsorption were lofted into the laze plume this could provide an explanation for elevated
342 concentrations of Al.

343 Silicate-corrected concentrations of Cd, Zn, Ag, Cu, Bi, Re are also elevated in the
344 laze plume above seawater. Cu and Cd enrichments were also observed in a study of
345 seawater close to Kīlauea's ocean entry in July 2018³¹. Due to the relatively high volatility of
346 all these elements ($\epsilon > 0.001\%$), it is likely that these elements are degassing from lava at
347 the ocean entry³². Critical factors that could explain the enhanced degassing of these
348 elements include the oxidation state of the lavas/gases and the availability of ligand-forming
349 elements, such as Cl and S. Basaltic melts have been shown to become more reduced
350 during S degassing⁶¹, therefore we would expect lava flow melts at the ocean entry to be
351 more reduced than those emitted at the source vent. However, we note that Lerner et al.⁶²
352 found that melts (matrix glass and melt inclusions) sampled from distal lava flows were more
353 oxidised than those at the source, potentially due to atmospheric interaction during sub-
354 aerial lava flow. Due to this uncertainty, we have investigated the effect of
355 increasing/decreasing the Cl content at seven different initial HCl gas concentrations (0.001,
356 0.01, 0.1, 1, 10, 100 and 1000 times the initial concentration measured in the magmatic
357 plume, **Methods**) on the speciation of trace elements in a gas mixture, at both comparatively
358 reduced ($V_A/V_M = 0$), and oxidised ($V_A/V_M = 0.33$) conditions (**Methods**). The S/Cl ratio of
359 the laze plume is comparable to the model run with ~100 times the amount of HCl gas in the
360 magmatic plume (see data in **Tables S8** and **S12**; and **Figure 8**).

361 Cu, Ag and Zn tend to complex predominantly with chloride, at both $V_A/V_M = 0$ and
362 $V_A/V_M = 0.33$ (**Figure 6**), and their affinity for chloride increases markedly when the HCl gas
363 content of the plume is increased ($V_A/V_M = 0$, $T = 1145^\circ\text{C}$, **Figure S16**; $V_A/V_M = 0.33$, $T =$
364 1016°C , **Figure 8**). At $V_A/V_M = 0.33$, and at 100 times the initial HCl gas content, ~100% of
365 Cu, Ag, Zn, Cd and Bi are present as chloride gases (**Figure 8**). At $V_A/V_M = 0$, Cu, Zn and

366 Ag are present almost exclusively as chloride gases, while only a small proportion of Bi and
367 Cd are complexed with chloride. Re displays opposite speciation behaviour to Cd and Bi: Re
368 is present as an chloride at $V_A/V_M = 0$ and as an oxide at $V_A/V_M = 0.33$. Without further
369 investigation of the oxidation state of degassing melts at the ocean entry, these models are
370 endmembers, whereas the true oxidation state of gases may lie somewhere in between.
371 From the results of the speciation model, we would also expect other elements with strong
372 chloride affinity to be elevated above seawater and silicate glass in the laze plume, such as
373 Pb and In. These elements were not above detection limits in both filter pack samples
374 (**Methods**); however, In was above detection limits in the size-segregated sampling (**Figure**
375 **2D**), and a small amount of Pb was detected in one of the UAS samples, as well as in a
376 previous study of a laze plume at Kīlauea³². The strong affinity of the degassed elements for
377 chloride speciation, either at or above magmatic plume chloride concentrations, suggests
378 that their degassing and/or detection at the ocean entry might be facilitated by the presence
379 of elevated chloride.

380 The availability of Cl at the ocean entry is likely to be higher than that at Fissure 8 for
381 two reasons. Firstly, fractional degassing of lavas between the source and the distal lava
382 flows will decrease the S/Cl ratio of the remaining undegassed volatiles (by Rayleigh
383 distillation)⁶³. For example, during the later stages of degassing of 2014–15 Holuhraun
384 eruption, S/Cl ratios in emissions were ~50 times lower than measured in the syn-eruptive
385 plume. Secondly, the Cl-rich environment created at the ocean entry due to the boiling
386 seawater to dryness, may facilitate the degassing of Cl-complexes. Our observations of the
387 critical role of chloride from speciation modelling are supported by recent experimental
388 work⁴⁴, which has shown that increasing the level of chloride available during degassing of a
389 phonolitic melt can increase the amount of Cu hosted in the resulting sublimates, and that
390 chloride sublimates can host significant amounts of Pb, Tl, As, Cu, Bi and Zn⁴⁴.

391 The absence of volatile elements that complex with sulfides on degassing (Se, Te and
392 As, **Figure 6B**) is notable in the laze plume, and may suggest that either 1) processes at the
393 ocean entry act to suppress the degassing of these elements, or 2) their concentrations in the

394 lava reaching the coast have been depleted by degassing as sulfides at the active vent
395 (Fissure 8) and along the lava flows. This is supported by the observation that up to 90% of
396 S in the melt is degassed at the vent^{62,64}.

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

404

405 **Synthesis**

406

407 The chemistry of volcanic plumes at basaltic intraplate volcanoes such as Kīlauea (and
408 other hotspot volcanoes, e.g. Iceland) provide tantalising analogues for the gas and PM
409 emissions during catastrophic volcanic events in Earth history such as flood basalt eruptions
410 (forming LIPs). Scaled up to the erupted (and therefore degassed) volumes of LIPs, the
411 composition of present-day plumes could be used to estimate the total emissions of volatile
412 trace elements during flood basalt events. For example, the total SO₂ emitted during the
413 eruption of the Deccan Traps LIP is estimated to be 3.5–6.5x10⁶ Mt⁶⁵. Using X/SO₂ ratios
414 from Kīlauea in 2018, over the total 4 million year duration of the eruption, the Deccan Traps
415 could have released long-term average daily emission rates of 5–100 kg Se/day and 7–13
416 kg Cu/day. However, given that the majority of the eruptive activity of the Deccan traps
417 occurred over more concentrated eruptive periods within this time, daily emissions sustained
418 over 10s–100s of years could be far greater than this long-term average⁶⁶.

419 Further, our results highlight the unique metal signature of lava-seawater interaction
420 plumes, which would have been a common phenomenon during oceanic plateau basalt
421 eruptions (e.g. Ontong-Java), and during continental flood basalt eruptions that reached

422 coastlines. Degassing of trace metals from late-stage lava flows at chlorine-rich ocean
423 entries, whose melts are already enriched in Cl over S due to fractional degassing^{61,62},
424 produces a fundamentally different fingerprint of trace metals to magmatic plumes. During
425 large basaltic eruptions, distal ocean entry environments are likely to have been important
426 sites where volcanogenic metals (particularly Cu) are transferred from magmas into the
427 environment, potentially hundreds of km⁶⁷ from magmatic source vents.

428

429 [5354 words]

430

431 **Figure captions**

432 **Figure 1. A:** Map of the final extent of the 2018 LERZ eruption lava flows (red area,
433 including extension of pre-LERZ coastline) and plume sampling locations during this study.
434 Small red triangles represent the location of individual fissures active during the eruption.
435 The yellow star marks the location of the Leilani Community Association, where UAS flights
436 into the magmatic plume were launched. White triangles mark the locations from which
437 UAS flights to sample the laze plume were launched. During the July-August 2018
438 campaign, we sampled the laze plume which was created near Isaac Hale Park. Inset map
439 of Island of Hawai'i with locations of Kīlauea summit (S), Pu'u 'Ō'ō (P) and Fissure 8 (F8).
440 Adapted from Neal et al³⁵. **B:** Aerial image (USGS) of Fissure 8 and the magmatic plume,
441 taken on 24 July 2018 during a sampling flight, looking ~SE. UAS sampling of the magmatic
442 plume was carried out ~300 m above the active vent. The cylindrical filter pack symbol
443 (**Figure S1**) marks the approximate location of ground-based sampling. **C:** Aerial image
444 (USGS) of the ocean entry and laze plume taken during a flight from Mackenzie State
445 Recreation Area on 24 July 2018, looking ~NE. UAS sampling of the laze plume was carried
446 out ~100 m above the ocean entry.

447
448 **Figure 2. Size segregated concentrations (not ash corrected) of elements in**
449 **particulate matter measured in the magmatic and laze plumes, in order of volatility.**
450 *Note the different emanation coefficient scales on figures A and B. A:* Refractory ($\epsilon <$
451 0.001%) elements in the magmatic plume, with emanation coefficients (ϵ) calculated for the
452 magmatic plume for the UAS and ground-based sample are also shown. **B:** Volatile ($\epsilon >$
453 0.001%) elements in the magmatic plume, with emanation coefficients (ϵ). **C:** Refractory ($\epsilon <$
454 0.001%) elements in the laze plume. **D:** Volatile ($\epsilon > 0.001\%$) elements in the laze plume. All
455 elements were measured by ICP-MS or ICP-OES except where indicated; IC = ion
456 chromatography. D = cut-off diameter as defined in methods. BDL = below detection limits
457 (of either the instrument, or below filter blanks).

458 **Figure 3. S, Cl, F, and N in the magmatic and laze plumes.** Concentrations (mol/m^3) of S
459 (measured as SO_4^{2-}), Cl (measured as Cl^-), F (measured as F^-), and N (measured as NO_3^-)
460 in the gas and PM phases of the magmatic (left, UAS and ground samples) and laze plumes
461 (right, Isaac Hale Park and Mackenzie State Recreation Area samples). Percentages
462 indicate the proportion of S, Cl, F, and N measured as gas and PM for each element. S/Cl
463 and Cl/F ratios are total (gas + PM) molar ratios. Cl in PM at Fissure 8 is comparable to
464 background levels measured in 2019 (**Table S8**, Ilyinskaya et al., *in review*).

465

466 **Figure 4. Trace element emission rates and relative abundances in volcanic plumes.**

467 **A:** Trace element emissions rates for a selection of basaltic volcanoes normalised to
468 emission rates in the Kīlauea 2008 eruptive plume⁹. Kīlauea 2018 emission rates are
469 calculated using an SO_2 emission rate of $39 \pm 11 \text{ kt day}^{-1}$ as described in this work.
470 Holuhraun 2015 data from⁶⁸. Etna 2001 data from⁷. Erta Ale data from¹⁰. **B:** Trace element
471 concentrations, X, ratioed to SO_2 gas (SO_2) concentration to account for variable plume
472 dilution, normalised to the X/ SO_2 ratios in the Kīlauea 2008 eruptive plume⁹. Arc volcanoes
473 are shown as shaded regions, the bounds of which represent the error on the data, where
474 errors are propagated from individual electron microprobe analyses of sulfur, which is
475 typically 5%, and errors on X/ SO_2 , as described in⁵⁵. Etna 2001 data from⁷. Stromboli 1993-
476 97 data from⁶. Masaya 2000-2001 data from⁸. Ambrym 2007-08 data from¹². Elements are
477 ordered by the average arc X/ SO_2 ratio for the volcanoes shown. Kīlauea 2018 data are an
478 average of non-saturated samples 8_1 and 8_5 and error bars are the standard deviation of
479 these samples.

480

481 **Figure 5. Emanation coefficients (ϵ) compared for a selection of volcanoes. A:**

482 Emanation coefficients at a selection of intraplate volcanoes, ordered to their magnitude in
483 Kīlauea 2018 (average of ground and UAS samples). All emanation coefficients are
484 calculated using X/ SO_2 ratios as outlined in **Methods**, with the exception of Holuhraun, for

485 which the values are those given in the paper, calculated using ϵ_{Pb} . **B:** Emanation
486 coefficients at a selection of arc settings. Data sources are as in Figure 4, in addition to a
487 study of degassed and undegassed melts⁴⁷, and a compilation (Rubin) of ϵ at a mixture of
488 tectonic settings⁵³. Data for the figure can be found in **Table S17** and a description of ϵ
489 calculations can be found in **Methods**. Error bars represent the emanation coefficients
490 calculated for the maximum and minimum X/SO₂ ratio measured during each measurement
491 campaign. Errors are not available for the Rubin compilation⁵³ or the Holuhraun 2014-15
492 data¹¹.

493

494 **Figure 6. Speciation of gases bearing a selection of trace elements in the Fissure 8**
495 **plume, modelled in the GEM module of HSC chemistry as detailed in the methods. A:**
496 The effect of atmospheric mixing (+ 78% N₂, 21% O₂, 1% Ar) on the speciation of major
497 sulfur-bearing gases in the volcanic plume, with the compositional discontinuity at ~15% air.
498 **B:** the speciation (gas phase only) of elements in the magmatic plume at 0% percent air
499 ($V_A/V_M = 0$; no atmospheric mixing). **C:** the speciation after the compositional discontinuity,
500 at 25% air ($V_A/V_M = 0.33$; the proportions of different species do not change significantly
501 between 20-25% air). The model inputs can be found in **Table S20** and the outputs can be
502 found in **Table S21**.

503

504 **Figure 7. Sources of elements in the laze plume.** The laze plume composition presented
505 as X/Cl ratios in the plume compared to X/Cl ratios in average global seawater (SW)⁵⁹.
506 Compositions corrected for a basaltic 'ash'/silicate glass contribution are also shown as star
507 symbols (when elements do not change position after the correction they are shown as stars
508 only). The solid blue line represents a 1:1 correspondence between the X/Cl ratios of the
509 laze plume and the seawater. Dashed diagonal black lines represent orders of magnitude
510 enrichments in laze plume above the seawater X/Cl ratio. Elements are coloured by
511 emanation coefficient.

512

513 **Figure 8. The effect of increasing/decreasing the chlorine content of the oxidised**
514 **magmatic plume on speciation.** Elements are shown in order of decreasing volatility from
515 top to bottom. From left to right, the input concentration (mol) of HCl(g) in the starting model
516 is increased by an order of magnitude per column, and each column represents a discrete
517 step of the model. The model uses the same input composition as in Figure 6 (**Table S20**)
518 and data outputs from the altered HCl(g) models can be found in **Table S21-27**. Results are
519 shown at $V_A/V_M = 0.33$ or 25% mixing with ambient atmosphere. Results at $V_A/V_M = 0$ or 0%
520 air are shown in **Figure S16**.

521

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

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539 **Author contributions**

540 EM, PW, EJM, EI and RCWW were the fieldwork team with local assistance from CK, TE,
541 DS, and PAN. TCW and AJSM collected SO₂ flux data, with assistance from EJM and TP.
542 EM carried out the majority of the lab work, along with EJM, EI and PW. EM created figures
543 and wrote the manuscript with assistance from all authors.

544 **Competing interests**

545 No competing interests to declare.

546 **Materials and correspondence**

547 All correspondence should be directed to EM. All data used can be found in the
548 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^{69,70}) was used to simultaneously measure concentrations of CO₂, SO₂ and H₂S, 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. SO₂ and H₂S 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 CO₂ 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. CO₂/SO₂ molar ratios were calculated using Ratiocalc⁷¹ (supplement section **S2**). Multi-GAS SO₂ 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 SO₂ 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 SO₂, which corresponds to the concentration baseline between SO₂ 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 technique⁷² 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 D_{p50} – the particle diameter retained with 50% efficiency on the given stage, and is dependent on Stokes number parameters⁷⁴. 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’^{75,76}. 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 **un**constrained. 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 southwestern 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 haze 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 (following^{77,78}). 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 SO_4^{2-} by ion chromatography were $\pm 10\text{--}18\%$. Errors for NO_3^- and F^- were around $\sim 25\%$. 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 spectrometer^{79,80} (**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 following^{82,83} 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/SO₂ ratio in the plume and the independently measured SO₂ emission rate, as:

$$\text{emission rate of } X = X/SO_2 * SO_2 \text{ emission rate}$$

The weighted mean of SO₂ 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 SO₂ emission rates of 71 ± 31 kt/day on the same day of sampling³⁷ – 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 SO₂ was reported⁸⁴. If X/SO₂ ratios remain constant with changing SO₂ 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 $X_{degassed}$ 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:

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

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:

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

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:

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

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 (ϵ_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:

$$\epsilon_x = \frac{(X_{aerosol}/S_{total}) * S_{degassed}}{(X_{aerosol}/S_{total}) * S_{degassed} + X_{degassed}}$$

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 composition⁴⁷ 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 work⁴⁷ suggests that 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 Kilauea. Therefore to cover the full range of possible $S_{degassed}$ values, we use a $S_{degassed}$ value of 1250 ± 300 ppm to calculate ϵ_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^{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 Thornber⁸⁶, 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 $\sim 1145 \pm \frac{1.6}{3.6}$ °C. Further cooling of gases may occur during adiabatic expansion of bubbles. Opehnerimer et al⁸⁷ 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 on 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:

$$T_{mixture} (^{\circ}C) = \frac{(T_1*m_1*c_1)+(T_2*m_2*c_2)+\dots+(T_n*m_n*c_n)}{(m_1*c_1)+(m_2*c_2)+\dots+(m_n*c_n)},$$

where $T_{mixture}$ 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 N₂, O₂ and Ar gases at 25°C are 1.0, 0.9 and 0.5 kJ/(kg*K), respectively; the specific heat for magmatic H₂O 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. H₂O, CO₂, SO₂, H₂S etc.) are from Gerlach⁸⁸, 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 Kīlauea plume and allows comparison with previous work⁵⁴. The data presented in Gerlach⁸⁸ display a similar CO₂/SO₂ ratio (~0.3) to that measured by the multi-Gas in this study (supplement section **S2**) and others⁸⁹. An approximate HBr concentration for the plume was calculated using a HBr/SO₂ 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:

$X_{source} (mol) = ((X_{FP}/S_T) * S_{source}) * X_{source}$ 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_{source} is the concentration (mol) of S in the plume at the point of emission. In this case S_{source} is the total sulfur concentration (measured as SO₂, H₂S, S₂ and COS gases) as determined by Gerlach⁸⁸. Organic compounds are excluded from the calculation because they are unstable at high temperatures⁵⁴. 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**).

[3412 words]

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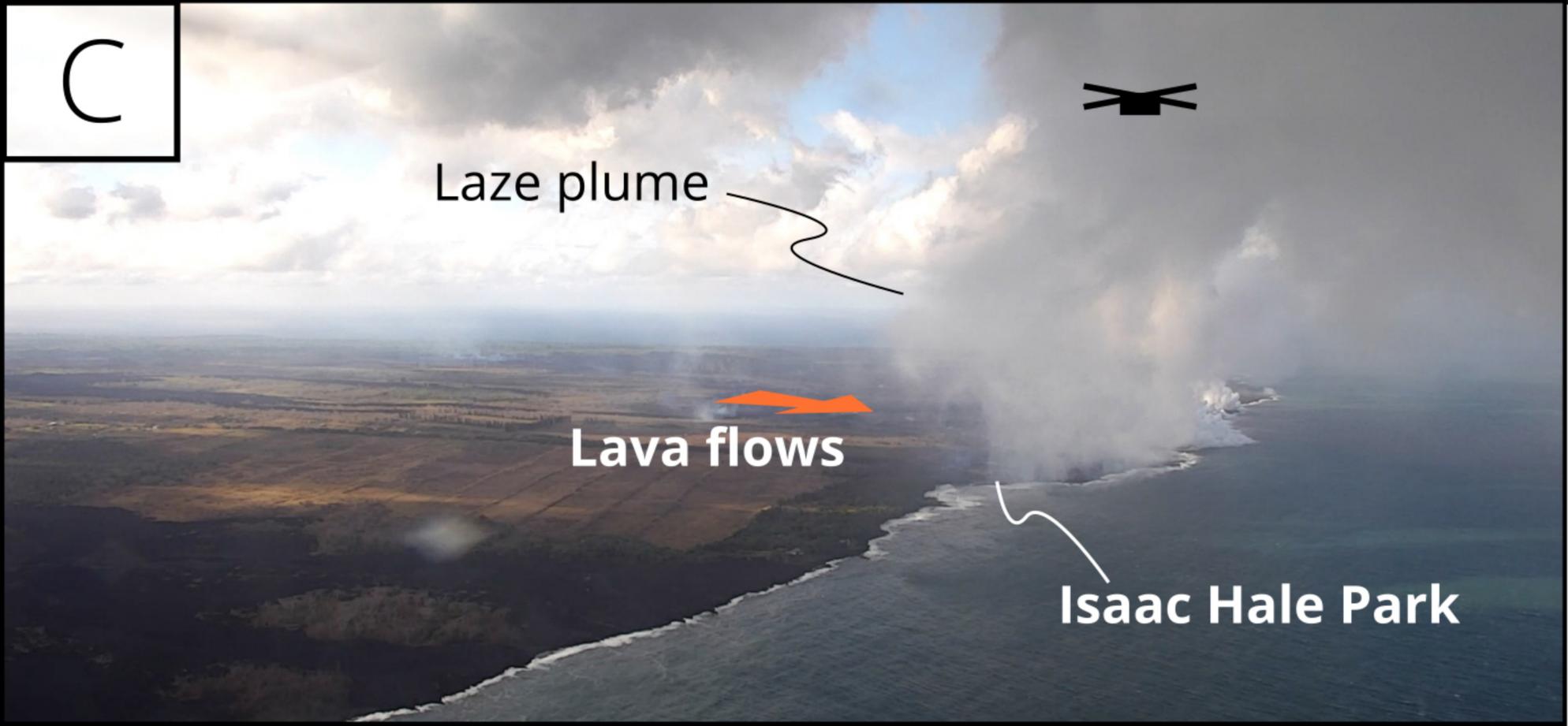
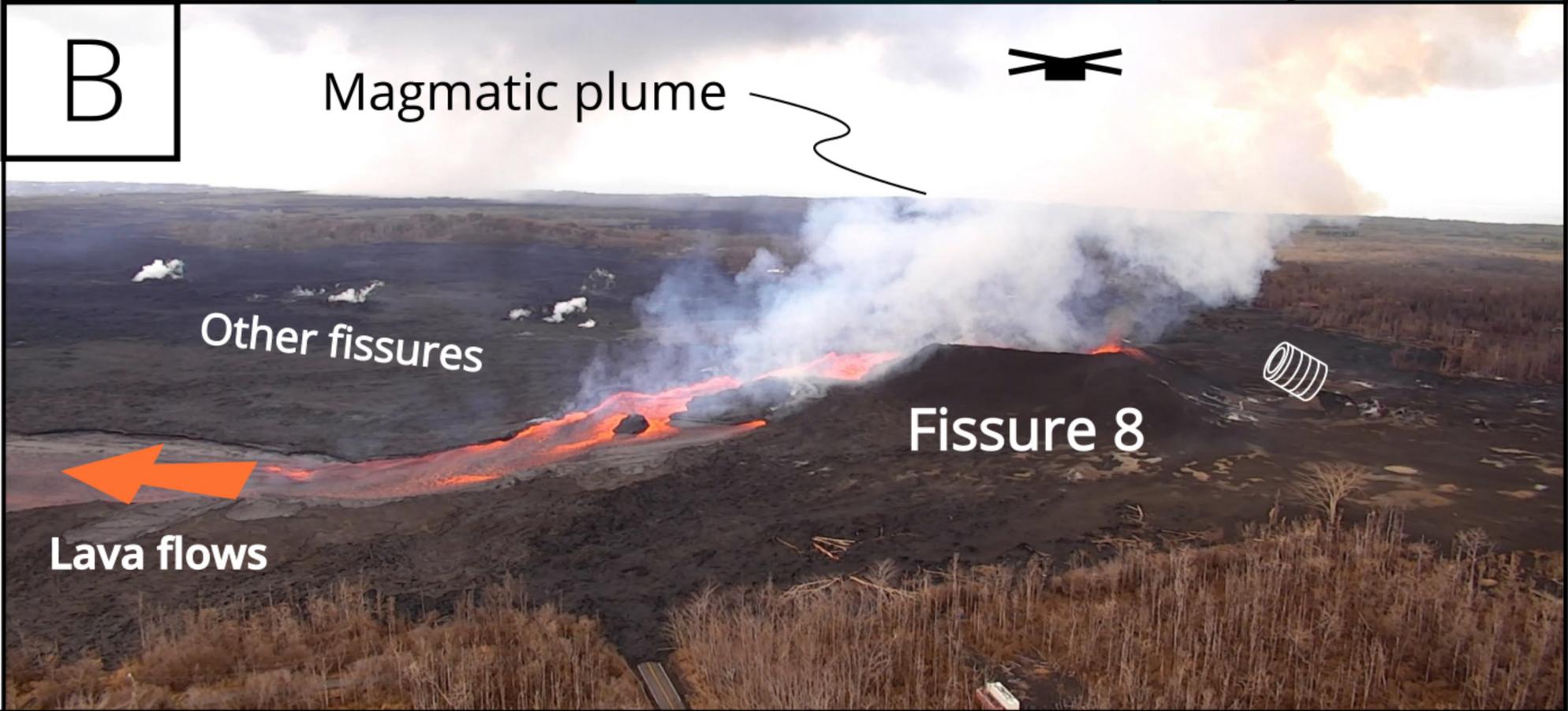
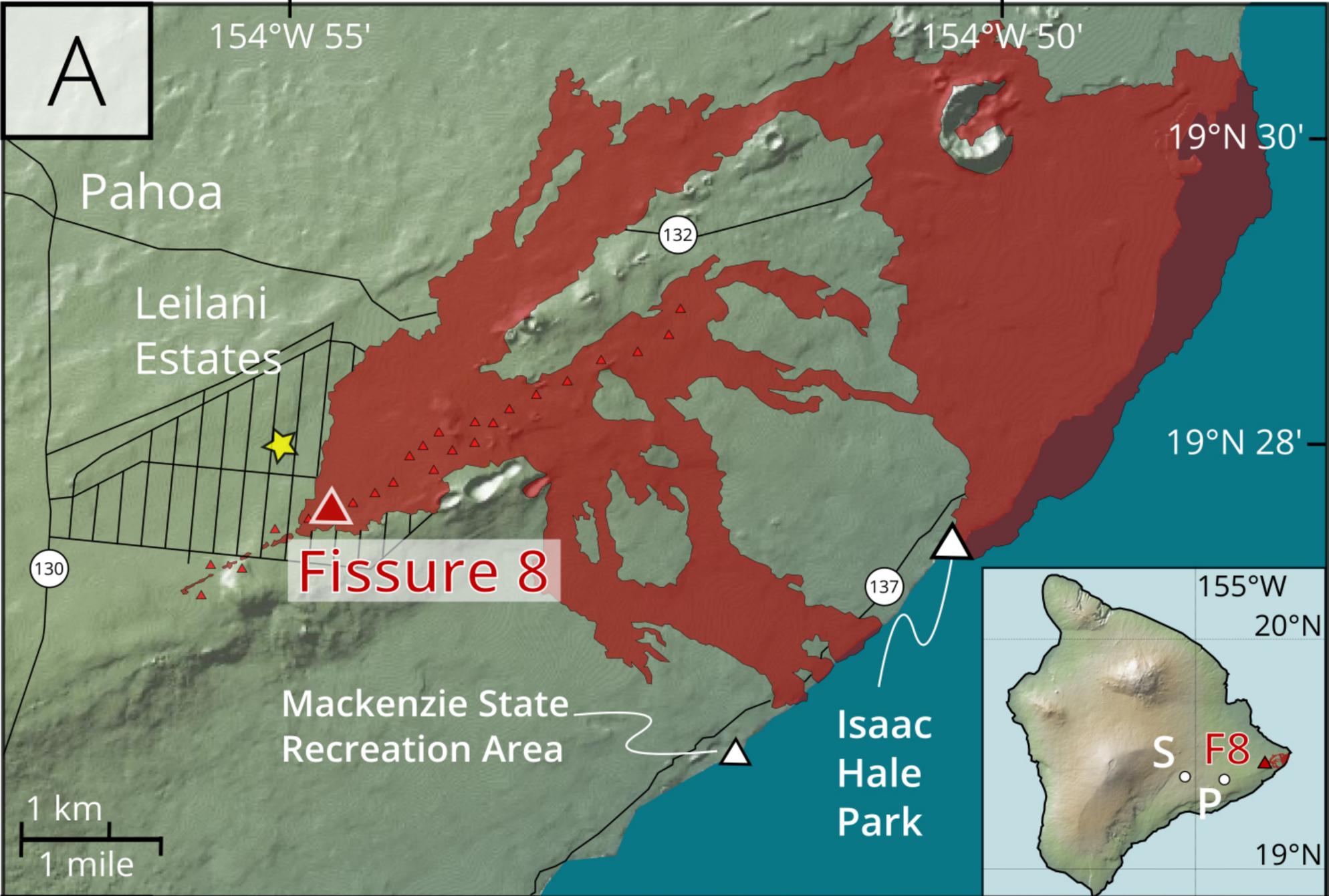
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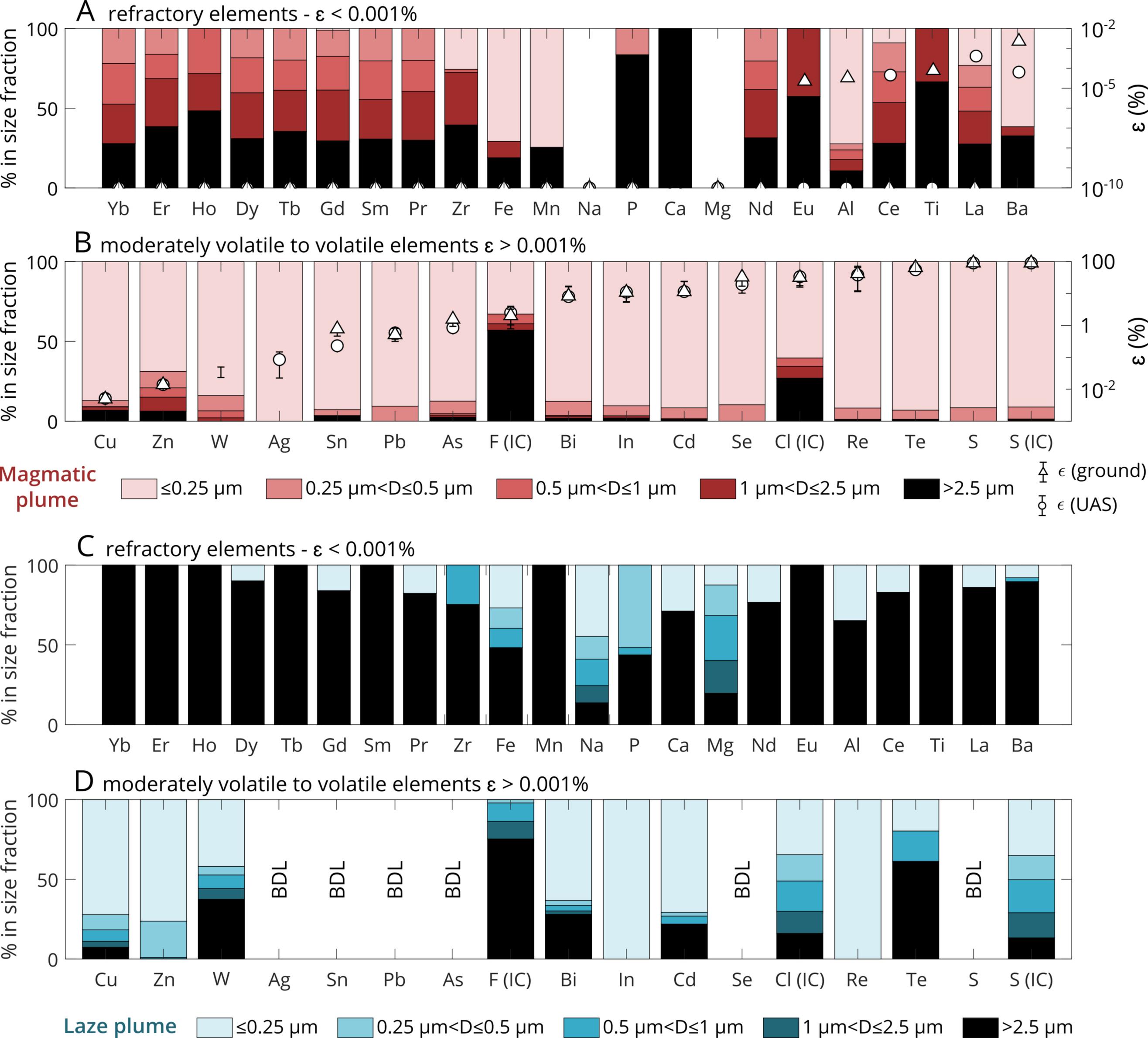
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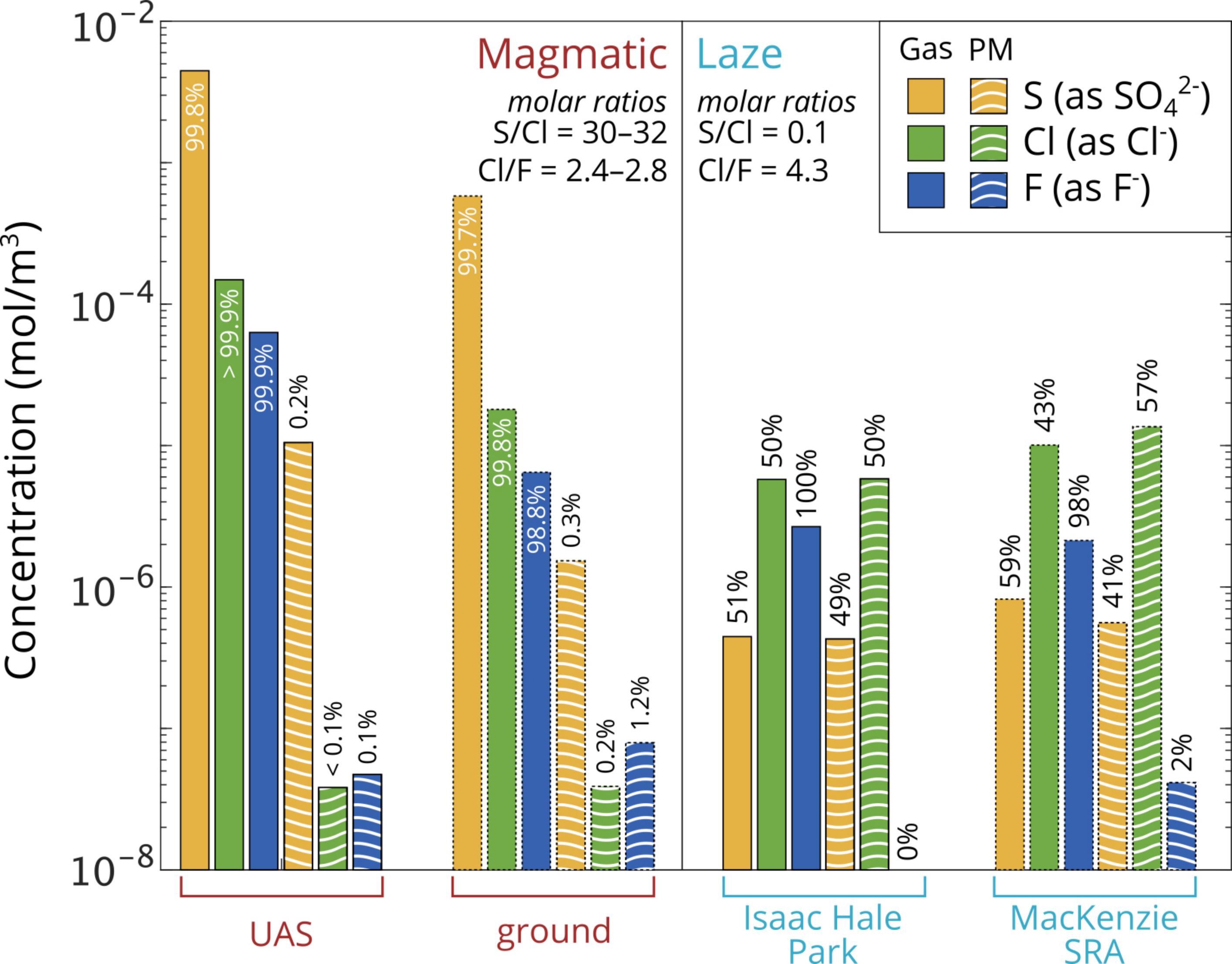
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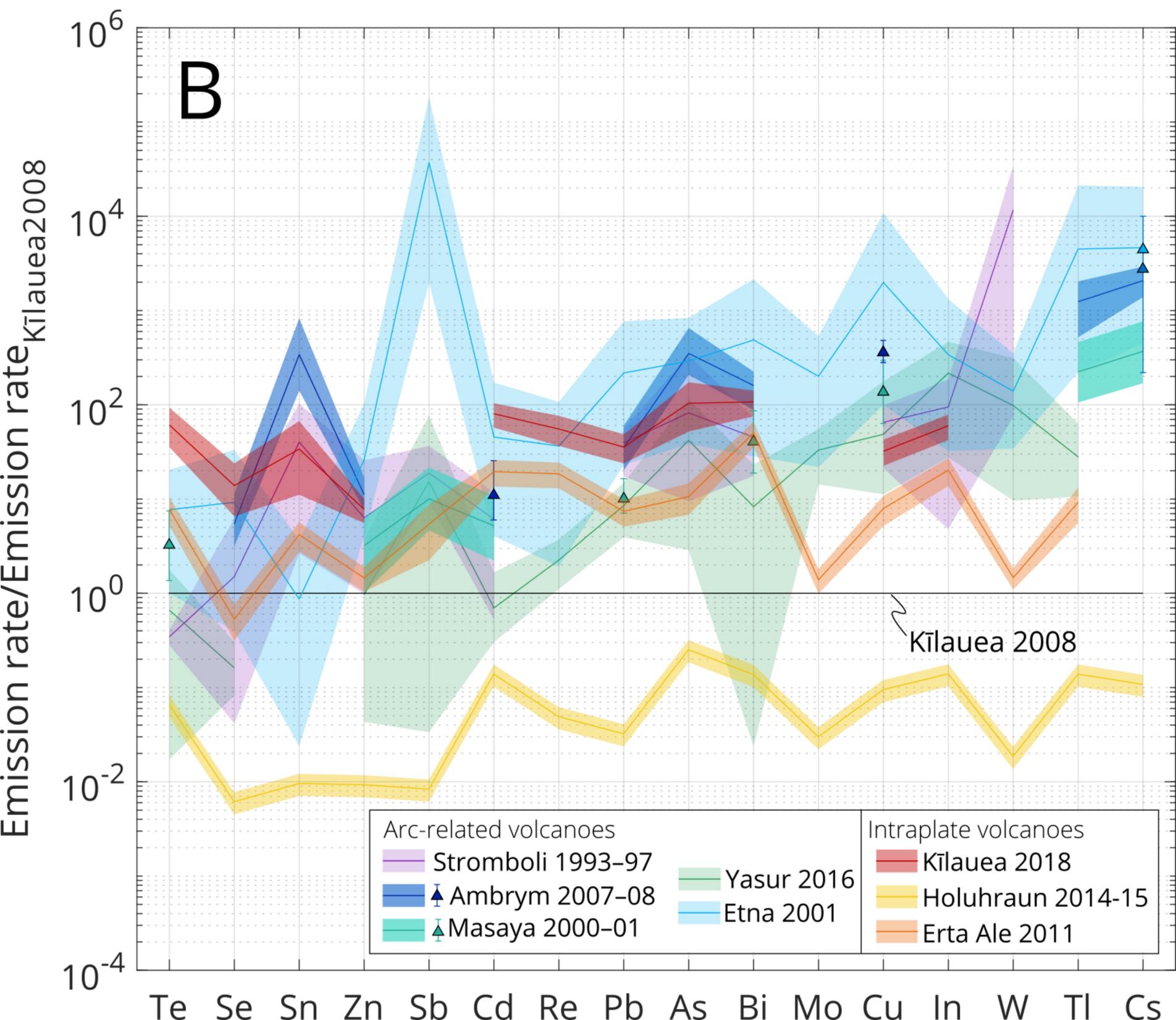
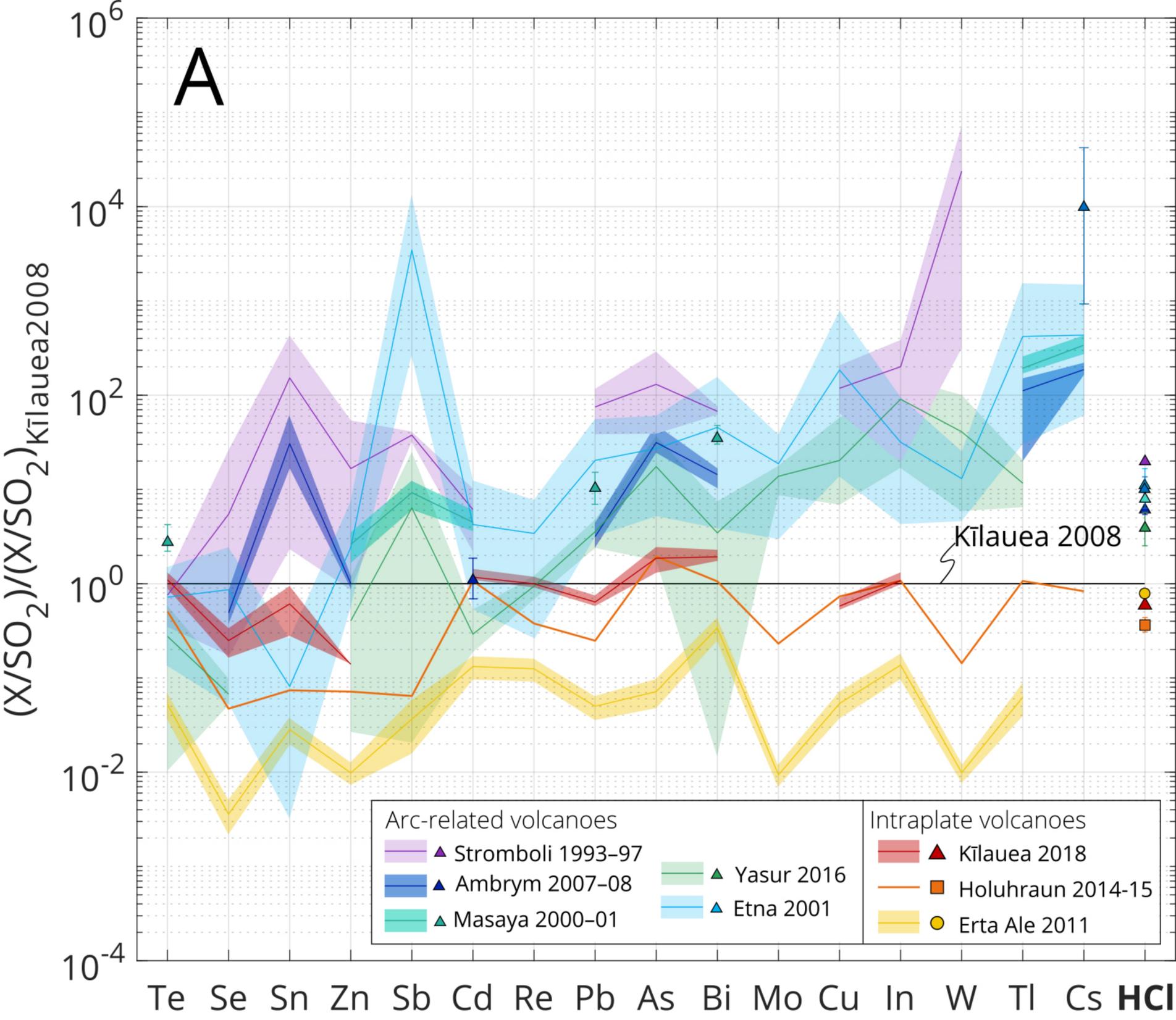
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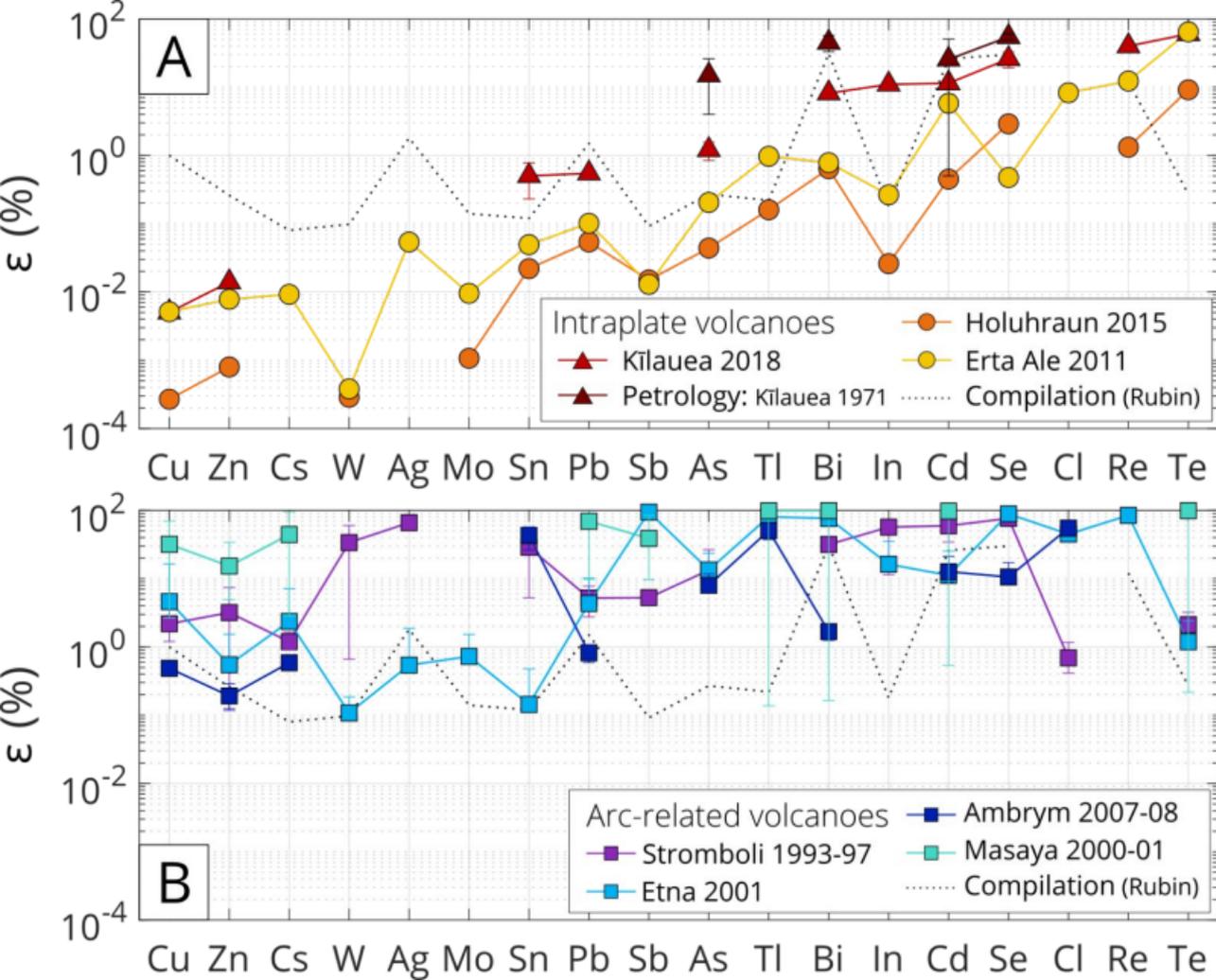
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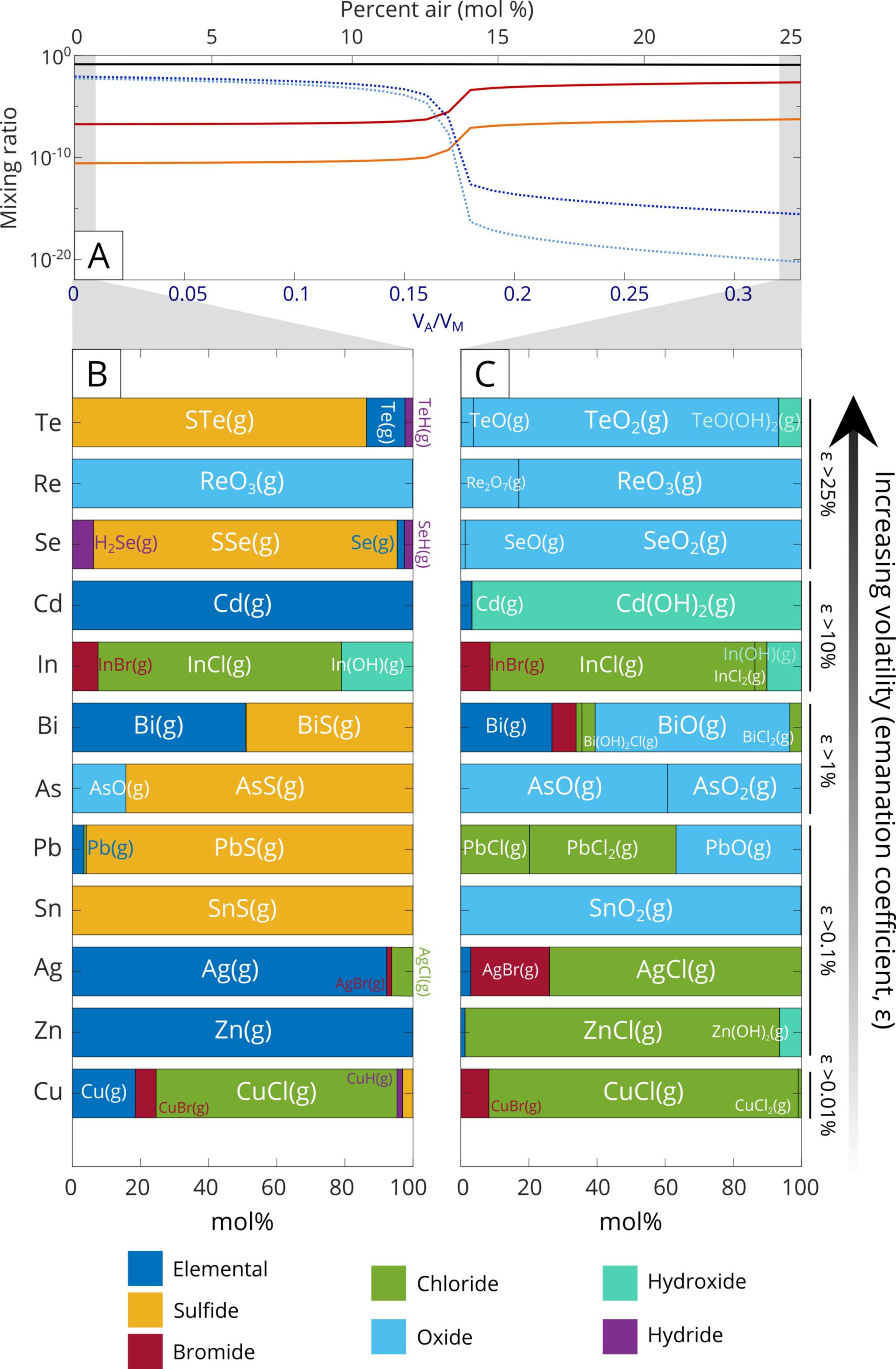


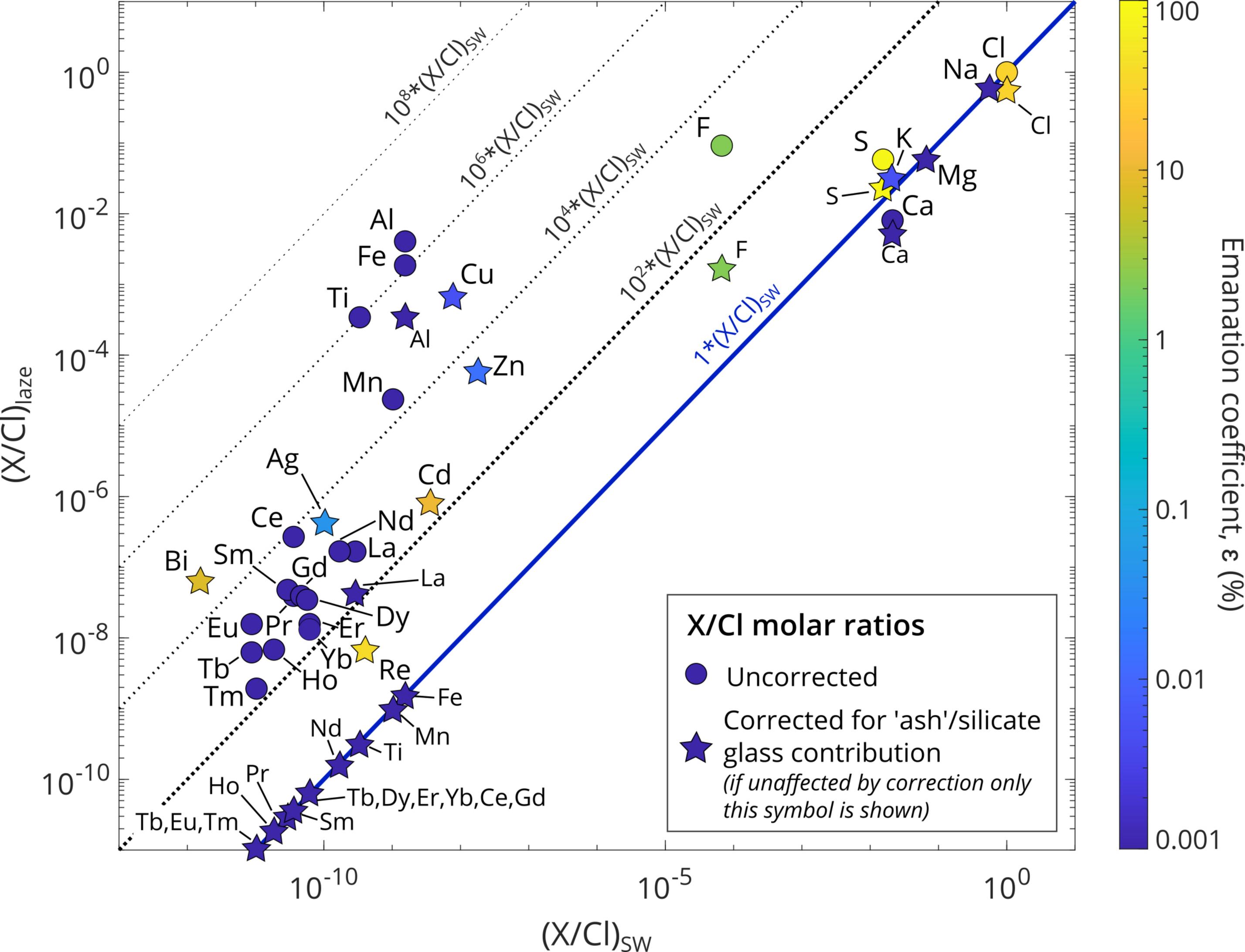




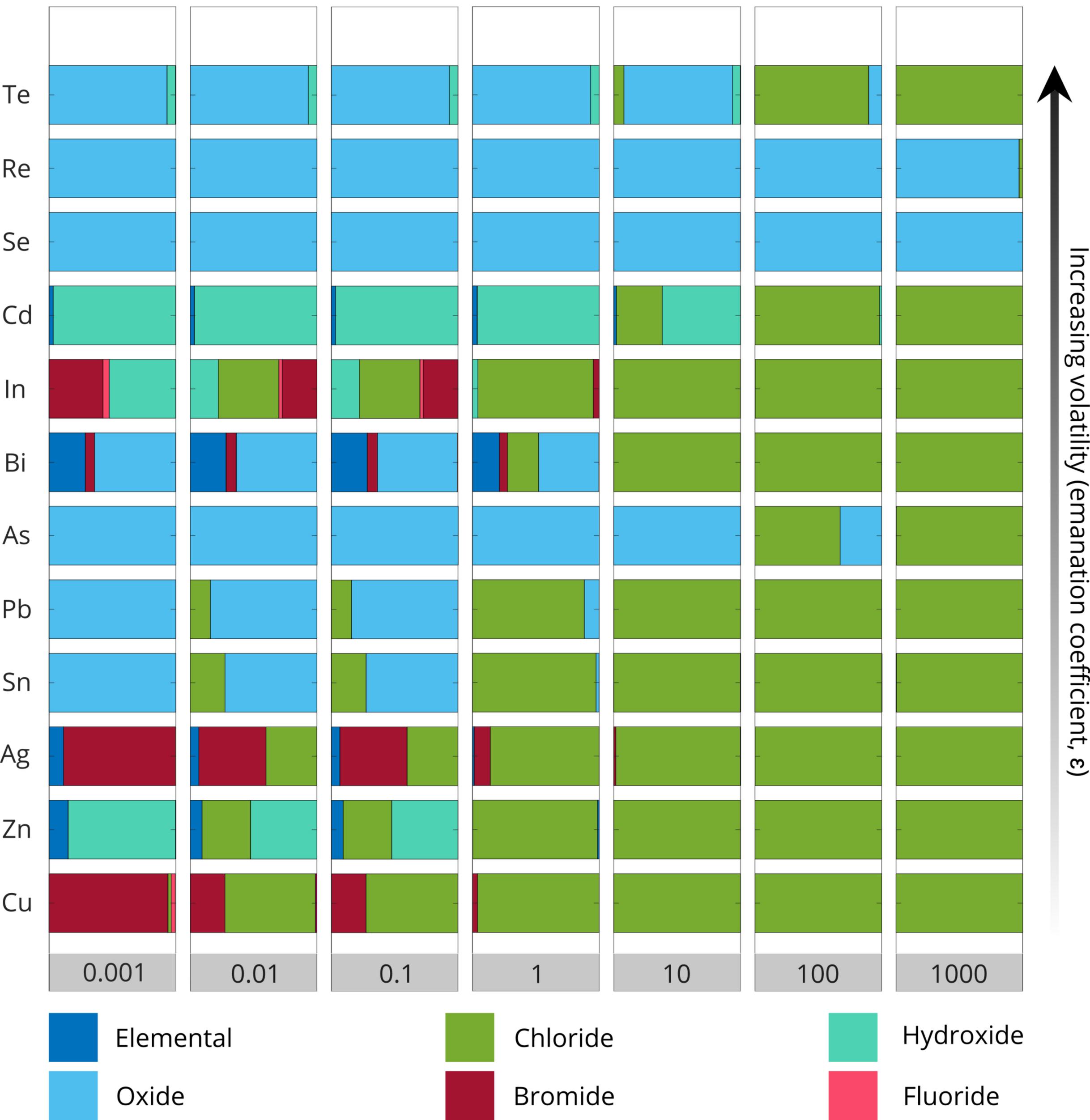


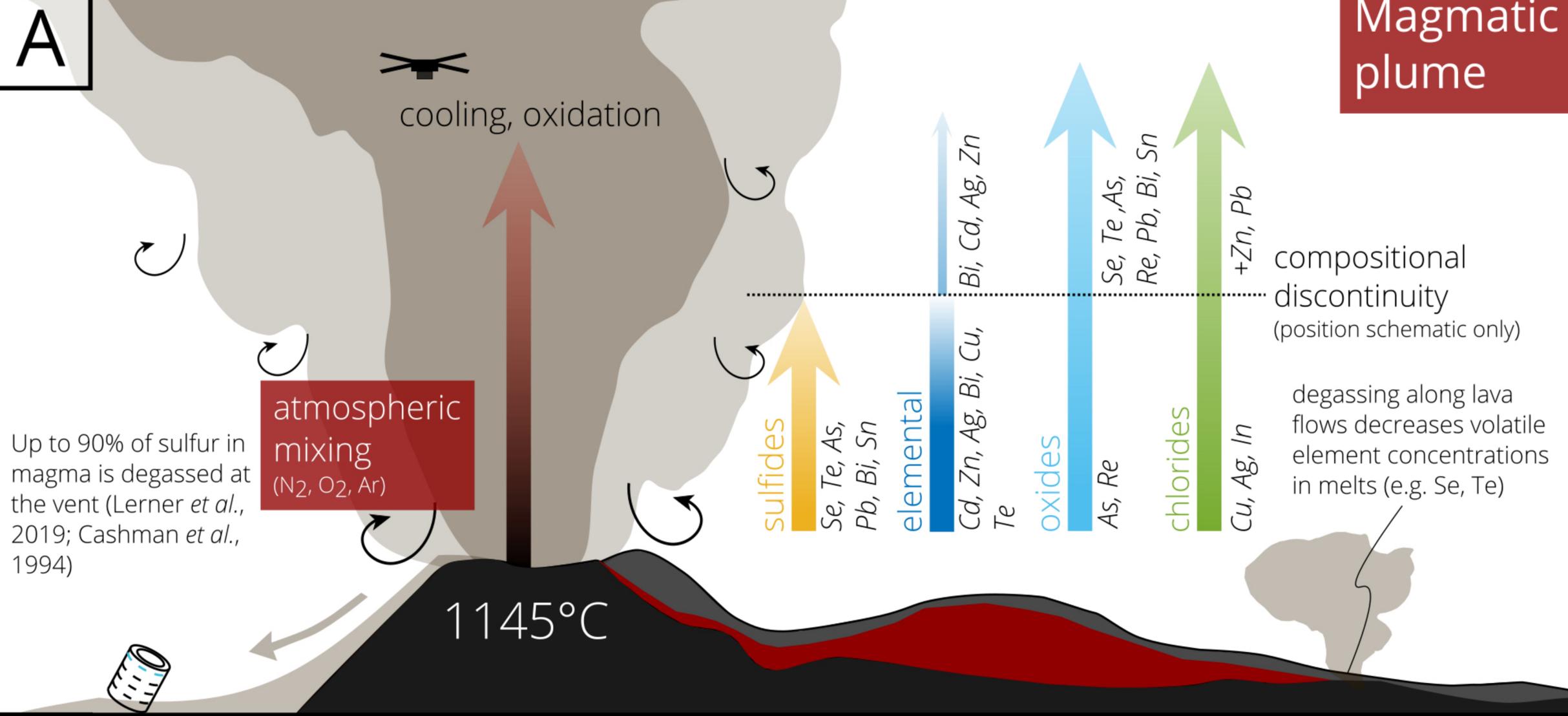
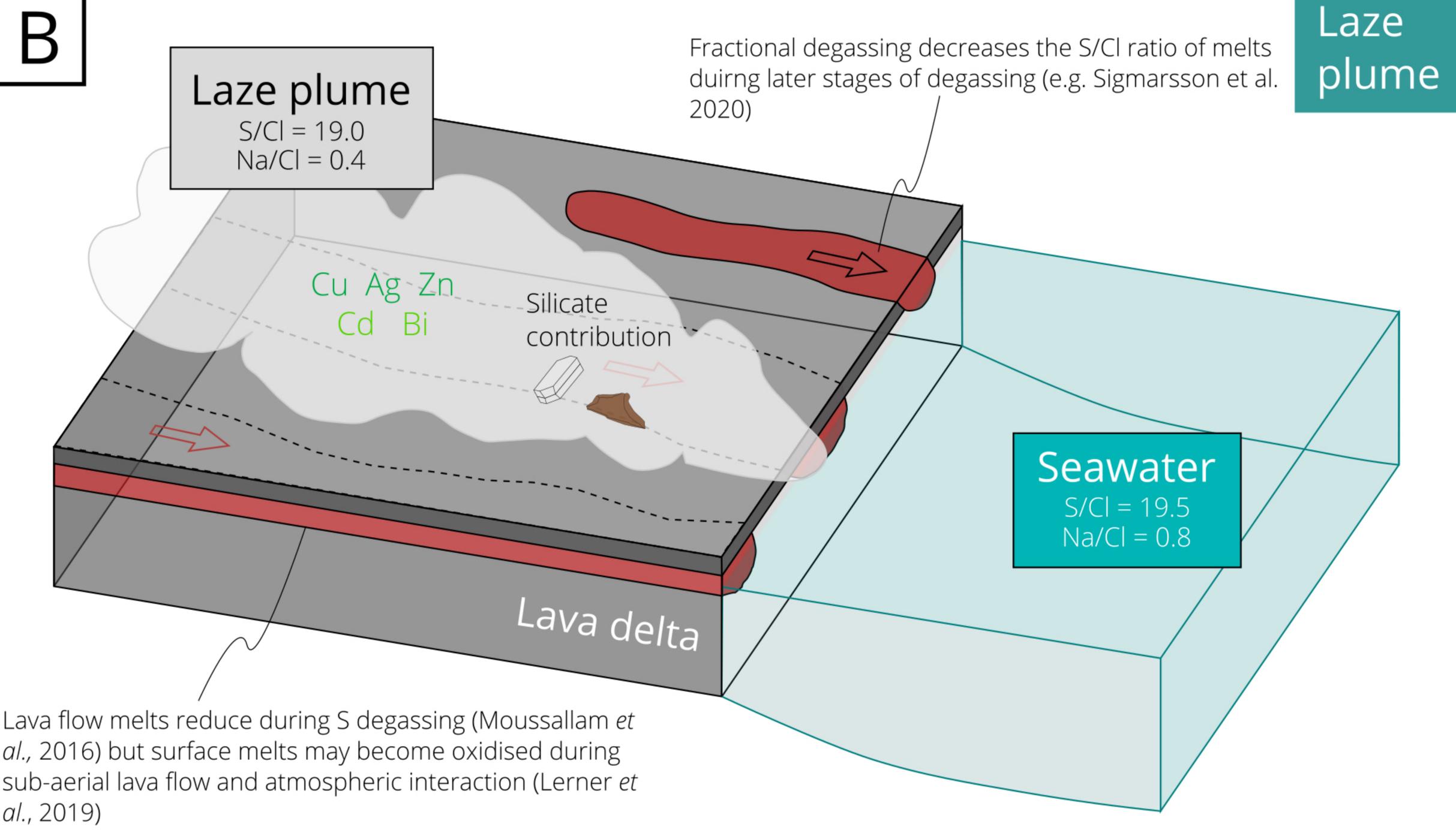






Proportion of original [HCl(g)] in model (at $V_A/V_M = 0.33$; 25% air)



A**Magmatic plume****B****Laze plume**

Response to Comms Earth and Environment reviews

Reviewer comments in black. Our response in blue. **Please note that the line numbers refer to the marked-up pdf (not the one without comments) – the line numbers are different in the two documents.**

1 Reviewer comments

1.1 Reviewer #1 (Remarks to the Author):

This paper is a well-written documentation of lava-seawater interaction, degassing and resultant metal emissions from both the gas and 'laze' (seawater vapor + particle haze) components of the 2018 eruption of Kilauea. The strengths of the paper are it is well-written and organized. The study is data-rich and an extremely comprehensive documentation of all variables affecting metal-loading from what was a crisis-eruption at the time in 2018. Of particular note are the partitions of different element families among different size classes of particles. I cannot find much if any flaws in the data collection, presentation or interpretations.

1.1.1

We thank the reviewer for their kind comments here and for their detailed review of our work.

Descriptions of and the use of the measurements require several assumptions in further calculations (enrichment factor or emanation coefficients) and in modelling. These important facets of the study required nearly twice the length of the paper as Supplemental Material. An example of the complexity is shown in Figure 6 and 8 – which can take a long look to pick through and understand even FOR a practiced reader in this research area. The point is some of the material and many facets of the study, were underplayed or raced through for space reasons.

1.1.2

We endeavoured to be as detailed and transparent as possible during the write-up of our study, hence the long supplementary material section. We have provided a level of detail that we argue that many papers on this topic often do not provide, which has been a source of frustration to us when reading some previous literature. As noted by reviewer 2, not all of this material is strictly necessary to support the paper, and so we have reduced or removed some of it where agreed it was appropriate.

While we appreciate the point that the reviewer makes when they say below that the paper would be more suited to a volcanology-specific journal, we argue that our paper has a broad appeal suited to the format of Communications Earth and Environment. The 2018 eruption of Kilauea was not only a very high-profile eruption in the media at the time, but also is and will continue to be a very important eruption for the volcanological community. The eruption represented the biggest shift in the

behaviour of Kīlauea since the 1980s, and provides countless opportunities to better understand how this extensively monitored volcano behaves. Further, our study presents the first comparison of genetically-related magmatic and laze plumes, and has important implications for the transfer of metals to the environment throughout Earth history (see response 1.1.5, below).

The shorter format of the journal also means that expert or particularly interested readers will be able to find all the information they require in the supplementary information, but those who might read the paper more out of general interest can do so without being burdened by the full expanse of information contained in the supplementary information.

Overall, and most importantly, as a reader one struggles to find much new or novel in what was actually observed. At the end of the day, many observations here on laze, metal emissions or the modelling of volcanic degassing mostly corroborate the previous work, as was cited throughout the study, including previous 2003 and 2008 Kīlauea eruptions. For example, I note there are several other studies cited on metals in laze, even by one of the co-authors, so one doesn't really see a new or novel story here. There are also other previous studies on metal behaviour and/or enrichment in laze, also cited here. Lastly, the modelling of volcanic gases herein has also been done before, as noted by the referenced work by Mandon, Wahrenberger, Hemley and Seward. The outcome here for gas resultant from seawater interactions was not particularly different. None of this is to dismiss the importance of the study, but the novelty or uniqueness of it did not ring out in several of the observations.

1.1.3

We thank the reviewer their reading of our work, and for their observation that the novelty of our work is not made clear enough in the manuscript. This is something we will address when updating the text in light of these reviews. However, we would like to challenge some of what the reviewer has said here.

1. **The novelty of our work on the laze plume.** As the reviewer points out, there have been some previous studies of the laze plume at Kīlauea, including:
 - a. One that used Fourier Transform InfraRed (FTIR) spectroscopy to study major gases (Edmonds & Gerlach, 2006) but **not metals/metalloids**
 - b. A recent study that looked at the metal/metalloid composition of seawater close to the ocean entry, **not the composition of the laze plume** itself (Hawco et al., 2020) – although they did not measure a number of the elements presented here (Bi, Re, Se, Te, As, Sn, Ag, In)
 - c. Two papers (both from the same authors: Resing & Sansone, 1999, 2002; both papers relate to the same sampling studies, carried out in 1990, 1991 and 1995) that looked at the deposition of metals from the laze plume close to the ocean entry related to lava flows emanating from the Pu‘u ‘Ō‘ō vent. This study did not consider the composition of the magmatic plume emitted from the Pu‘u ‘Ō‘ō vent at the same time, and they also did not measure a number of the elements presented here (Bi, Re, Se, Te, As,

Sn, Ag, In). We also note that the 2018 activity was of a much higher intensity than that observed during activity from the Pu'u 'Ō'ō vent in the 1990s, and therefore we propose that the bulk gas emission rate, as well as the emission rates of individual trace metals, would have been far greater in 2018 than in the 1990s.

We did not (or did not mean to appear to) present our study as the 'only' study of the laze plume – this is clearly not the case. However, we do believe that this aspect of the paper is interesting and novel for several reasons:

- We emphasise that the lofted laze plume has **never** been measured in situ before using a UAS. This enabled more proximal sampling of the concentrated plume than previously possible, and was important for collecting low concentrations of metals above the detection limits of ICP-MS analysis. reaching the detection limits of trace metals/metalloids.
- The remarkably different compositions (both major components and metals/metalloids) of **simultaneously produced, genetically-related, laze and magmatic plumes** have also **never been studied and presented together** in the way we do here. Further, the potential mechanisms we propose for the enrichment in metals/metalloids that complex with chloride, have not been suggested before. Finally, the idea that a laze plume could produce more copper than the magmatic plume is unexpected, and has never been proposed before.

2. Modelling of speciation in volcanic gases. While we of course have referenced all previous studies that modelled the speciation of volcanic gases, we also note the following important factors that bring novelty to our work:

- a. The speciation of trace elements has **never** been modelled in this way for Kīlauea. In fact, to our knowledge, all previous models of speciation in volcanic gases have been done for arc volcanoes only and this is in fact the first time a model has been presented for a hotspot-related volcano.
- b. Most studies of speciation in volcanic gases typically **only consider the effect of temperature on speciation**. Again, to our knowledge, ours study is the first to present the rapid changes in speciation at the vent, considering both atmospheric mixing and associated cooling simultaneously. These results represent the initial chemical conditions that could go on to be used in low-temperature atmospheric dispersion modelling.
- c. We also believe that our study is the first to assess the sensitivity of a volcanic gas mixture speciation model to chlorine concentrations, and it is also certainly the first to consider the laze plume in terms of speciation modelling.

In response 1.1.5 (below) we also note that the two other reviewers did note the novelty of our research and we highlight quotes from their reviews.

I applaud the many measurements and they are surely worthy of publication.

1.1.4

We thank the reviewer for their kind words about our work.

At the end, the reader struggles to go beyond more than the following: (1) a large eruption of lava reached seawater and created laze, (2) the laze shows enrichment in Cl, and (3) the laze is enriched in Cu, an element known to complex with Cl. Many points (1) to (3) have been recognized previously. In this way, no case for any greater impact of the study or of 'laze' is made. Whether laze itself is more than a transient signal to metal loading over earth history was not really addressed or developed here more than a back-of-the-envelope calculation applied to a sub-aerial eruption (Deccan Traps) that questionably never interacted with seawater.

1.1.5

Where we reference the Deccan Traps in the synthesis section of the manuscript, we are mainly using it to demonstrate the trace metal/metalloid emissions possible from a **magmatic source** during extremely extended periods of basaltic volcanism, independently of the presence of any laze plume. However, there is evidence that some lava flows from the Deccan Traps (specifically the Rajamundry Traps, which are proposed to be the longest on Earth) could have reached at least a shallow marine environment (Self et al., 2008).

Other examples of flood basalts interacting with seawater:

- Several lava flows from the **Columbia River Basalt Group** reached the Pacific Ocean and advanced onto the continental shelf (Wells et al., 2009; see also a [USGS page](#) on this).
- **Kerguelen Plateau** – it is thought that much of the plateau was emplaced near the surface ocean (Coffin & Eldholm, 1994). Two groups of volcanic islands remain subaerial today (French Southern and Antarctic Lands, and Heard Island and McDonald Islands).
- **North Atlantic Igneous Province** (bulk of emplacement between 56 and 54 Ma) – recent evidence (Stokke et al., 2020) suggests a substantial hydromagmatic component to erupted material, with a transition through time from dominantly subaerial activity to dominantly submarine activity. Laze plumes may well have been a feature of the early transition period. In general, most episodes of continental rifting are thought to have resulted in volcanism that initially took place close to sea level and subsequently subsided beneath the sea surface (White & McKenzie, 1989).
- **Ontong Java Plateau** (~120 Ma) – there is evidence from the presence of volcanoclastic sediments that near-surface ocean volcanism was taking place at seamounts on the plateau at the time of its emplacement (Chambers et al., 2004; Tarduno et al., 1991; Thordarson, 2004).
- **Manihki Plateau** (66 Ma) – much of the emplacement of this plateau was interpreted to have taken place at or near the sea surface (Schlanger et al., 1981; Beirsdorf et al., 1995).

We have added these examples into the introduction text as follows (lines 74–87):

“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, such as: when lava flows from continental flood basalts reached coastlines (e.g., Columbia River Basalt group [Wells et al., 2009], Deccan Traps [Self et al., 2008]); in periods of subaerial eruption during ocean plateau basalts emplacement (e.g., the Kerguelen [Coffin & Eldholm, 1994], Ontong Java [Chambers et al., 2004; Tarduno et al., 1991; Thordarson, 2004], and Manihiki [Beiersdorf et al., 1995; Schlanger et al., 1981] Plateaus); and in the early stages of continental rifting (White & McKenzie, 1989) (e.g., the North Atlantic Igneous Province; Stokke et al., 2020).”

In these cases, laze-type lava-seawater interactions may have continuously transferred elements to the marine biosphere over hundreds or even thousands of years. We have shown that these plumes deliver a suite of trace metals/metalloids that are distinct from those emitted from magmatic plumes. The emissions of Cu from laze plumes during very high rates of lava effusion in Earth’s geological past may have particular significance for the marine biosphere.

We have altered the text in the synthesis section to better reflect this (lines 668–674):

“Our results suggest that laze plumes have the potential to produce higher emission rates of Cu than even large magmatic plumes. Laze plumes can transfer elements directly to the marine biosphere (Hawco et al., 2020; Resing & Sansone, 2002; Wilson et al., 2019), where elements such as Cu can act as both pollutants (e.g. Leal et al., 2018) and important nutrients for microorganisms (Walsh et al., 2015). During large basaltic eruptions, distal ocean entry environments are likely to have been important sites where volcanogenic metals are transferred from magmas into the environment and the biosphere, potentially hundreds of km (Self et al., 2008) from magmatic source vents.”

We would also note that both reviewers 2 and 3 recognise the novelty of our study.

Reviewer 2: *“This is definitely a quite interesting piece of research, which has implications as diverse as the environmental impact of lava flow reaching the sea, the trace geochemistry signature of flood basalts and massive shallow water volcanism in the ancient Earth. It is only the second time such a detailed trace metal geochemistry study is conducted for such a massive eruption, and the first time it is conducted in lava-seawater interaction plume. The methodology of gas and aerosol sampling and analysis is at state-of-art level.”*

Reviewer 3: *“Very little is known about the chemistry of laze compared to magmatic plumes. Their case study provides an analogue for the gas and PM emissions during catastrophic volcanic events in Earth history such as flood basalt eruptions, which bring constraints on their environmental impacts. The synthesis is well thought out*

and well constructed. I am happy to recommend its publication after some minor to moderate modifications.”

In addition, metal loading estimates from volcanoes also exist in the literature.

1.1.6

It is certainly true that estimates of metal emissions from volcanoes exist in the literature. However, this does not mean that it is not worth publishing further estimates of metal emissions from volcanoes. In fact, due to the paucity of data available for volcanic metal/metalloid emissions, we would argue that all new measurements of these elements make an important contribution to the state of our knowledge. We would like to emphasise that the fact that the 2018 eruption of Kīlauea was the largest eruption at the volcano in nearly 200 years, and produced some of the highest SO₂ emission rates of any tropospheric eruption on record. This eruption therefore had significant potential to do harm in terms of metal pollutant dispersal and deposition into the environment. We note a comment from reviewer 2 that also highlights this point:

“It is only the second time such a detailed trace metal geochemistry study is conducted for such a massive eruption, and the first time it is conducted in lava-seawater interaction plume.”

My point is not to downplay any of the excellent work that went into this study, more about its impact and novelty, which I think is the emphasis of a paper in Communications Earth & Environment. If the Cl and Cu in laze has a big impact on metal loading or environmental degradation, that point was not really demonstrated in this study. The excellent, further documentation of the 2018 eruption shown here truly belongs in a volcanological journal, where it can be fleshed out and not hidden in Supplemental that goes unread by most non-experts.

1.1.7

While we understand the points that the reviewer is making here, we feel strongly that Communications Earth and Environment is a suitable journal for publication of our work.

First, we would challenge their assertion that our work lacks novelty, and we have given our reasons for this above in responses 1.1.3, 1.1.5, and 1.1.6. Further, we disagree that a long supplementary material document means that our paper is not suitable. We have made every effort to be as transparent with our collection, processing and subsequent use of our data. As reviewer 2 points out below, some of this is not strictly necessary to support the paper, and we will cut down on some of this in response to their comments. We argue that the information presented in the main paper and methods is sufficient for non-experts to assess and understand the work, and when experts read the paper, all the additional information they require is available in the supplement. In this format, we imagine that the paper will have broader appeal and will be read by more non-experts overall.

1.2 Reviewer #2 (Remarks to the Author):

Review of “Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kīlauea Volcano, Hawai‘i, submitted by Mason and co-workers for publication in Communications Earth & Environment

The manuscript reports on measurements of concentrations and fluxes of trace metals in the atmosphere caused by the 2018 eruption of Kīlauea volcano. The authors conducted their sampling using filter packs and cascade impactor both located on the ground and on an unmanned aerial vehicle (UAV). Using this strategy they were able to measure separately the plume emanating from the magmatic degassing (lava fountains) and from the ocean entry.

This is definitely a quite interesting piece of research, which has implications as diverse as the environmental impact of lava flow reaching the sea, the trace geochemistry signature of flood basalts and massive shallow water volcanism in the ancient Earth. It is only the second time such a detailed trace metal geochemistry study is conducted for such a massive eruption, and the first time it is conducted in lava-seawater interaction plume. The methodology of gas and aerosol sampling and analysis is at state-of-art level. Thermodynamic modelling looks solid (although it is not my area of specialty) and the manuscript is well-written.

1.2.1

[We thank the reviewer for their kind comments and we are grateful for the perspective and comments on our work that they have provided here.](#)

However, the study presents several shortcomings that need to be addressed before publication

1°) The quantification of the HCl flux from the ocean entry, which is one of the cornerstones of this research, needs be improved. The estimation method the HCl emission rate based on the basalt effusion rate is pure hand waving, because it is currently not known what percentage of seawater is effectively heated to ebullition when a lava flow enters the sea. There are many other ways to dissipate the thermal energy of the lava when it enters the sea: among them fragmentation and heating seawater to sub-boiling temperature. The original article of Edmonds et al., argues that 1 to 10 % of the thermal energy is effectively used to boil sea water, so it point out that this method of estimation is affected by one order of magnitude of uncertainty and not directly scalable to larger flow.

1.2.2

[We agree with the reviewer that the uncertainty in the HCl flux calculations is very large, and we note that we took care to point this out in the manuscript we submitted.](#)

[However, we disagree with the reviewer that the quantification of the HCl flux is a ‘cornerstone’ of the research, or at least we had not intended for it to come across in](#)

this way. It was not our goal to calculate the HCl emission rate during the field campaign, if it had been, we would have made plans to quantify the emission rate in a more rigorous way in advance. As we point out in the manuscript, there are large uncertainties associated with any quantification of HCl emission rate from laze plumes. Without a spectroscopic measurement of the HCl emission rate, any quantification of the rate will rely heavily on assumptions and perhaps feel ‘hand waving’.

For this reason, we have decided to move the quantification of trace metal/metalloid emission rates into the supplement (which we have also reduced and modified, see response 1.3.3). We have also explored another approach to calculating these emission rates using data from lava-seawater interaction experiments carried out by Resing & Sansone, (2002). We thank the reviewer for pointing out that we had not included the fact that “1 to 10 % of the thermal energy is effectively used to boil sea water”. We have now added a further term to our calculations to account for this (as described in the updated supplementary section). This extra term adds further uncertainty to the quantification of laze plume emission rates which, as calculated here, span around 2–3 orders of magnitude. All we can say using this quantification is that emission rates of copper *might* be as high or slightly higher than those from the magmatic plume, but without being able to narrow down the parameters of the lava-seawater interaction further, or using a spectroscopic method to quantify emission rates, we have no way of determining the true emission rates with more certainty and precision. It does not feel appropriate to include such broad ranges of emission rates in the main text.

2°) Similarly, the authors should try to improve the accuracy of the SO₂ flux reported in the study. The authors state that the measurements were conducted with the PySpec 3D-printed spectrometers. Wilkes et al. (2028) reported that their PySpec spectrometers are affected by a higher straylight than most of the commercial spectrometers. At the extreme concentration reported by the authors, straylight is a tremendous source of error that is added to the atmospheric scattering effects reported by Kern et al (2012). All these errors generally produce an underestimation of the SO₂ column densities and emission rate. I would suggest that the authors consider using satellite data (OMI or TROPOMI), whose measurements of SCD downwind of the plume, once they undergo a sufficient dilution, are less subject to errors (e.g. Beirle et al., 2014).

1.2.3

The reviewer suggests the use of satellite data to corroborate ground-based measurements of SO₂ emission rates. Whilst we agree that cross-validation between satellite and ground-based approaches is certainly a necessary avenue of research more generally, we argue that this is beyond the scope of this paper, and could form a considerable standalone piece of publishable work in itself. Indeed, the Kern et al. (2020) study that we cite, focuses specifically on SO₂ emissions from the 2018 fissure eruption and also proposes the exploration of satellite data for validating results. However, even in this focused study they do not directly address this in their

work as such work demands a detailed and dedicated investigation. In this low-lying (essentially sea-level injection) tropospheric plume we may also anticipate that satellite data will suffer from significant radiative transfer complications as the instruments are required to look through the entire atmosphere.

We also acknowledge that in the past ground-based and satellite measurements have not always shown strong agreement; furthermore, using satellite measurements from an older downwind plume (to avoid the high concentrations and complicated radiative transfer of the nascent plume) will be subject to the losses of SO₂ to sulphate aerosol and precipitation out of the plume, which would require an accurate correction.

Regarding the accuracy of the SO₂ measurements, we highlight that they agree very well with those of Kern et al. (2020) who have performed an incredibly detailed and robust retrieval of SO₂ emission rates throughout the eruption. Their probability distribution of emission rates provides unprecedented detail into the uncertainties of DOAS SO₂ emission rate retrievals. Taking on board the reviewers remarks, we have emphasised these points more clearly in the manuscript.

From methods (new lines 1005–1006):

“Another highly detailed study found SO₂ emission rates of 71 ± 31 kt/day on the same day of sampling (Christoph Kern et al., 2020) – these are within 1 SD of this study’s average.”

Regarding the reviewer’s comment on stray light of the PiSpec instrument: Whilst the reviewer notes that stray light internal to the spectrometer can be larger for the PiSpec than for some commercial Ocean Optics spectrometers, one analysed instrument had almost identical stray light to the PiSpec (0.12 vs 0.13), therefore this is very dependent on the individual piece of equipment. Furthermore, this effect can be managed in the retrieval software to essentially reduce the impact of this effect. Correction for stray light is performed by assuming a uniform distribution of stray light across the sensor; subtraction of the average pixel intensity between 280-290 nm, where no sky radiance is expected (due to strong Ozone absorption of these wavelengths), from all pixels in the spectrum therefore gives a relatively good stray light correction. Since the sensor in the PiSpec is so small (≈ 3.7 mm wide) this assumption is perhaps more valid than for commercial spectrometers which use long linear array detectors (≈ 28.7 mm in the Ocean Optics instruments); the stray light within the latter instrument is therefore more likely to vary across the full extent of the detector. The quality of the DOAS fit further suggests that stray light has not caused significant errors. We may expect that if the uniform correction was not adequate we may see degradation of the fit, or some parts of the spectrum fitting better than others; we do not see this. We also highlight that previously published side-by-side tests between the PiSpec and Ocean Optics spectrometers found no systematic

differences, with the PiSpec displaying only a slightly larger increase in random error (Wilkes et al., 2017).

3°) In absence of geochemical analysis of the concentrations of the several trace metals in the melt at different stage (melt inclusions, channel lava and lava having interacted with sea water), many processes suggested by the author to explain the trends in their data remain speculative. I annotated the pdf document to highlight points where rock geochemistry could be an utterly useful complement to the gas/particle geochemistry reported here.

1.2.4

We did collect samples close to the active Fissure 8 vent and we present matrix glass analyses for these samples, which we use for both the ash correction and emanation coefficient calculations. We collected two samples, both from a similar location, one of which was a recent overflow from the channel, and one of which was a direct lava channel sample. However, due to the hazards of collecting lava samples during an active eruption, we were not able to obtain any further lava channel samples, including any samples close to the ocean entry.

There are significant analytical challenges associated with measuring Se-As-Te in silicate glasses. Even in our Fissure 8 samples, there were too many microlites to find the 110 μm spot of clear glass needed to detect Se, As and Te. We also note that it has been shown in previous work that even degassing at the vent is almost unresolvable from analytical noise using *in situ* petrological analysis (for all elements apart from Se; Wieser et al., 2020). It is therefore unlikely that we would be able to resolve variations within variably degassed matrix glasses taken along the channel, as we would expect the extent of this degassing to be less than that at the vent. As for melt inclusions, Wieser et al., (2020) also showed that chalcophile concentrations in melts are significantly affected by sulphide formation, making their interpretation far from straight forward. Further, melt inclusions at Kīlauea are unlikely to be directly connected to the specific event from which they are sampled (Wieser et al., 2019).

Our intention in this response is not to say that these measurements would not be worthwhile attempting, only that there are significant challenges and complexities to overcome, amplified by the extremely limited availability of samples. We feel that we have made the best use of the available reliable data and samples at this time.

In particular it could:

- 1) Elucidate whether the apparent **depletion in chalcophile element** in the haze plume compared to the magmatic plume is due to one of the two hypothesis proposed by the authors, or to another unconsidered process (such as dilution of the magmatic signature by an oceanic signature and S-depletion in the melt).

1.2.5

In the paper, we hypothesise that some sulphide-complexing elements* (e.g. Se, As, Te) are not measured in the laze plume because there is insufficient sulphur remaining in the melt at the ocean entry to allow them to degas. As we describe in the manuscript, previous work on the 2018 eruption of Kīlauea has shown that up to 85% of the sulphur held in the magma is degassed during ascent and extrusion at the surface (A. H. Lerner et al., 2019). Further, we show using speciation modelling, that it would take far more Cl than that present in the laze plume to allow elements such as Se, Te and As to degas as chloride complexes. So we argue that **‘S depletion in the melt’ is in fact the mechanism we suggest** and is not ‘unconsidered’ as the reviewer suggests above. We have reviewed the text proposing this mechanism in the manuscript, to better understand where the miscommunication occurred, and we have rephrased as follows (line 525–533):

*“In contrast, volatile elements that complex with sulphide on degassing (Se, Te and As, **Figure 6B**) appear to be absent from the laze plume. Previous studies at Kīlauea have shown that up to 90% of the sulphur in the melt is degassed during ascent to and extrusion from the source vent (**Figure 6A**) (Cashman et al., 1994; Allan H. Lerner et al., 2019), while significantly lower proportions of Cl (~10%) and F (as little as 2%) are lost during this initial degassing (Greenland et al., 1985). We suggest that there is insufficient sulphur remaining in the melt in distal ocean entry lavas to facilitate significant degassing of Se, As and Te, and/or Se, As and Te concentrations in the lava reaching the coast are themselves extremely low, due to extensive degassing at the active vent (Fissure 8) and along the lava flows.”*

As to mixing and dilution of the magmatic signature with seawater, it is possible that seawater has contributed to the dilution of the magmatic concentrations of Se, As, and Te to the extent that they were not measured above detection limits in the laze plume. However, we note that their degassed concentrations would still be very low compared to the other elements that are enriched in the laze plume relative to seawater (Bi, Cd, Cu, Zn etc.).

We have clarified that the ‘absence’ of sulfide-complexing elements in the laze plume actually means that they are below detection limits, not necessarily completely absent in the laze (lines 525–526):

*“... volatile elements that complex with sulphide on degassing (Se, Te and As, **Figure B6**) appear to be absent from (i.e., below detection limits in) the laze plume.”*

*We note that the use of the word chalcophile is tricky here, as while for example Cu does not predominantly complex with sulphide during degassing (instead mainly complexing with chloride instead), in igneous systems and in terms of silicate melt–sulphide partitioning, Cu is a major chalcophile. Therefore, to avoid confusion between the igneous petrology/geochemistry use of chalcophile, and that implied here, we have removed all use of the word chalcophile from the manuscript and instead use sulphide-complexing to indicate the elements that complex with sulphide during degassing in our speciation model of the magmatic plume.

2) Identify unambiguously the processes responsible for the distinct geochemical signature of the laze plume. I suggest that the author consider a leaching/evaporation process as being responsible for it rather than some kind of degassing from the lava.

On the PDF the reviewer elaborates:

Lines 400–403: I would suggest a third mechanism : The leaching of the freshly fragmented glassy silicate rock by a high salinity temperature brine that is finally evaporated. Upon evaporation elements that can form volatile compounds with Cl ligands get enriched in laze the plume.

1.2.6

We note that we do consider the potential effects of leaching bulk basalt on the composition of the seawater close to the ocean entry, and subsequently therefore the composition of the laze plume. In Figure 7A, we correct the composition of the laze plume for a silicate composition. If any dissolution of basalt at the ocean entry is congruent, rather than selectively dissolving some species over others, then this correction accounts for both silicate fragments in the plume, and the effect of congruent dissolution of basalt by seawater.

Lava-seawater experiments

Solid line: regressions of coastal ocean samples. Open symbols: seawater experiments; closed symbols: DIW experiments

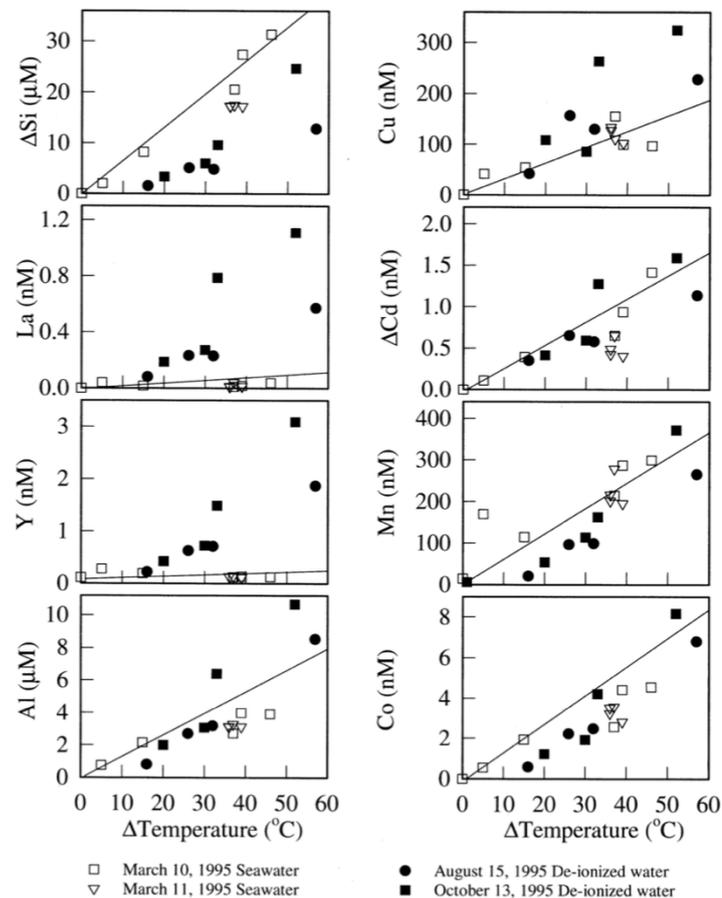


Fig. 8. Elemental concentrations vs. change in water temperature for lava-seawater experiments. The line in each graph is a regression of March 1, 1991, coastal ocean data for element concentration vs. temperature. For the seawater experiments, $\Delta[E] = [E]_{\text{sample}} - [E]_{\text{background}}$ where $[E]_{\text{sample}}$ is the concentration of an element in a sample and $[E]_{\text{background}}$ is the background concentration of that element in the seawater.

The reviewer's proposed third mechanism is plausible and we thank them for bringing it to our attention. In this case, we would expect there to be a noticeable difference in the leaching ability of Cl-rich seawater versus pure distilled water (DIW), i.e. that seawater would preferentially leach chloride-complexing elements such as copper over e.g. REEs, while DIW would show no preference. Resing & Sansone, (2002) carried out experiments where they exposed molten lava to these two different water compositions and found that there was no significant difference in the leaching potential between seawater and DIW, as shown in Figure 8 from their paper above. Therefore, leaching by high temperature brine at the ocean entry, while certainly plausible, is not supported by lava-seawater interaction experiments.

We have added text to the manuscript to reflect this (lines 541–568):

“Alternatively, high-temperature Cl-rich seawater at the ocean entry may act to preferentially dissolve chloride-complexing elements such as Cu over refractory elements, such as the REEs. However, lava-water (either seawater or distilled water, DIW) interaction experiments (Resing & Sansone, 2002) showed that seawater produced no preferential dissolution of chloride-complexing elements compared to DIW.”

Our study is not the first to suggest that degassing of magmatic gases plays an important role in the composition of the laze plume (Resing & Sansone, 1999, 2002). (Resing & Sansone, 2002) “effectively modelled using a simple two-part equation, which combines the congruent dissolution of a fraction of the lava with the volatile emanation of elements from the lava based on their emanation coefficients.” These authors did not go on to recognise the suppression of sulphide complex (SeS, TeS, AsS) degassing in favour of chloride-complex degassing as we have done here (they did not measure sulphide-complexing elements such as Se, Te and As), but their results suggest that it is reasonable to some degassing of lavas could be occurring at the ocean entry.

We have clarified that there is previous evidence for degassing in lines 448–452:

*“Silicate-corrected concentrations of Cd, Zn, Ag, Cu, Bi, Re remain elevated in the laze plume above seawater (**Figure 7A**). Cu and Cd enrichments were also observed in a study of seawater close to Kīlauea's ocean entry in July 2018 (Hawco et al., 2020). Due to the moderate to high volatility of all these elements ($\epsilon > 0.001\%$), it is likely they are, to some extent, degassing from lava at the ocean entry (as previously proposed for Cu and Cd (Resing & Sansone, 2002)).”*

Further, more specific, comments are written directly on the PDF.

We have pasted in these comments below to keep our response in one document.

Lines 383–385: Although the S/Cl ratio in the gas does increase in distal gas emission from lava flows, the absolute amount of degassed Cl is probably decreasing monotonously as the flow goes away from its emission source. So I don't think the increase availability at the ocean entry results from magmatic Chlorine.

1.2.7

We agree that Cl is likely degassing along the lava flows. We do not argue that the absolute availability of magmatic Cl is higher at the ocean entry than at the source vent (Fissure 8), rather we argue that the **relative** availability of magmatic Cl versus S will be higher at the ocean entry, and that this may favour the emission of chloride-complexing elements **over sulphide-complexing elements**. This matches what we observed in our measured laze plume composition.

However, we agree that for the chloride-complexing metals/metalloids, the dominant and overwhelming source of Cl with which they can complex, will come from the seawater, not from the magmatic Cl.

We have adapted this part of the manuscript slightly to reflect this (new lines 534–541, new text in **bold**):

*“The **degassing of chloride-complexing elements may be enhanced relative to sulphide-complexing elements** at the ocean entry 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)(Sigmarsson et al., 2020). For example, during post-eruptive 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 of seawater to dryness, may facilitate the degassing of Cl-complexes. **This second mechanism is a much greater potential source of Cl than fractional degassing alone.**”*

Lines 392–396: I would suggest a third explanation: There is not enough S available to enable the degassing of these element above the detction limit in the plume. Here Rock analysis from subaerial lava flows at different points of the flow and in the lava fragments drifted from the entry could clarify the dilemma.

1.2.8

We have addressed these points in responses 1.2.4 and 1.2.5 above.

SO₂ and multi-element flux section of methods: I think the two references cited here do not correspond to what is described. These are papers dealing with H₂O retrievals.

1.2.9

The reviewer comments that the two references relating to the saturation effect refer to H₂O DOAS retrievals. This is indeed true, however, the principle of the saturation effect and the procedure for modelling and correcting for this effect, which is outlined in those two papers, can be directly applied to DOAS retrievals of other gas species where high column densities and/or a low spectral resolution relative to the species' absorption lines lead to a non-linear instrument response. The PiSpec's spectral resolution (≈ 1.0 nm) is slightly lower than that of commercial spectrometers typically employed for SO₂ retrievals (≈ 0.6 - 0.7 nm). Furthermore, column densities of SO₂ encountered during the Fissure 8 measurements were well beyond those commonly measured in volcanology ($>10,000$ ppm·m). These factors combine to make the atypical non-linearity correction of PiSpec retrievals a requirement in this work. We therefore maintain that these references are pertinent here.

We have clarified that these are the correct references in the methods text as follows (lines 989–993):

“Due to extremely high column densities of SO₂ (at times exceeding 10,000 ppm·m) the spectrometer retrievals were corrected for non-linearity following a H₂O saturation correction (which can also be applied to DOAS retrievals of other gas species)(C. Kern et al., 2017; Wagner et al., 2003), using a modelled PiSpec response to account for the saturation effect.”

These comments are meant to improve and consolidate this research work before its publication and not to reject it. I do support the publication of this high-quality research in this journal after these moderate revisions/additions are done.

1.3 Reviewer #3 (Remarks to the Author)

The manuscript by Mason et al. entitled "Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kilauea Volcano, Hawaii " reports a thorough chemical investigation of the emissions of volatile trace metals in magmatic and laze plumes during the 2018 eruption of Kilauea. The manuscript is well written and well illustrated. The amount of work the authors have put in this study is significant and the study is interesting. Very little is known about the chemistry of laze compared to magmatic plumes. Their case study provides an analogue for the gas and PM emissions during catastrophic volcanic events in Earth history such as flood basalt eruptions, which bring constraints on their environmental impacts. The synthesis is well thought out and well constructed. I am happy to recommend its publication after some minor to moderate modifications.

1.3.1

We thank the reviewer for the time and thought they have put in whilst reviewing our work.

General comment:

A lot of the details regarding methods and such are pushed into the supplement (34 pages in total with 18 figures + 7 tables + two excel files). It is thus sometimes hard to follow the main thread of the paper because I needed to constantly check the supplement files, there's no dataset table in the main ms for instance. I suggest adding some of this information in the main text.

1.3.2

At this stage, as nearly all the data is presented in figures in the manuscript, we would prefer not to add any large tables to the paper, as we believe that the figures are more illustrative (and that computer readable tables in the supplement are more accessible from an open data perspective), and we are under the impression that this is not the style in which Communications Earth and Environment articles are published.

There are two excel files as the speciation datasets are very large so these are separated from the other data. We appreciate that there is a lot of supplementary data, and this is in part because we have made every effort to provide both the raw data, and the results of any calculations we have made. Most readers will not look at this data, but it is fully available for any interested readers to access in a useable way.

However, considering the ms as a whole (the main text and the supplements) it's already a very long paper with a lot of information, and I feel that one can easily lose track of the main points. I would suggest to delete or shorten some sections of the ms: sections that (i) do not bring important information/results for the conclusions such as the REE behaviour (S8) and/or (ii) are already well described in previous papers (such as S1.1 and the S5, Fig. S5, Table S5 about the volatility and choice between enrichment factors and emanation coefficient). S1.4 and Table S2 could be also explained more concisely for instance. The whole ms could be thus shortened and re-organised to aid communication of the most important findings.

1.3.3

We have removed the REE section as suggested, as well as most of section S5. We have also cut down on section S1.4 and removed table S2. However, we strongly believe most of the supplement should stay to maximise the transparency of our work.

Minor comments:

The way the emanation coefficients are calculated needs more explanation in the main text and/or methods (better define C_i and C_f).

1.3.4

We do not use the terms C_i and C_f in the paper, we define emanation coefficients in the text as follows:

*“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 $[X]_i$ is the concentration of X in the melt just prior to syn-eruptive degassing, and $[X]_f$ is the final degassed concentration of element X in the melt, respectively (originally defined by (Lambert et al., 1985))... 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. (Mather, 2015); data sources in **Table S15**).”*

In methods we add further details, as quoted below. We would need further clarification on what the reviewer did not understand to be able to address this comment fully.

“We calculate emanation coefficients (ε_x) using the ratio of element concentration to sulphur (X/S) in the volcanic plume, combined with an estimate of total S degassed during subaerial eruption:

$$\varepsilon_x = \frac{(X_{aerosol}/S_{total}) * S_{degassed}}{(X_{aerosol}/S_{total}) * S_{degassed} + X_{degassed}}$$

*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 (P. Wieser et al., 2020) or preferred BHVO values were used (**Table S15** contains more detail).*

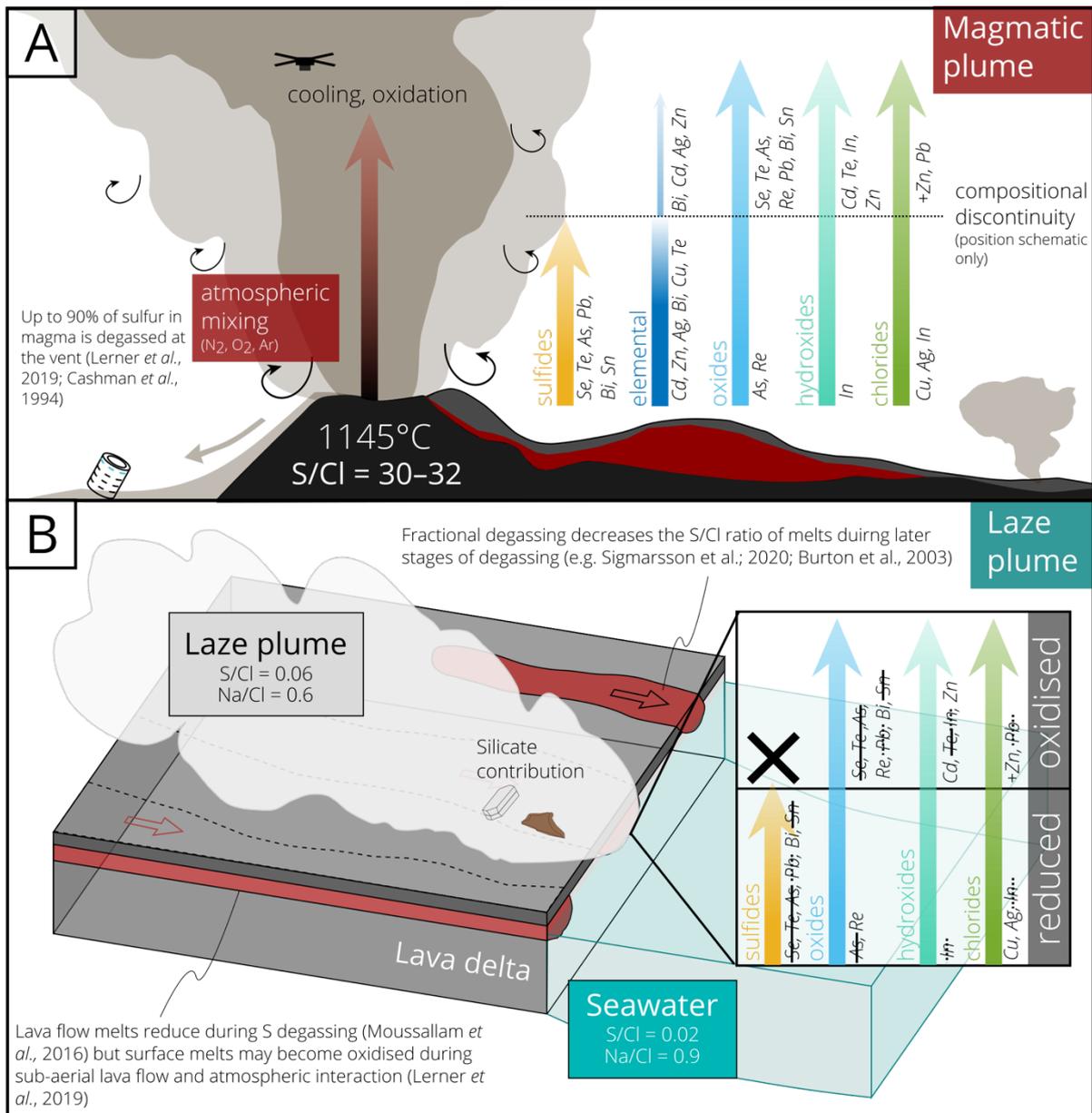
Ideally, $S_{degassed}$ is the concentration of S (in ppm) degassed from the melt from which the measured emissions are released, measured by comparing degassed and undegassed glass compositions. However, this data is not yet available for the

Fissure 8 lavas. Recent work (P. Wieser et al., 2020) suggests that 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 ϵ_x . We note that, we calculate emanation coefficients using silicate-corrected plume composition data, our emanation coefficients are relative, i.e. during the ash-correction some elements are assumed to be only present in a silicate phase, and therefore these elements have emanation coefficients of zero, but may degas in the gas phase to a limited extent.”

The figures are well done. The summary of processes (Fig. 9) is important and well illustrated. However, in order to focus on the comparison between magmatic and laze plumes, some data are missing (S/Cl for magmatic plume, indication of the speciation of trace elements in the laze plume for instance).

1.3.5

We agree with the reviewer that these details would be useful here so we have adapted Figure 9 as suggested. See below:



Response references

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27th Jan 21

Dear Ms Mason,

Please allow me to apologise for the long delay in sending a decision on your manuscript titled "Volatile metal emissions from volcanic degassing and lava-seawater interactions at Kīlauea Volcano, Hawai'i". It has now been seen by 2 reviewers, and I include their comments at the end of this message. Reviewer #3 is the same as in the previous round, Reviewer #4 is a new reviewer. As you will see, Reviewer #4 raises some important points regarding the justification and clarity of your analytical methods. We are still very interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter) and the completed checklist:

[link redacted]

** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Joe Aslin

Associate Editor,
Communications Earth & Environment
<https://www.nature.com/commsenv/>
Twitter: @CommsEarth

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Please refer to our data policies at <http://www.nature.com/authors/policies/availability.html>.

REVIEWER COMMENTS:

Reviewer #3 (Remarks to the Author):

The authors did a very good job taking into account all the comments and suggestions. I recommend the publication of this paper.

Reviewer #4 (Remarks to the Author):

The manuscript is well-written and provides very interesting findings. In light of this, the paper deserves publication. The technical concerns from the previous round of review have been sufficiently addressed. However, there are other important points that require a further revision of the manuscript.

Sampling

Why did not the authors sample and analyze local seawater? The authors use seawater composition from: <https://www.mbari.org/summary-table-of-mean-ocean-concentrations-and-residence-times/> There are many other more recent references (especially for Cu).

Filter packs:

The authors have to provide IC analytical results for each elution solution (for each filter) in order to make clear that the whole pack was able to trap acidic gases. Filter-packs are subject to errors. As a rule, when the last filter of the pack contains non-negligible amounts (>10%) of the total trapped species, results should be discarded. In Wittmer et al. (2014) the authors can find all the necessary details to apply an appropriate sampling and analytical technique.

Filter packs represent a well-established method only depending on the fact that it is cheap and easy-to-transport tool for sampling volcanic gases but this does not mean that it is a good method. The glycerol affects the beginning of the chromatogram and overlap with the fluoride peak and H₂O₂ causes baseline effects that can lead to an inaccurate quantification especially for anions with short retention times. How did the authors solve these problems? What is the amount of used H₂O₂?

SO₂ does not form SO₄²⁻ as counter-anion. SO₂ needs to be oxidized to form SO₄²⁻.

Multigas data:

Figure S5 and dataset

There is a typing error in the caption “measured on measured on”

Is it still possible to measure 356 ppm of atmospheric CO₂? (see “344_1_data_set_7467_qjjbwk” file)

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What is the background value used to compute the CO₂ excess? It seems the authors assumed 370 ppm. Is this value realistic? The NOAA data show about 407 ppm for that period.

Time series of CO₂, SO₂, and H₂O concentrations measured on the tephra field behind Fissure 8 on 24/07/18 are not provided as supplementary material (.xls). How did the authors retrieve H₂O concentration?

Modelling

Speciation modelling only accounts for thermodynamic equilibrium. Can the authors rule out kinetic and/or catalytic processes?

Finally, the authors neglect some important literature relative to the emission of volatile trace elements from other volcanoes (e.g. Mt. Etna, Nyiragongo etc).

REVIEWER COMMENTS:

Reviewer #3 (Remarks to the Author):

The authors did a very good job taking into account all the comments and suggestions. I recommend the publication of this paper.

We thank the reviewer for their comments, and for the time they have given to reviewing this work, and our responses.

Reviewer #4 (Remarks to the Author):

The manuscript is well-written and provides very interesting findings. In light of this, the paper deserves publication. The technical concerns from the previous round of review have been sufficiently addressed. However, there are other important points that require a further revision of the manuscript.

We thank the reviewer for the time and expertise they have dedicated to the review of this work.

Sampling

Why did not the authors sample and analyze local seawater? The authors use seawater composition from: <https://www.mbari.org/summary-table-of-mean-ocean-concentrations-and-residence-times/>

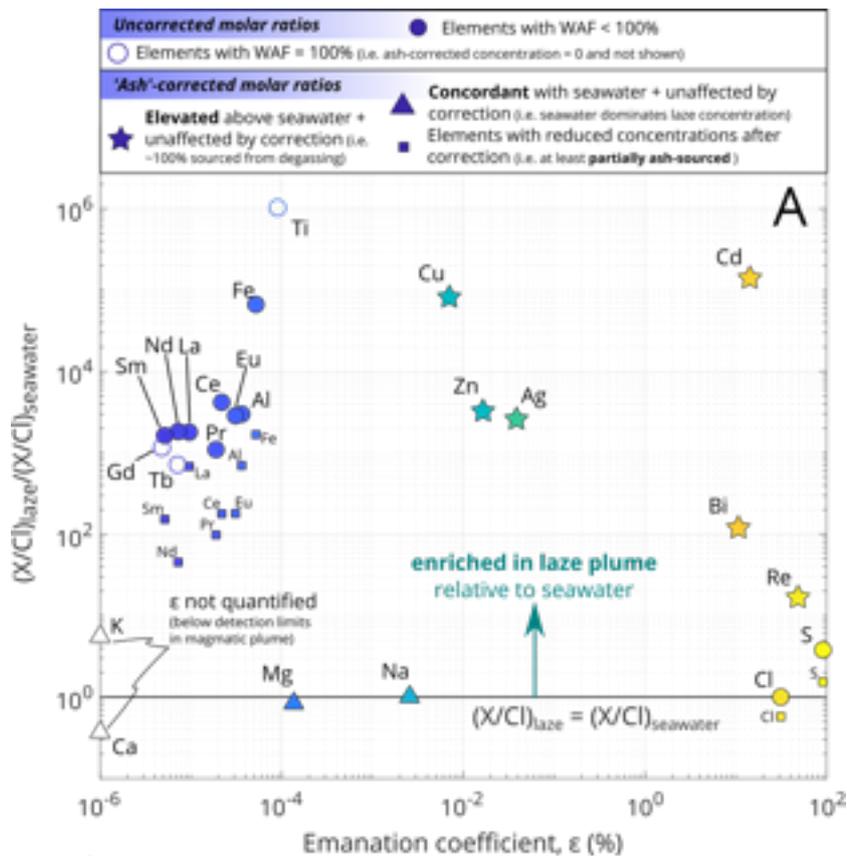
There are many other more recent references (especially for Cu).

We thank the reviewer for raising this point here. We agree that a more recent composition, and ideally a North Pacific seawater composition would be ideal. However, to our knowledge, dissolved and insoluble concentration data for North Pacific seawater have not been published recently. Therefore, where possible we have replaced the previous data with new data sources, prioritised as follows:

1. Hawaiian seawater compositions (e.g., Fröllje et al., 2016);
2. North Pacific seawater compositions (including standards, e.g., Biller & Bruland, 2012);
3. Global database values from Sarmiento & Gruber (2006) or values from Resing & Sansone (2002), who also use seawater composition to compare to a lava-seawater interaction plume.

The new data and sources can be found in the updated Data S16.

These changes have only a minor effect on Figure 7A. The only exception is Al, which is no longer as enriched in the laze plume. But we note that there are significant analytical challenges to measuring Al in seawater (Tria et al., 2007), which can lead to orders of magnitude variation in measurements. We have added a comment on this to the caption of Figure 7.



New figure 7A caption:

Figure 1. A: 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 a compilation of seawater compositions (data sources in Data S16) and discriminated using symbol colours according to emanation coefficients (see Methods). Ash-uncorrected compositions are shown as circles (unfilled when the silicate correction can account for ~100% of their concentration in the laze plume; see Methods). Corrected compositions are shown as either: 1) a small square when concentrations are reduced after correction, but still elevated above seawater; 2) a triangle when concentrations are concordant with seawater and unaffected by correction; and 3) star symbols when concentrations are elevated above seawater, and do not change position after correction. It should be noted that challenges with measuring Al in seawater (Tria et al., 2007) can lead to high (several orders of magnitude) variability in measured concentrations, therefore values for this element should be treated with caution. WAF = weighted ash fraction.

Filter packs:

The authors have to provide IC analytical results for each elution solution (for each filter) in order to make clear that the whole pack was able to trap acidic gases. Filter-packs are subject to errors. As a rule, when the last filter of the pack contains non-negligible amounts (>10%) of the total trapped species, results should be discarded.

We have added this information to the supplement (Data S8 and S12).

We also provide further discussion of the reasons for exclusion of some samples in the supplementary information (S1.4). We realise this was unclear in the main text, and have added clarification in the methods section (lines 641–645):

We note that, due to limitations of access to the hazardous sampling area close to Fissure 8 and saturation of some samples, we were only able to acquire two non-saturated ground-based samples (FP_8_5 and FP_8_6 on 31/07/18). We assess the saturation of samples in the Supplementary Information and individual gas filter concentrations are given in Supplementary Data S7 and S11.

We have also more explicitly referenced the ~10% threshold in the supplementary information, and explain sample inclusion/exclusion criteria, illustrated with a new figure. We have included this section in the updated supplementary information, and in **Appendix 1 of this document.**

The reviewer will note that the saturated samples are different to those originally stated in the text – this was due to a data processing error and we are grateful to the reviewer for helping to bring this to our attention. All figures and manuscript text have been corrected to reflect these changes.

In Wittmer et al. (2014) the authors can find all the necessary details to apply an appropriate sampling and analytical technique. Filter packs represent a well-established method only depending on the fact that it is cheap and easy-to-transport tool for sampling volcanic gases but this does not mean that it is a good method.

We accept that filter packs have their limitations, and discuss these in the manuscript in lines 645–649.

Filter pack samples can show broad compositional variations in element to SO₂ ratios (X/SO₂; sometimes several orders of magnitude; e.g., Aiuppa et al., 2003; Mandon et al., 2019) between sampling periods, even when these are only a few hours apart. However, we note that differences in X/SO₂ ratios between samples in this study are comparatively small (and always well within an order of magnitude).

However, we maintain that for simultaneous sampling of acid gases, metal and metalloid-bearing particulate matter, filter packs are appropriate. We are not aware of any other robust field-portable instruments that allow sampling of metal and metalloid-species, in particular in hazardous environments. In addition, their small size and relatively low mass of filter packs mean that they can be used on Unoccupied Aerial Systems (UAS), critical in this study, particularly for the laze plume, which would otherwise have been inaccessible.

The glycerol affects the beginning of the chromatogram and overlap with the fluoride peak and H₂O₂ causes baseline effects that can lead to an inaccurate quantification especially for anions with short retention times. How did the authors solve these problems? What is the amount of used H₂O₂?

Thank you for raising this here. This is indeed a problem for fluoride. We did not remove the effects of the H₂O₂ using MnO₂ or similar as outlined in Wittmer et al. (2014). On further reflection, due to the effect of the H₂O₂ and the glycerol on measured F- concentrations we have decided to remove the fluoride data from the paper. We have now added the amount of H₂O₂ we used to the methods (250 μl of H₂O₂ in 20 ml of milli-Q water; thank you for spotting that we had overlooked this detail).

We have also added a description of the problem introduced by the H_2O_2 in the methods as follows, to address the potential effects on the SO_4^{2-} and Cl^- data that we include in the paper (lines 736–744):

The H_2O_2 used to oxidize captured acidic gases during sample extraction is highly reactive, and can cause baseline effects during IC analysis that may lead to inaccurate quantification, especially for anions with short retention times (e.g., F^-) (Wittmer et al., 2014). Excess H_2O_2 was not removed (e.g., by reaction with MnO_2 (Wittmer et al., 2014)) before analysis. Glycerol used to pre-treat filters before sampling can also interfere with the F^- signal. Therefore, we do not present F^- data here. Based on experimental results (Wittmer et al., 2014), excess H_2O_2 can introduce errors for SO_4^{2-} concentrations of ~30% (however we note that this may vary depending on the concentration of excess H_2O_2 in the solution). This source of error is incorporated into the propagated errors for IC measurements to give $\pm 33\%$ for Cl^- and $\pm 35\%$ SO_4^{2-} .

Omission of the F^- data has little bearing on the discussion or interpretation of our results, and does not change the key findings of the paper.

SO_2 does not form SO_4^{2-} as counter-anion. SO_2 needs to be oxidized to form SO_4^{2-} .

We agree that use of counter ion for the conversion of SO_2 is a simplification. Therefore, we have changed this sentence as follows (lines 633–634):

Base treatment of gas filters captures acidic gases (e.g., SO_2 , HF and HCl).

Multigas data:

Figure S5 and dataset

There is a typing error in the caption “measured on measured on”

Thank you for noticing this. It has now been corrected.

Is it still possible to measure 356 ppm of atmospheric CO_2 ? (see “344_1_data_set_7467_qjjbwk” file)

This value is indeed too low for atmospheric CO_2 . We believe that some process was acting to offset the baseline (background) concentration during our measurement periods. However, a stable, background CO_2 concentration of 370 ppm (when $SO_2 = 0$) was measured, and it is this that has been subtracted from the measured signal. As for the CO_2/SO_2 ratios we are considering only the relative change in concentration, this does not affect these values (which are in close agreement with those measured by the USGS using a different instrument – pers. comm.). Further, in this study we mainly rely on the multi gas data for the SO_2 concentrations which we use to determine ‘time in plume’ for the very intermittently exposed ground-based filter pack samples. Further analysis of multi gas data was included for interest. We now include all the raw data in the supplement, as well as the processed data, so that others can reprocess the data from both sampling days should they wish to.

We have also added more detail to the methods as follows (lines 609–614):

The multi-GAS was calibrated at the University of Palermo prior to and following the field campaign; no sensor drift was identified. CO₂/SO₂ molar ratios were calculated using Ratiocalc 3.2 (Tamburello, 2015) (supplement section S2). A stable, background CO₂ concentration of 370 ppm (when SO₂ = 0) was subtracted from the measured signal (we note that this is lower than the expected background but this does not affect the derived CO₂/SO₂ ratios, which are based on relative changes in concentration).

What is the meaning of negative values for H₂? (see “344_1_data_set_7467_qjjbwk” file)

Thank you for raising this. Having looked at the H₂ data more closely, it is clear that the H₂ sensor was not operating normally during our sampling campaign. The H₂ data do not have a bearing on the discussion in this study, so we have removed these data from the supplementary information altogether.

What is the background value used to compute the CO₂ excess? It seems the authors assumed 370 ppm. Is this value realistic? The NOAA data show about 407 ppm for that period.

See response above.

Time series of CO₂, SO₂, and H₂O concentrations measured on the tephra field behind Fissure 8 on 24/07/18 are not provided as supplementary material (.xls).

We have now added two data sheets to the supplement for the multi gas data, one for each of the measurement days. The tables include both raw data and the processed data plotted in figures in the supplement.

How did the authors retrieve H₂O concentration?

We have also added detail to the methods regarding our calculation of H₂O as follows (lines 615–617):

H₂O concentrations were calculated from measured temperature and relative humidity, using an ambient pressure of 1003.5 mbar (according to the Arden Buck equations relating the pressure of vapor saturation to temperature for moist air) (Buck, 1981).

Modelling

Speciation modelling only accounts for thermodynamic equilibrium. Can the authors rule out kinetic and/or catalytic processes?

The equilibrium speciation modelling does not take into account kinetic effects, as we discuss in lines 235–239:

Kinetic effects also play an important role in determining speciation (Roberts et al., 2019), and are not accounted for in the model presented here. Therefore, 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 are assumed to attain equilibrium rapidly, and subsequent kinetic effects are assumed to be negligible (Gerlach, 2004; Martin et al., 2006).

We appreciate that this is a simplification of the processes occurring in the plume, and outline the assumptions inherent in this in the passage above.

There is a considerable amount of observational data on major species in volcanic gases that supports rapid attainment of equilibrium in volcanic gas mixtures under conditions of changing P, T etc (e.g., Heald et al., 1963). For high-T gas mixtures, like those at Kīlauea that we consider in this study, this is a robust assumption. Assuming equilibrium at the point of sampling is a pragmatic way to link models and observations – a full kinetic treatment is unwarranted owing to complex and poorly constrained rate constants for many species. Further work is needed to better understand these reactions before kinetic and catalytic processes can be realistically incorporated into these models (Roberts et al., 2019).

Finally, the authors neglect some important literature relative to the emission of volatile trace elements from other volcanoes (e.g. Mt. Etna, Nyiragongo etc).

Without more specific references here, we are not sure exactly which literature is missing. However, we compare the volatile trace element data generated in this study with those from Mt. Etna in Figure 4, and include references to works of Aiuppa et al., 2003; Buat-Ménard & Arnold, 1978; and Gauthier & Le Cloarec, 1998, which discuss the volatile trace element emissions, and Burton et al., 2003, which discusses fractional degassing at Mt. Etna.

We accept that reference to studies at Nyiragongo is missing here, however this is because the focus of this study is basaltic to basaltic andesitic composition volcanoes. Nyiragongo's peralkaline magma composition means that it is not suitable to compare it to the other volcanoes included in any global comparison presented here. However, we note that measurements made at Nyiragongo are important to the overall picture of our understanding of metal/metalloid degassing at volcanoes and therefore we have added reference to this where most relevant (lines 180–186):

It is important to note that the differences in relative abundances of volatile metals and metalloids between arc and intraplate settings (Edmonds et al., 2018) are only consistent for mafic magma compositions (i.e., basaltic to basaltic andesite). More evolved or peralkaline intraplate volcanoes (e.g., Nyiragongo (Calabrese et al., 2015), Erebus (Wardell et al., 2008; Zreda-Gostynska et al., 1997)) can produce higher volatile trace element emissions than those at mafic intraplate volcanoes – this has been attributed to the higher halogen contents of gases emitted at these volcanoes (Mandon et al., 2019).

Appendix 1

S1.3 Summary of samples

Table S1. Samples taken at Fissure 8 and the ocean entry. FP = filter packs; SKC = sioutas cascade impactor. UAS = unoccupied aerial system. Flow rate accuracies are $\pm 5\%$ for UAS samples and $\pm 10\%$ for ground-based samples.

Sample name	Location	Date	Mean flow rate (L min ⁻¹)	Sampling duration (min) ¹	Sampling platform	Included/excluded (with reasons)?
Fissure 8						
FP_8_1	~300 m above vent (UAS flown from Leilani Estates community centre)	24/07/18	9.3	23	UAS (Matrice 600 Pro)	Excluded (saturated)
FP_8_2	Tephra field	24/07/18	14.85	177	Ground-based	Excluded (saturated)
FP_8_5	Tephra field	31/07/18	22.0	16	Ground-based	Included
FP_8_6	Tephra field	31/07/18	21.2	99	Ground-based	Included
SKC_8_2	~300 m above vent (flown from Leilani Estates community centre)	29/07/18	9.0	35	UAS (Matrice 600 Pro)	n/a
Ocean entry						
FP_9_1	~100-150 m above sea level (flown from Mackenzie State Recreation Area)	29/07/18	9.5	51	UAS (Matrice 600 Pro)	Excluded (saturated and only sampled the very dilute and distal laze plume)

FP_9_2	~100-150 <i>m above sea level (flown from Isaac Hale Park)</i>	02/08/18	10.0	15	UAS (Matrice 600 Pro)	Included
SKC_9_2	~100-150 <i>m above sea level (flown from Isaac Hale Park)</i>	02/08/18	9.0	40	UAS (Matrice 600 Pro)	n/a

Fissure 8 (magmatic plume) filter pack samples were excluded on the basis of two factors:

- The gas filters had become saturated; and/or
- There was evidence of fumarolic activity (see section **S2**).

As a general rule, gas filters are assessed to be saturated when the final filter contains non-negligible concentrations (<10% total concentrations of species). We assess this for the samples considered here in **Figure S5**.

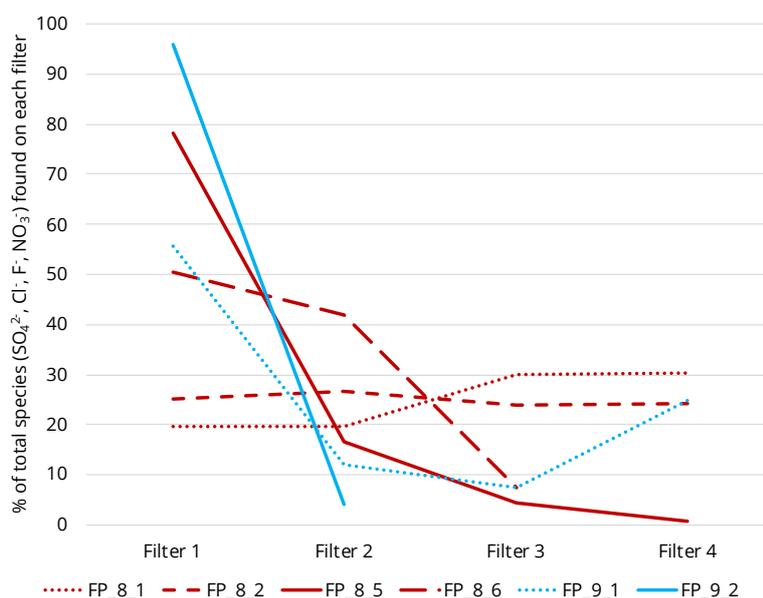


Figure S2. Assessing whether filter pack samples were saturated. Total percentages of all anions measured on each filter are shown as a percentage of the total concentrations of all species across all filters in each sample. Red lines denote samples collected at Fissure 8 (only FP_8_1 was collected using a UAS, all others were ground-based), blue lines denote samples collected from the laze plume. All samples contained 4 filters, except FP_8_6, collected at Fissure 8, which contained 3 filters, and FP_9_2, both collected from the laze plume using a UAS, which contained 2 filters. Samples FP_8_1, FP_8_2 and FP_9_1 are excluded from further analysis of their gas compositions as their high concentrations of the final filter show that they are likely to be saturated.

Gas filters from several samples were found to be saturated (see **Figure S5**). However, the concentrations of particulate matter measured on the first (PTFE) filter may still be used, particularly to calculate trace element ratios, and are therefore included in enrichment factor and weighted ash fraction calculations (**Table S11**, supplementary excel file 1). One laze plume sample was discarded from use in our analysis as it likely only sampled the very distal and dilute plume (FP_9_1).

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