We thank the reviewer for their thorough assessment and constructive feedback. We are confident that we can revise the manuscript to address reviewer 1's concerns. Below are point-by-point responses addressing each comment, with corresponding revisions that will be implemented in the manuscript accordingly. Key changes are substantiated by data from our observations and established literature.

RC1: "48 Use standard MKS units and notation, e.g. 8-9 cm-3"

Authors: All instances of concentration notation (e.g., "8-9 #/cm^{3}") will be standardized to MKS units as "8–9 cm^{-3}" throughout the manuscript. This aligns with conventions in atmospheric science literature.

RC1: **"**71 Where does a VEI of 6 for Hunga-Tonga eruption come from? Needs a reference. The Global volcanism network states 5 and others have rated it lower".

Authors: We thank the reviewer for pointing this out. The Smithsonian Institution Global Volcanism Program currently classifies the 15 January 2022 Hunga Tonga–Hunga Haʻapai eruption as VEI-5 based on erupted volume estimates. However, some peer-reviewed studies have suggested that the eruption may fall within the VEI 5–6 range based on geophysical and seismic analyses (e.g., Tarumi & Yoshizawa, 2023).

To ensure accuracy and avoid overstatement, we will add the following footnote to Table 1: "The eruption has been classified as VEI-5 by the Smithsonian Global Volcanism Program, with some studies suggesting VEI 5–6 (Tarumi & Yoshizawa, 2023)."

Reference to be added:

Tarumi, K., & Yoshizawa, K. (2023). Eruption sequence of the 2022 Hunga Tonga-Hunga Ha'apai explosion from back-projection of teleseismic P waves. Earth and Planetary Science Letters, 602, 117966. https://doi.org/10.1016/j.epsl.2022.117966

RC1: "Table 1. What is the meaning of the column labeled injection altitude. Is this the top of the injection layer, as suggested by the Hunga-Tonga entry, or the height of the primary injection layer for the most material as suggested by maybe Nabro and Raoikoke? If it is the peak, then it is clearly wrong for Pinatubo. Also what are the references for these height measurements?"

Authors: The column name will be changed to Primary injection altitude along with an additional column with references corresponding to each eruption. See below the proposed changes to table 1.

Abbreviation	Full name	Erupted on	Lat, Lon	Primary Injection Altitude (Km)	VEI	Amount of SO2 injected (Tg)	Reference	e-folding time in months (m) (SAOD)
El	El Chinchon	03/28/1982	17.3º N, 93.2° W	~31	5	7.5	(Matson, M., 1984)	22 m (0.04168)
Pi	Pinatubo	06/15/1991	15.14º N, 20.3°E	~18-25	6	20	(Quaglia, I., et al., 2022)	15 m (0 .08465)
Sa	Sarychev	06/11/2009	48º N, 153.2º E	15	4	0.9	(Rybin et al., 2011)	13 m (0.00763)
Na	Nabro	06/12/2011	13.3º N, 41.7º E	21	4	1.65	(Clarisse et al., 2012)	10 m (0.00859)
Ca	Calbuco	04/22/2015	15 41.3º S, 72.6º W	~15-22	4	0.35	(Matoza et al. (2018)	10 m (0.00874)
Ra	Raikoke	06/22/2019	48.2º N, 153.2ºE	~13-17	4	1.5	(Vernier et al., 2024)	14 m (0.01193)
HTHH	Hunga Tonga Hunga Ha'apai	01/15/2022	22 20.5º S, 175.3º W	57	5-6	0.45	(Proud et al., 2022)	21 m (0.01362)

RC1: " 130 The last 35 years? This would extend back to 1990, barely including Pinatubo and certainly not El Chichon."

Authors: "The last 35 years" will be revised to "the last 45 years" to include both eruptions.

RC1: "144-151 This paragraph needs work as it is currently confusing. SAOD from GLoSCAC does not represent sulfate sSAOD. GLoSSAC cannot distinguish the components of SAOD. So the second half of the first sentence does not make sense. GLoSSAC cannot be used in the way suggested."

RC1:149 What is semi-annual sulfate? Better to state exactly what Fig. 1b) is showing, that is: SO2 injection compared to SAOD averaged over the 6 months following each volcanic eruption. It is not clear why 6 months is chosen. It would be better to use a quantity more reflective of each volcanoes character and so2 injection amount, such as a similar e-folding time, e.g. when SAOD reaches 1/e of its initial value. This might provide a more consistent way to compare the volcanoes.

Authors: The paragraph will be rewritten to clarify that GloSSAC measures total SAOD, not sulfate-specific SAOD.

We appreciate the recommendation of using a quantity that reflects the characteristics of each volcano (e-folding time approach). We followed the approach proposed and added in the table the e-folding time as well as the mean e-folding-SAOD which was calculated between the peak SAOD reached by each volcano until SAOD reaches 1/e from the peak. However, we decided to choose the peak SAOD value in the scatter plot (fig.1b) since this variable should be correlated with the total SO2 injected. Overall, the scatter plot shows similar behavior than before which suggests that HTHH's SAOD is higher than expected when considering earlier SO2 estimates (0.42Tg).

The following new plot will be added to the manuscript:

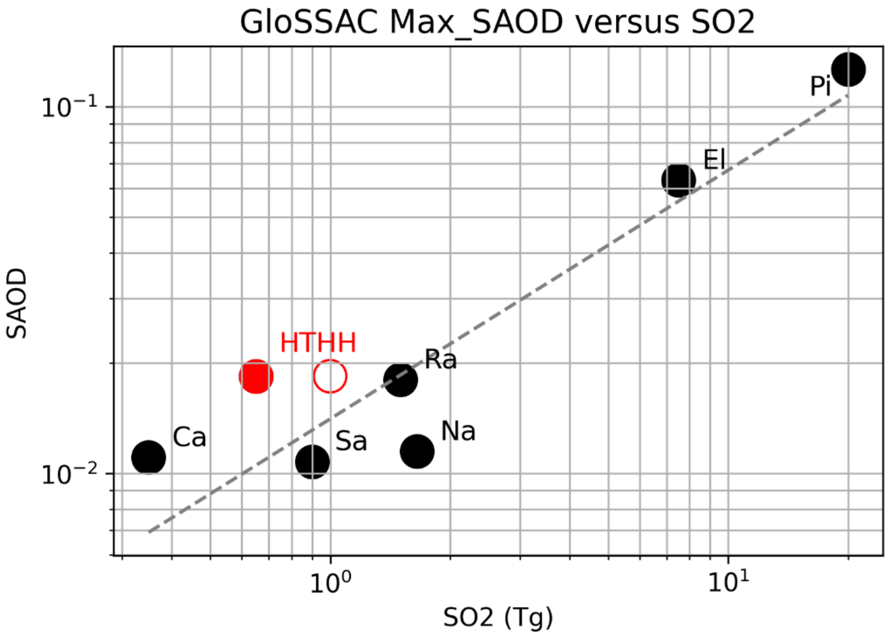


Fig. 1b. Scatter plot of maximum SAOD values and SO2 injected reach after the most significant eruptions

RC1: "222 Is there a reference for the impact of the SAA on CALIOP measurements?"

Authors: We thank the reviewer for this suggestion. The South Atlantic Anomaly (SAA) is known to affect spaceborne instruments due to enhanced energetic particle flux, which can increase background noise and reduce signal-to-noise ratio. In the case of CALIOP, reduced detectability of stratospheric layers due to low signal-to-noise ratio has been documented (e.g., Taha et al., 2022; Kar et al., 2019). We have added this reference and clarified in the manuscript that reduced data availability over Brazil is associated with signal degradation and data screening in regions influenced by the SAA.

RC1: **“**237 POPC is not a good acronym for this new instrument. There is another instrument with a very similar acronym POPS (portable optical particle spectrometer). Thus is seems unfortunate to use an acronym that will soon conflate these two different instruments. Profiling also is not unique to the POPC. All OPCs designed for stratospheric measurements are profiling instruments.**”**

Authors: We thank the reviewer for this thoughtful comment. We would like to take the liberty of choosing the acronym of the measurement sensor we have developed in partnership with a private company.

RC1: **“247 Corrected to what?”**

Authors: We thank the reviewer for this clarification. The size thresholds are initially defined using calibration with polystyrene latex (PSL) spheres. Because atmospheric particles (e.g., sulfate and sea salt) have different refractive indices than PSL, the optical diameters derived from PSL calibration were converted to equivalent diameters representative of stratospheric sulfate aerosol using Mie-theory-based corrections. This correction accounts for differences in scattering efficiency between PSL and ambient aerosol particles.

The text will now specify: "Corrected for refractive index differences between PSL and Sulfate/Sea Salt using Mie theory “

RC:1 “Fig. s1. The text claims the instrument is sensitive to particles 0.3 – 10 µm, yet the figure only extends to 2 µm. It would be helpful to also show the instrument’s response to the PSL calibration aerosol here, that is the laboratory measurements confirming the instrument response including their error bars.

But exactly what does Fig. s1 show? The text for Fig. s1 includes the following, “… Figure S1 shows the scattering efficiency for individual particles derived from Mie calculations (Hagan et al., 2022) for PSL, sulfate (70%H2SO4/30%H20) (Knepp et al., 2024), and sea salt (Bi et al., 2018) by…” So Hagan, Knepp, Bi did the Mie calculations for the instrument or are they supplying the index of refraction for these compositions of aerosol? The text should be clear, and there are no entries for Knepp, Hagan, or Bi et al., in the reference list. The title for Fig. s1 is POPC Theoretical Response. This implies it is the counter response function, but then the ordinate should have units of volts, or photon energy, or something similar. Instead no units are provided and the caption states that it is "mean scattering efficiency." Thus it seems that this figure has nothing to do with POPC, as this would be the same without any consideration of an OPC. If it is the counter response function then it should be so stated and the appropriate labels added to the graph along with the results of the measurements with PSL."

Authors: We thank the reviewer for the opportunity to clarify the details of Figure S1 (now Figure [X]).

- **Instrument Specificity:** The reviewer is correct that the scattering efficiency depends on the instrument configuration. Figure S1 is indeed specific to the POPC; the Mie calculations were performed using the POPC's specific laser wavelength (785 nm) and detector collection geometry (58°-118°).
- **Source of Calculations vs. Refractive Indices:** The Mie code was developed by Hagan et al. (2022), while Knepp et al. (2024) and Bi et al. (2018) provided the refractive indices for the specific aerosol compositions. We will add these entries to the reference list.
- **Units and Labels:** The ordinate represents the scattering amplitude (C_{scat}) with units of cm^2/particle. We have updated the axis label and the figure caption to reflect this.
- **Calibration Data:** While a full technical paper dedicated to the POPC characterization is in preparation, we have updated Figure S1 to extend to 10 μm as requested. Furthermore, we have added a new panel (Figure S1b) showing the theoretical response to PSL particles. The following figure will be used in supplementary materials.

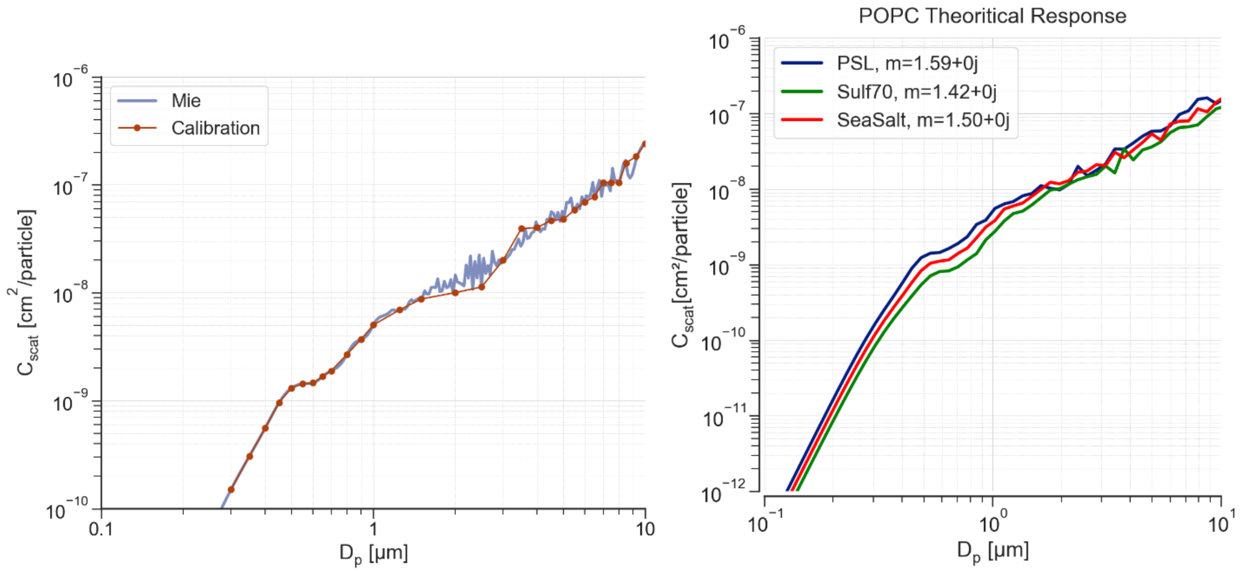


Figure (left). Theoretical response of the POPC to PSL particles (blue line/Mie) and extracted values at the size threshold location (red point/calibration). (right) Same as left for all 3 types of aerosols.

RC1: "252-253 What is the backscatter ratio measurement? Is this the ratio of backscattered light to the emitted light? How does the backscatter ratio compare to the scattering ratio?"

Authors:

The backscatter ratio is defined as the ratio of the total backscattered light (from both molecules and particles) to the backscattered light from molecules alone also known as scattering ratio. It is not the ratio of backscattered light to emitted light, but rather a normalized measure of how much more backscattering occurs due to the presence of aerosols or particles compared to a purely molecular atmosphere. Mathematically, it is expressed as:

$$\text{Scattering Ratio}=\textbf{Backscatter Ratio} = \frac{\boldsymbol{\beta}_{\textbf{total}}}{\boldsymbol{\beta}_{\textbf{molecular}}}$$

where $\boldsymbol{\beta}_{\textbf{total}}$is the total backscatter coefficient (molecules + particles) **and** $\boldsymbol{\beta}_{\textbf{molecular}}$is the backscatter coefficient due to molecules only. We will use the term Scattering Ratio (same quantity as Backscatter Ratio) in the paper.

RC1: "255 Such concentrations are usually written 8-9 cm^{-3}."

Authors: We thank the reviewer for pointing this out. We will revise the units in the text to read "8–9 cm^{-3}" for consistency with standard notation.

RC1: “259-261 Why is Fig. s2 in the supplementary material? It should be in the paper.”

Authors: We will include Fig. S2 in the revised version of the paper.

RC1: “In Fig. s2, there is no reason to show the POPC measurements with no correction from PSL for index of refraction. Everyone knows there is no PSL in the stratosphere and all OPCs have to be corrected to the aerosol expected in the stratosphere. The first row of Fig. s2 just misleads the reader, including this one.”

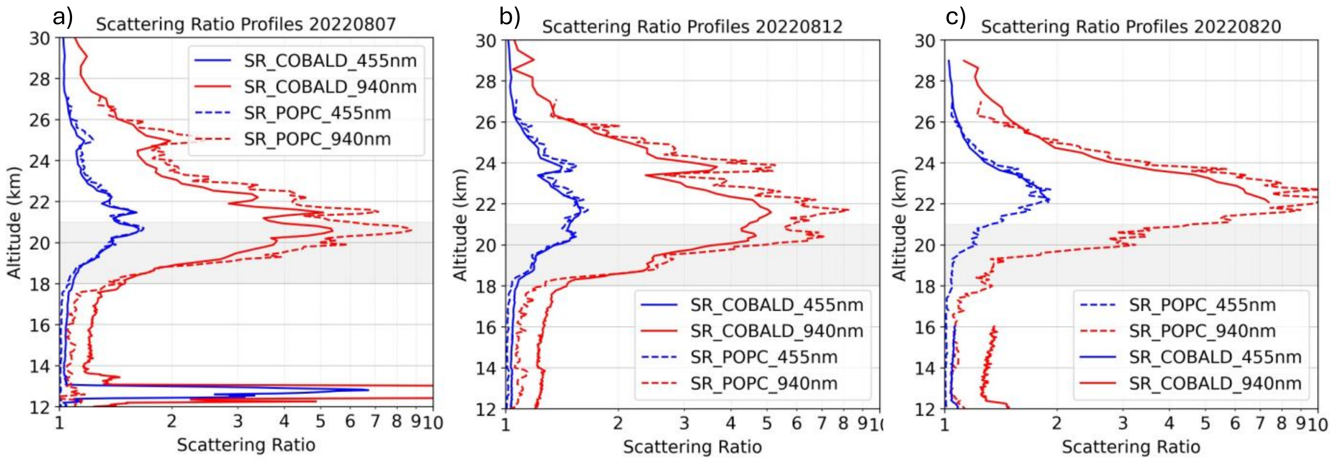
Authors: We will include Fig. S2 in the main text of the revised version of the paper and remove the case with no correction.

RC1: “Fig. 3 Why are these profiles interesting? More interesting would be to show the POPC estimates of the COBALD scattering ratios, which would also illustrate the same point, that is that both instruments clearly detect the Hunga-Tonga plume.”

Authors: We agree with the reviewer that demonstrating the consistency between the POPC and COBALD instruments is a powerful way to substantiate the detection of the Hunga-Tonga plume.

In Figure 3, we have included the Scattering Ratio (SR) estimates derived from the POPC at both 455 nm and 940 nm (dashed lines), alongside the standard COBALD SR profiles (solid lines). To derive the POPC SR, we integrated the particle size distributions measured by the POPC and applied Mie theory to calculate the expected scattering ratio.

The high degree of correlation between the two independent measurement techniques—one based on in-situ backscatter (COBALD) and the other on single-particle counting and sizing (POPC)—provides strong confidence in the vertical structure and magnitude of the aerosol layers observed following the Hunga-Tonga eruption.



New Fig.3. From left to right. Scattering Ratio profiles from COBALD and POPC at 455 nm and 940 nm on 08/07, 08/12 and 08/20.

RC1: “299 “Positioned into a dry to …” Something missing here.”

Authors: We thank the reviewer for pointing out this incomplete sentence. The text will be corrected to clarify that the samplers were immediately placed in a dry-ice container upon recovery to preserve volatile components and minimize post-collection chemical changes. The revised sentence will read:

“The internal temperature of the sampler air flow ranged between 17 and 35 °C during the flight (Fig. 4c) and remained below 36 °C until recovery, after which the samplers were immediately placed in a container with dry ice to prevent the loss of volatile components and minimize post-collection aerosol loss or chemical reactions.”

RC1: “In general there should be more explanation of how the various filter samples were kept sealed from outside contamination both before and after exposure. It would seem difficult to keep them at the pressure of their exposure, but maybe that’s the case? Or were they somehow bathed in dry nitrogen before and after exposure to not have to deal with the pressure differentials? This needs to be clarified.”

Authors: We thank the reviewer for raising this important methodological point. The filters were handled following established clean protocols previously applied in stratospheric aerosol sampling (Vernier et al., 2022). Prior to flight, filters were stored in sealed glass Petri dishes and handled exclusively with sterilized stainless-steel tweezers in a controlled laboratory environment to minimize contamination.

After recovery, the sampler was immediately transferred to dry ice to limit volatilization and post-collection chemical reactions. Filters were then removed using sterilized tools, placed in pre-cleaned glass Petri dishes, sealed with aluminum foil, and maintained under cold-chain conditions until extraction and analysis.

Regarding pressure conditions, the filters were not maintained at stratospheric pressure after sampling. As is standard practice in balloon-borne aerosol collection, the sampled particles equilibrate during descent within the closed sampler housing. No active gas purging was applied post-collection.

The manuscript will be revised to clarify these handling procedures

RC1: "330 ...Filters from positions P 1-P 5 were extracted and analyzed by ion chromatography. Each extract ..." What is the extract and how does that differ from the filters on which the extract is deposited? Most readers aren't going to be so familiar with ion chromatography."

Authors: We thank the reviewer for this helpful comment. The term "extract" refers to the aqueous solution obtained after dissolving the water-soluble aerosol components collected on the filters. Following sampling, each filter was immersed in ultrapure water to dissolve the soluble ionic species; this solution (the extract) was then analyzed by ion chromatography to quantify major anions and cations. To clarify this procedure, we will revise the text as follows:

"Filters from positions P1–P5 were immersed in ultrapure water to dissolve the collected water-soluble aerosol components, and the resulting extracts were analyzed by ion chromatography to quantify major inorganic ions."

RC1: "423 ...This helps identify non-marine sources or processing. ... What does or processing mean?"

Authors: We appreciate the reviewer's request for clarification. In this context, "or processing" refers to atmospheric processes that can alter the chemical composition of aerosols after their emission or formation. These processes may include:

- Chemical reactions (e.g., oxidation, acidification, or neutralization) that modify the ionic composition of aerosols.
- Physical processes such as evaporation, condensation, or mixing with other air masses, which can enrich or deplete certain ions relative to their seawater ratios.
- Interaction with non-marine sources (e.g., volcanic emissions, anthropogenic pollution, or dust) that contribute additional ions or remove existing ones, further deviating the aerosol composition from the expected marine signature.

For example, sulfate (SO_4^{2-}) may be enriched due to volcanic SO_2 oxidation or depleted due to reaction with ammonia, even if the original source was marine. The MEF analysis helps distinguish between direct marine contributions and these secondary modifications.

To improve clarity, we will revise the text to read: "This helps identify non-marine sources or atmospheric processing that alters the ionic composition relative to seawater."

RC1: "4.1 "Theoretical considerations ..." Why theoretical? Aren't the authors presenting measurements, albeit based on some assumptions?"

Authors: We thank the reviewer for this insightful comment. We agree that the term "theoretical" may be misleading, as the mass estimates are derived from measured POPC size distributions combined with standard microphysical assumptions (log-normal fitting and assumed aerosol density). We have therefore replaced the term "theoretical" with "Methodological Framework.

RC1: "463-466 If a size distribution has been fit to the OPC data, why isn't that used to directly calculate the aerosol volume along the flight path? Then the mass is given by V*d. Isn't that what is done? The authors are not converting number concentration to mass concentration. They are using the number concentration to calculate volume by an integration. If that is the case then, aside from the uncertainty of the density, isn't the mass measured? And if so why is it referred to as theoretical?"

In fact what the authors are doing, which is reasonable, is to assume that the stratospheric aerosol size distribution they measured from 8/07-12 would be similar to the distribution that existed on the day of the flight. It's not a theory, it is an assumption. And if this is really what the authors are doing, why don't they plot in Fig. 6a a vertical profile of the aerosol mass concentration, rather than number concentration which has already been done? They could do it for all three days, and take the average for the mass to be used for the flight on 8/16. The step by step approach is detailed in the supplementary material, but the authors could eliminate a lot of confusion by a clearer explanation here and by adding some of the supplementary material to the text."

Authors: We agree that "assumption" is a more accurate description than "theoretical" in this context, and we will revise the text to reflect that we are using a derived volume from the measured size distributions.

- **Calculated Volume vs. Number Concentration:** As suggested, we will replace the number concentration profile in Figure 6a with the Aerosol Volume Concentration (cm^3/m^3) derived from the three POPC flights (Aug 7, 12, and 20). This provides a more direct link to the mass concentration calculations used for the August 16 sampler flight.

- **Mass Derivation:** We will clarify the methodology: the total aerosol mass is indeed a derived measurement obtained by integrating the POPC-fitted size distributions to find total volume (V) and multiplying by the assumed aerosol density (ρ).
- **Averaging Strategy:** We will clarify that the Aug 16 values are based on the average volume concentration derived from the surrounding POPC flights, which we assume to be representative of the stratospheric background during that period.
- **Refining the Text:** To reduce confusion, we will move the key step-by-step methodology from the supplementary material into the main text and updated Figure 6a. Note: The volume concentration profiles are shown for altitudes above 11 km, as the fitting algorithm was optimized for the stratospheric plume and did not converge reliably in the troposphere.

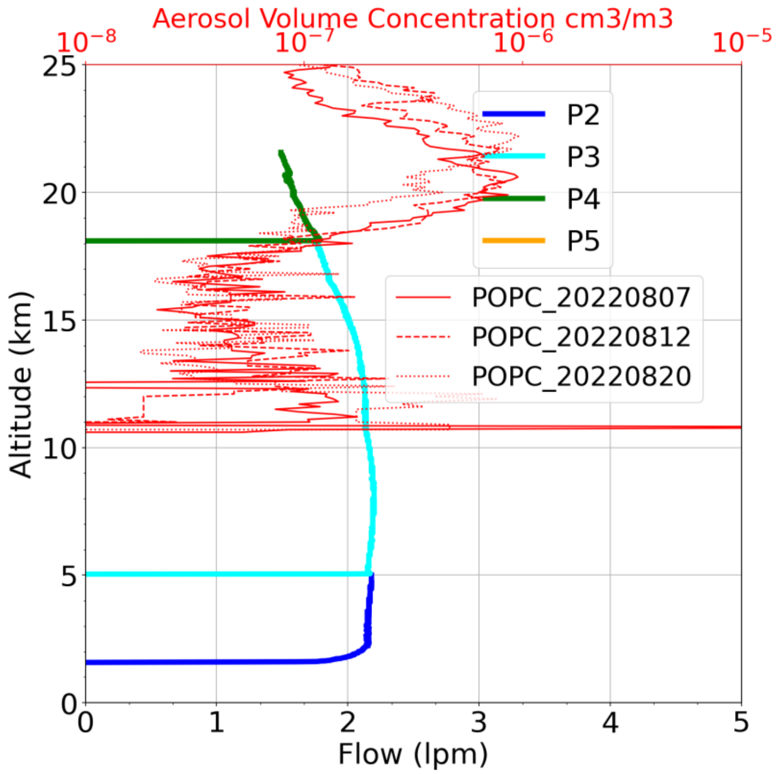


Fig.6a (new). Aerosol Volume Concentration derived from the 3 POPC flights and flow measurements from the sampler on 08/16.

RC1: “Fig. 6b) Why are masses calculated for d > 0.3 and > 0.45 µm? What is the pore size of the filters, or what is the minimum size of particle that the filters will capture? This should determine where the OPC size distribution should be integrated from to get the comparable volume. How is the right hand axis, arrived at? The label is mass, but the OPC only provides mass/volume sampled. So what volume is used to obtain mass? Then shouldn’t the axis be labelled accordingly?”

Authors: We appreciate the reviewer’s focus on the integration limits. To ensure a direct comparison between the in-situ POPC data and the physical sampler, we have clarified the following:

- **Filter Cutoff vs. Integration Limit:** The sampler uses filters with a pore size of 0.45 µm. Therefore, to obtain a comparable mass estimate, we integrated the POPC size distribution from d > 0.45 µm to the upper limit of the instrument (10 µm).
- **The 0.3 µm Comparison:** We also included the integration from d > 0.3 µm (the lower detection limit of the POPC) to illustrate the mass contribution of the smaller aerosol fraction (0.3-0.45 µm) that may pass through the filter pores.
- **Right-Hand Axis (Mass Accumulation):** The right-hand axis in Figure 6b represents the **c**umulative mass (µm) collected on the filter every second. This was derived by multiplying the POPC-derived mass concentration (M_{conc}) by the instantaneous volumetric flow rate measured by the sampler (Q_{vol}) and integrated over 1s.

  $$\text{Total Mass}\} = \int (M_{conc})\ (Q_{vol})\ dt$$

  We will update the axis label to "Cumulative Mass (µg)" and clarify in the caption that this is the mass integrated along the flight path based on the sampler's flow measurements.

RC1: “475-476 “The theoretical mass derived from POPC data is near 42–43 ng for the first two flights and 27 ng …” Again why theoretical? There is nothing theoretical about integrating a size distribution or assuming a density. What do the numbers 42, 43, 27 represent? Is this the total mass that would have been collected by the filter in the altitude range of 18-21 km, and was calculated by using the OPC mass concentration times the total volume to which the filter P4 was exposed? This is what it should be but it is extremely unclear what was done.”

Authors: We agree that the term "theoretical" is misleading in this context and have removed it from the manuscript. These values represent the total cumulative mass that would have been collected by the filter (P4) during its specific sampling altitude (e.g., 18-

21km), based on the integrated POPC size distribution and the sampler's measured volumetric flow rate.

To clarify the methodology:

1. We calculated the instantaneous mass concentration (M_{conc}) from the POPC size distribution (d > 0.45 μm) using the assumed aerosol density (ρ).
2. This concentration was multiplied by the sampler's instantaneous volumetric flow rate (Q_{vol}) to obtain the mass collection rate (dm/dt).
3. The values of 42 ng, 43 ng, and 27 ng represent the time-integral of this collection rate over the duration of the respective sampling intervals.

The text will be updated to explicitly describe this integration process to ensure the derivation of the collected mass is transparent.

RC1: "476 Is 513 ng the total mass obtained from washing the filter? Is an ion mass different than the total mass? A much clearer explanation of how the OPC size distributions were used, and a profile of the mass concentration derived from the OPC measurements would go a long way in understanding how to compare these numbers. At present this comparison is a black box to the readers, and 513 ng is over 10 times the other masses listed."

Authors: We thank the reviewer for raising these important points and agree that further clarification is needed.

Clarification of Mass Units: The 513 ng refers to the total mass of ions extracted from the filter and quantified by ion chromatography, not the total particulate mass collected on the filter. The filter collects all aerosol particles, but ion chromatography only measures the water-soluble ionic components (e.g., SO_4^{2-}, Cl^-, Na^+) extracted from the filter. Thus, the 513 ng represents the mass of all ions alone, not the total aerosol mass.

This discrepancy in magnitude is expected because the total aerosol mass includes non-ionic components (e.g., organics, crustal material) that are not captured by ion chromatography.

We recognize that this comparison may not be immediately transparent to readers. To improve clarity, we will:

- Add a brief description of the OPC-to-mass conversion process in the manuscript.

- Explicitly state that the 513 ng is the mass of all ions, while the OPC-derived mass represents the total aerosol mass (including non-ionic components).

We will add the following text:

“The hypothetical mass collected derived from POPC measurements is significantly lower than those measured through IC by a factor 10. This could be explained by several reasons:

- The Hunga volcanic plume was still inhomogeneous, and a higher concentration layer may have been present during the sampler flight on 8/12 and not during the POPC flights before and after.
- The POPC mass concentration might be underestimated if the aerosol density in the plume was much higher than the one used in our calculations (1.8kg/L) especially due to the presence of refractory aerosols (volcanic ash).
- The refractive Index used in these calculations may deviate significantly especially if a mixture of sea salt, sulfate, and/or nitrate was present in the plume (ten Brink et al., 1997).
- Additional aerosols on the filters may have been present due to an unknown contamination problem

RC1: “481-590 The text here describes, briefly, a dozen chemical scenarios to explain the observations that were made. These scenarios are beyond my expertise and need to be reviewed by a qualified chemist to substantiate their reasonableness.”

Authors: We thank the reviewer for this important comment Our intention was not to assert conclusive pathways, but rather to discuss plausible processes consistent with established atmospheric chemistry and prior volcanic plume studies.

To address this concern, we will revise the Discussion to:

1. Clearly distinguish between observations and interpretation.
2. Reframe the chemical processes (e.g., acid displacement, gypsum formation, ammonia neutralization) as plausible mechanisms supported by prior literature rather than definitive conclusions.
3. Reduce redundancy and streamline the discussion to focus on the most relevant processes.
4. Clarify the limits of our dataset in constraining specific reaction pathways.

All mechanisms discussed are supported by peer-reviewed studies in volcanic and marine aerosol chemistry (e.g., Mather et al., 2003; Ayris & Delmelle, 2012; Allen et al., 2000), which are now more explicitly cited to substantiate their reasonableness.

The revised Discussion will now read as:

4.2 Na^+:Cl^- Ratios and Marine Source Identification

Ion chromatography analysis of the aerosol samples reveals variations in Na^+:Cl^- molar ratios that are broadly consistent with a marine contribution modified by subsequent chemical processing.

At Position 2 (1.6–5 km), the Na^+:Cl^- ratio of 0.98 is close to the seawater molar ratio (~0.86), suggesting a predominantly marine influence. Although this altitude range lies above the marine boundary layer, previous studies have documented vertical transport of sea salt aerosols into the free troposphere through convection and large-scale uplift (e.g., Murphy et al., 2018). Thus, the observed ratio is consistent with lofted marine material.

At Position 3 (5–18.1 km), the elevated Na^+:Cl^- ratio (1.23) may indicate partial chloride depletion. Acid displacement reactions involving volcanic acids (e.g., H_2SO_4, HCl) have been shown to release HCl(g) from sea salt particles, increasing the Na^+:Cl^- ratio in the residual aerosol phase (e.g., Mather et al., 2003). The observed deviation is therefore consistent with acid-mediated chloride loss, although alternative mixing processes cannot be excluded.

At Position 4 (18.1–21.6 km), the Na^+:Cl^- ratio (0.76) remains within the range expected for partially processed marine aerosol. Such values may reflect a combination of chloride volatilization and re-partitioning onto larger particles, as described in volcanic plume studies (e.g., Allen et al., 2000). Overall, the vertical variability in Na^+:Cl^- ratios suggests progressive chemical modification with altitude, though the precise pathways cannot be uniquely constrained by IC data alone.

4.3 Stratospheric Sea Salt Signature

The near-marine Na^+:Cl^- ratio observed at Position 4 is consistent with the presence of sea salt aerosol at 18–22 km. While slight deviations from seawater stoichiometry are evident, the ratios remain within the range reported for transported marine particles subjected to acidic processing.

Submarine eruptions such as Hunga Tonga–Hunga Haʻapai are capable of injecting both seawater-derived material and volcanic gases into the upper troposphere and lower stratosphere. Previous modeling of this eruption indicates strong water–magma interaction (e.g., Colombier et al., 2023), which may facilitate marine aerosol entrainment. However, we emphasize that IC measurements alone cannot distinguish between freshly injected sea salt and previously lofted marine background aerosol.

4.4 Calcium-Rich Ash and Sulfate Partitioning

The elevated Ca^{2+} concentrations and high Ca^{2+}/Na^{+} ratios suggest a significant contribution from Ca-bearing volcanic ash. The large Ca^{2+}/SO_4^{2-} ratios observed at certain positions are consistent with heterogeneous interactions between ash and sulfate species.

Under Ca-rich conditions, sulfate may partition into relatively insoluble phases such as $CaSO_4$ (gypsum), a process thermodynamically favored in mineral dust–sulfate systems (e.g., Stumm & Morgan, 2012). Laboratory studies of ash–gas interactions (e.g., Ayris & Delmelle, 2012) have demonstrated that such reactions can alter the partitioning of sulfate between soluble and insoluble fractions.

While our IC analysis quantifies the water-soluble sulfate fraction, it does not directly measure insoluble sulfate phases. Therefore, the elevated Ca^{2+}/SO_4^{2-} ratios are consistent with, but do not definitively prove, heterogeneous sulfate consumption.

4.5 Marine Enrichment Factors (MEFs)

Marine enrichment factors calculated relative to seawater composition provide additional insight into source contributions.

At Position 2, Cl^{-} and Mg^{2+} MEFs near unity are consistent with marine influence, while enhanced SO_4^{2-} MEF may reflect contributions from volcanic SO_2 oxidation.

At Position 3, reduced Cl^{-} MEF values are compatible with chloride depletion processes. The absence of detectable SO_4^{2-} at this altitude may indicate sulfate partitioning into non-soluble phases, dilution effects, or analytical limitations.

At Position 4, near-unity Cl^{-} MEF values again support a marine contribution, while suppressed Mg^{2+} and SO_4^{2-} MEFs suggest mixing with ash-rich material or modified partitioning.

These MEF patterns are consistent with mixed marine and volcanic sources but do not uniquely constrain specific chemical pathways.

4.6 Implications for Stratospheric Aerosol Composition

The combined $Na^{+}:Cl^{-}$ ratios, Ca^{2+}/SO_4^{2-} relationships, and MEF analysis suggest co-existence of marine-derived material and Ca-rich volcanic ash in the sampled plume.

The data are consistent with heterogeneous interactions between acidic volcanic species and sea salt or ash particles. However, because IC measurements quantify only the water-soluble fraction, the full speciation and phase state of sulfate cannot be determined from these measurements alone.

4.7 Factors Contributing to Low Soluble Sulfate

The relatively low SO_4^{2-} concentrations observed in IC analyses at Position 4 may reflect several non-exclusive mechanisms:

(1) Partitioning into Insoluble Phases
Sulfate may be incorporated into $CaSO_4$ or other mineral-associated phases not fully recovered in aqueous extraction.

(2) Rapid Chemical Processing in a High-H_2O Environment
The exceptional water vapor injection associated with Hunga Tonga–Hunga Haʻapai (e.g., Millán et al., 2022) likely enhanced aqueous-phase chemistry, potentially accelerating sulfate formation and repartitioning.

(3) Acid Displacement Reactions
Reactions between volcanic acids and sea salt particles may alter sulfate and chloride partitioning (e.g., Finlayson-Pitts & Pitts, 2000).

(4) Ammonia Neutralization

Neutralization by background NH_3 may convert acidic sulfate into ammonium salts. Variability in NH_4^+ concentrations across altitudes suggests this process may have influenced sulfate speciation, although dissolution efficiency during extraction cannot be independently verified.

(5) Analytical Constraints
Ion chromatography measures water-soluble ions and may underestimate total sulfate if present in coarse or insoluble forms. Satellite retrievals, by contrast, are sensitive to total column sulfate and SO_2, potentially explaining apparent discrepancies.

Taken together, the observations are consistent with substantial chemical processing of the aerosol population, but the relative importance of individual pathways cannot be uniquely determined from IC measurements alone.

RC1: “543-544 What are the discrepancies with ACE-FTS? This is explained in the supplementary material, but should be more clearly included here, along with how it is resolved.”

Authors: We thank the reviewer for highlighting the need for clarification. The discrepancy refers to the contrast between (1) low soluble SO_4^{2-} concentrations measured by ion chromatography at 18–22 km and (2) coincidental ACE-FTS observations showing persistent sulfate/H_2SO_4 spectral signatures associated with aerosol extinction at similar altitudes (Fig. S4).

To address this, we will transfer the information about ACE-FTS from supplementary materials into the main text. We will revise Section 4.7 and propose the following:

“The low SO_4^{2-}concentrations measured by ion chromatography (IC) at Position 4 (18.1–21.6 km) seems to contrast with the nearest ACE-FTS collocated profile, on August 15th near 24.3°S, 45°W. ACE-FTS indicates persistent sulfate/H_2SO_4 absorption features at similar altitudes (Fig. S4). ACE-FTS spectra show characteristic H_2SO_4 signatures 1200 cm-1 at and associated increase in 1-μm extinction in the 19–22 km layer, whereas the soluble SO_4^{2-} fraction measured in our extracted filters is near or below detection limits.

This apparent discrepancy arises because the two techniques quantify different aerosol fractions. IC measures only the water-soluble ionic component recovered during filter extraction. In contrast, ACE-FTS and ACE-Imager are sensitive to total aerosol extinction and spectroscopic absorption, including insoluble sulfate phases and non-extracted material.

If a significant portion of sulfate at these altitudes was partitioned into insoluble $CaSO_4$ aggregates or coarse particles (>1 μm), it would contribute to satellite extinction but may be incompletely recovered during aqueous extraction and therefore underrepresented in IC analyses. Thus, the IC and satellite observations are not contradictory but reflect differences in measurement sensitivity and phase detection.”

RC1: “561 “(Finlayson-Pitts & Pitts, 2000) …” Neither of these references are in the bibliography.”

Authors: We thank the reviewer for noting this omission. The full reference for Finlayson-Pitts & Pitts (2000) will be added to the bibliography, and all in-text citations will be verified to ensure consistency.

Reference to be added: Finlayson-Pitts, B. J. and Pitts Jr., J. N.: Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, Academic Press, 2000.

RC1: “589-590 Are these discrepancies shown or discussed somewhere?”

Authors:

These discrepancies will be more clearly described in the revised manuscript, as detailed above. We will explicitly state the contrast between low soluble SO_4^{2-} measured by IC and the persistent sulfate/H_2SO_4 signatures observed by ACE-FTS at similar altitudes (Fig. S4).

We will also include contextual discussion of Martinsson et al. (2025), who examined sulfate formation and sea–volcanic interaction following the Hunga eruption. Their results similarly emphasize the complexity of sulfate partitioning in the stratospheric plume. Our in situ ion chromatography measurements provide complementary constraints on the water-soluble ionic fraction, helping to interpret differences between satellite-derived total sulfate signals and extracted aerosol composition.