

Response to Referees

Atmospheric Chemistry and Physics

Taquet et al.: “New insights into the 2021 La Palma eruption degassing processes from surface and direct-sun spectroscopic measurements”

We thank both reviewers for their very constructive comments, which really helped to prepare an improved revised manuscript.

Response to Reviewer #1: Yves Moussallam

General comments

There are a few things which I find amazing about this study. First, the authors are able to derive not only SO₂, HCl and HF from their solar-occultation FTIR measurements but also CO and CO₂. This is a major advance because unlike the other volcanic gas species listed, CO₂ has a very high (>400 ppm) background concentration, making the volcanic contribution over the large path length of solar occultation measurement (the entire atmosphere) too low to resolve prior to the latest generation of portable FTIR used here. Second the authors provide measurements of the gas compositions over the entire duration of the eruption which is a beautiful dataset. Third, the authors performed measurements at two sites, one close to the eruption on La Palma and one 140 km away on Tenerife.

I would encourage the authors to publish the code they used to analyse the FTIR spectra as they have made significant modifications in their retrieval strategy compared to the openly available code. I also encourage the authors to upload all the spectra they used on an open platform (this might be a journal requirement anyway).

Reply: The retrieval algorithms for EM27/SUN FTIR data are accessible via the KIT-COCCON website: <https://www.imk-asf.kit.edu/english/COCCON.php>. With respect to the specific retrievals used in this study, some aspects are still under consideration for a new specific contribution and will be made public after its publication. In any case, any modifications to the standard input files and all the datasets used in this study, can be obtained from the co-authors upon request.

I also encourage the authors to look for OCS in their FTIR spectra. Retrieving OCS is probably possible given the authors were able to retrieve volcanic CO. If you can retrieve OCS then you will have two redox species (e.g., <https://www.nature.com/articles/s41561-018-0194-5>) and may be able to tell a lot more about magmatic evolution during your observation period (see: <https://comptes-rendus.academie-sciences.fr/geoscience/articles/10.5802/crgeos.158/>).

Reply: We thank the reviewer for this insightful suggestion and the references. OCS can be retrieved in the mid-infrared spectral region (2030–2050 cm⁻¹), and in the context of this study, this range is only available using the high-resolution IFS125-HR measurements from the Izaña Atmospheric Observatory (Tenerife, 140 km from the Tajogaite volcano), which covers an extended MIR–NIR spectral range. OCS is part of the standard NDACC products routinely retrieved from Izaña’s IFS125-HR spectra (García et al., 2021), and we have examined the complete time series to investigate potential anomalies attributable to volcanic plumes. Over the course of the eruption, OCS strong enhancements (i.e., above natural variability) were observed on only two occasions. The first one (28/09/2021) coincided with elevated ΔCO and SO₂ levels (see Figure R1 below), and a ΔOCS/SO₂ ratio of 0.00015 was estimated (ΔOCS corresponds to the anomaly above the background). However, no ΔCO₂ anomaly was detected at that time (i.e. ΔCO₂ remained below the detection limit), preventing further investigation about the redox state of the magmatic system. During the second event, the OCS signal was too weak to establish any correlation with SO₂. For these reasons, we chose not to include these results in the manuscript.

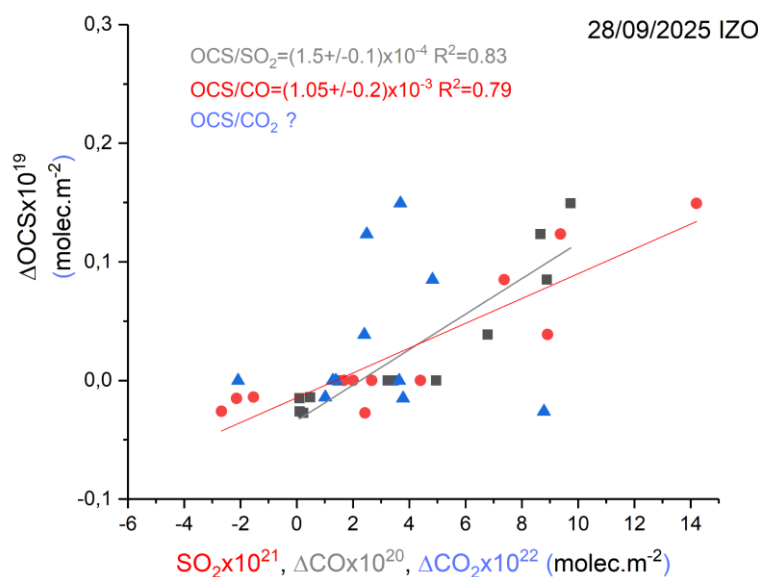


Figure R1: Correlation plot between ΔOCS , ΔCO_2 , ΔSO_2 and ΔCO during the 28/09/2021 event during which the volcanic plume was detected at IZO.

Specific comments

Reply:

Please add “e.g.,” in front of all citations which are examples.

Done. We added “e.g.,” in front of citations which are examples.

Line 51: “...CO₂ and H₂O are among the deepest exsolved gas species, followed by SO₂ and halogens in sub-surface.” This is not entirely/always true I suggest taking out this sentence.

We thank the reviewer for pointing out this unclear sentence and we replaced it with: “CO₂ and H₂O are **usually** among the deepest exsolved gas species” (l. 52 of the new version of the manuscript).

Line 59-64: Overly vague statements.

We rephrased these lines in the new version of the manuscript (l. 59-63) with:

“Volcanic plume compositions, when combined with seismic and structural data, help constrain volatile fluxes, magma ascent rates, and the architecture of the magmatic plumbing system. Integrating gas measurements with petrological constraints from matrix, melt inclusions (MI), and fluid inclusions (FI) enables reconstruction of pre-eruptive volatile contents and degassing pathways, which are key to modeling eruption dynamics (e.g.: Ubide et al., 2023; Longpré et al., 2025).”

Line 107: “...Lava evolved from a ‘a’ to fluid basaltic flows with changing composition.” You mean basanitic flows no?

We thank the reviewer for pointing out this unclear sentence and we replaced “basaltic” with “*basanitic*”.

Line 170: “...Base map was obtained from © Google Earth (©Google).” Add the original sources of the satellite data. 0

We added the original source for the SO₂ satellite data in the legend for Figure 1: “*The base layer was sourced from Google Earth (© Google), while the SO₂ distribution map was derived from TROPOMI data accessed through the Sentinel Hub platform.*”

Figure 2: A photograph of the real setup would be better here than the Schematic (or in addition to).

Done: We replaced the schematic with a photograph in Figure 2 corresponding to our measurement set-up (combined EM27/SUN - DOAS) at the FUE station.

Line 398: “*We also report Cl, F and S contents in tephra glasses that were measured during the analyses published in Gonzalez-Garcia et al. (2023).*” I don’t understand this, if these are already published you are not reporting them here. Or were these analysed for major elements but not S, Cl, F? Please explain.

The major elements and S, Cl and F were measured together, but only the major elements were published in Gonzalez-Garcia et al. (2023). We rephrased this sentence as follows (l. 303-305 of the new version):

“We also report Cl, F, and S contents in tephra glasses that were measured alongside major elements during the analytical session described in Gonzalez-Garcia et al. (2023), although only the major element data were published in that study.”

Figure 3: Maybe add the data from Asensio-Ramos et al., (2025) too.

The figure R2 shows our data together with the HCl/SO₂ and ΔCO/SO₂ ratios reported by Asensio-Ramos et al. (2025). As shown, including the full set of literature data might obscure the internal consistency of our dataset, which relies on only two, well-characterized measurement techniques (i.e., solar absorption FTIR measurements and in situ surface observations), both compatible with long term atmospheric monitoring networks. This could lead to misinterpretations. Therefore, in the figure 3 of the new version of the manuscript, we chose to represent the literature values only as shaded areas, in order to preserve the clarity of our time series.

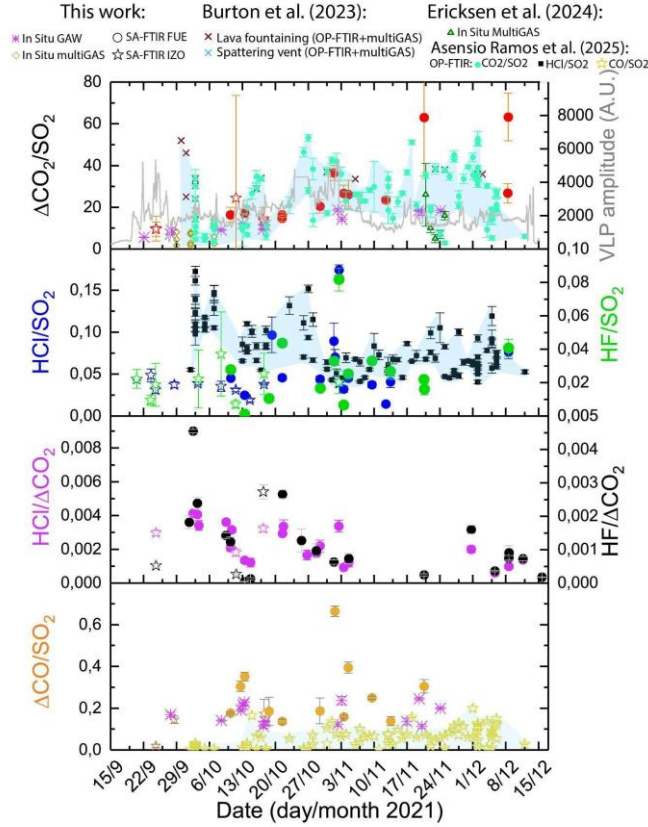


Figure R2: Comparison between the gas-species to SO₂ ratios found for this study and the literature data.

As shown in Figure R2, our $\Delta\text{CO}_2/\text{SO}_2$ and HCl/SO_2 ratios fall within the range reported in the literature. The observed differences can be attributed to variations in measurement techniques, viewing geometries, and plume sampling locations, particularly for species like CO and CO₂, which exhibit substantial atmospheric background levels. Our measurements are based on solar absorption spectroscopy conducted at distances of up to 140 km from the volcanic source, but benefit from high signal-to-noise ratios and traceability through participation in international networks such as NDACC and COCCON. This enables robust background corrections, even at significant distances from the source. In comparison, the study by Asensio-Ramos et al. (2025) employs an Open Path approach, using lava as a source of infrared emission (emission-absorption spectra) over shorter optical paths. This technique involves both absorption and emission processes, and requires consideration of temperature gradients across the atmospheric layers. Differences in radiative transfer effects, methodological approach and retrieval strategies, and measurement geometries could easily account for the observed small discrepancies. The significantly higher $\Delta\text{CO}/\text{CO}_2$ and $\Delta\text{CO}/\text{SO}_2$ ratios observed in our study compared to those reported by Asensio-Ramos et al. (2025) likely stem from differences in CO enhancements, as our $\Delta\text{CO}/\text{CO}_2$ ratios (Figure 4 of the new version of the manuscript) are also substantially higher than theirs. As mentioned in the manuscript (1.697-704), this discrepancy can be explained by the location of their measurement sites, mostly NNW of the eruptive vent and upwind of biomass burning plumes, whereas our FUE and IZO sites were more exposed to CO emissions from vegetation and building fires triggered by advancing lava flows. Furthermore another possible explanation could be the different contribution of emissions from effusive vs. explosive vents in the optical path of the instrument. We added this alternative hypothesis in the manuscript (1.689-692): “Tajogaite volcano presented notable differences in eruptive behaviour between the different vents along the volcanic fissure, the higher elevated ones being more explosive than the lower ones. Recent studies suggest that eruptive dynamics may affect the abundance of redox-sensitive species (e.g.: Oppenheimer et al. 2018, Moussalam et al. 2019).”

Figure 3: You could have HF/SO₂ and HF/CO₂ plotted in their own panel to make the figure a bit clearer.

In our view, it is essential to display all the time series within a single figure to clearly highlight the co-variability of the ratios. Adding two additional panels to the figure would either exceed the page size limit or hinder the readability of the figure. Moreover, the HF/SO₂ and HCl/SO₂ ratios exhibit similar trends and variability, as do HCl/CO₂ and HF/CO₂. Therefore, we chose to group these ratios into two panels, offering a comprehensive overview of all species and their co-variations in a single plot. For these reasons, we prefer to retain the original version of Figure 3.

Figure 4 and CO/CO₂: You say the data from the FUE and IZO observation sites are similar but it rather looks like the CO/CO₂ ratios measured at IZO tend to be lower than the ones measured at FUE. This may be evidence of oxidation of the gas plume during transport.

We thank the reviewer for this very insightful comment. To investigate this further, we have added the in situ surface $\Delta\text{CO}/\Delta\text{CO}_2$ ratios measured at IZO (GAW measurements) in Figure 4 of the new version of the manuscript. These ratios fall within the same range as those observed at FUE and their similarity with the FUE FTIR ratios rules out the hypothesis of systematic oxidation during plume transport between IZO and FUE. This new data bring further constraint on the amplitude of the intraday and day-to-day variability of this ratio (up to 0.005 over 1 day, i.e. $\sim 1/3$ of the full observed variation range) at IZO. It is noteworthy that at IZO, the in situ surface $\Delta\text{CO}/\Delta\text{CO}_2$ ratios are systematically higher than those derived from FTIR measurements. The above-mentioned short-term variability could explain this difference (only 1/5 coincident measurements), but other considerations due to measurement geometries have to be taken into account. On the days when FTIR retrievals were possible (i.e., when the correlation coefficient exceeded 0.6), the correlations were generally weak and only marginally above the threshold, except on October 17. Despite the detection of SO₂ on these days, confirming the presence of volcanic plume in the line of sight of the instrument, the FTIR retrievals showed limited correlation with SO₂. In parallel, TROPOMI S5P imagery (available on the Mounts project website) indicates that the FTIR instruments at IZO may have been affected by aged plume components during those episodes. This suggests that the FTIR-derived $\Delta\text{CO}/\Delta\text{CO}_2$ ratios at Izaña likely reflect a mixture of fresh and aged plumes, while the in situ surface measurements are more indicative of more directly transported plumes.

We added the following lines in the manuscript (l. 503-518):

“Figure 4 presents the time series of $\Delta\text{CO}/\Delta\text{CO}_2$ ratios derived from FTIR solar absorption measurements at the FUE and IZO stations throughout the eruption, alongside with in situ surface measurements at IZO (GAW data). The $\Delta\text{CO}/\Delta\text{CO}_2$ values observed at both sites and using both techniques are of the same order of magnitude, and exceed by more than one order of magnitude the average atmospheric background ratio at IZO (~ 0.0002). At FUE, the FTIR-derived ratios show a progressive increase from 0.0016 to 0.016 during the first 30 days of the eruption, followed by a decrease to lower values before mid-November. The surface $\Delta\text{CO}/\Delta\text{CO}_2$ ratios at IZO fall within a similar range to those derived from FTIR at FUE, with some coinciding values in very good agreement. On average, the surface ratios at IZO are higher than the FTIR-derived ones at the same site. This discrepancy may be explained not only by the strong short-term variability in the $\Delta\text{CO}/\Delta\text{CO}_2$ ratios (only a few data points are coincident), but also by the fact that, although all these points coincide with the presence of SO₂ (indicating the presence of volcanic plume), the correlation between ΔCO and SO₂ is relatively weak ($R^2 < 0.6$), suggesting additional sources contributing to the CO enhancements. Furthermore, satellite imagery suggests that, on these days, the line of sight of the IZO FTIR instrument may have intersected aged volcanic plumes, potentially altering the retrieved $\Delta\text{CO}/\Delta\text{CO}_2$ ratios due to both geometric and compositional effects. The difference between the surface $\Delta\text{CO}/\Delta\text{CO}_2$ ratios observed at FUE and IZO and those (shaded area) reported by Asensio-Ramos et al. (2025) is discussed in Section 5.”

The comparison between SO₂ flux and TADR is interesting, I would suggest citing this article which found the same thing during the Fagradalsfjall eruption: <https://www.sciencedirect.com/science/article/pii/S0377027324000568>

The following sentence has been added at lines 715-716 to comment on this previous observation: *“A similar correlation between SO₂ emissions and effusive volumes has previously been observed during the 2021 Fagradalsfjall eruption (Pfeffer et al., 2024).”*

Line 745: The difference in S content of the glass may between your data and previous publications may be related to the type of sample (flow vs tephra) used in each study. Please specify if these are all from the same type of samples.

We thank the reviewer for this suggestion. All the analyses arise from the tephra matrix.

The most comprehensive matrix dataset published to date is that of Longpré et al. (2025) with >500 EMPA distributed over the eruption. All the individual analyses previously published and our new dataset is consistent with Longpré et al. (2025). Our analyses were mainly collected from samples of 23/09, during one of the most explosive phases of the eruption, which emitted the tephra with the highest matrix S contents (up to 800 ppm) of the eruption. Our average is thus consistently slightly higher than that of the average for full literature data, for which the vast majority of samples have 300-500 ppm.

In this sentence, our point was both comparing our new data with literature values and suggesting that the matrix value used by Dayton et al. (2024) for their S degassing calculation is probably a little low, resulting in higher emissions. We rephrased this section as follows (l.812-817):

“Note that the matrix S contents we present (average 534 ppm; $N=52$; $\sigma=130$ ppm; Supplementary Table S1) are consistent with previously published datasets for the eruption (average of 403 ppm; $N=438$; $\sigma=10$ ppm; Burton et al., 2023; Longpré et al., 2025). These data are nevertheless substantially higher than the value reported by Dayton et al. (2024). Using these values in the MonteCarlo degassing simulation of Dayton et al. (2024), the full degassing of 0.25 km³ of magma would produce emissions of 1.93 ± 0.21 Mt SO₂. This is compatible with the TROPOMI-derived total SO₂ emissions (1.81 ± 0.18 Mt).”

Line 753: You say that sulfide droplets are “...absent from the matrix.” But then you show a picture of Sulfide droplets in the matrix glass (Figure B1). This is confusing please rephrase and improve the explanations. Do you see any sulfide inclusions in minerals? Can you plot the S content of Melt inclusions versus FeO to see when the melt reached sulfide saturation?

We thank the reviewer for spotting this confusing section. Rare sulfide droplets have indeed been observed in the matrix of Tajogaite eruption products by Day et al. (2022) and Pankhurst et al. (2022). We have only been able to observe sulfide inclusions in the matrix, but the recent paper of Andujar et al. (2025) describes “a few” sulfide inclusions in CPx cores and magnetites. Here we meant that the S making up these sulfides is neither in the matrix analyses nor degassed. We rephrased it and explained as follows (l. 818-832):

“A possibly unaccounted repository for initial S in the degassing balance could be the rare sulfide droplets, previously described to be present in the eruptive products matrix (Fig. B1; Day et al., 2022; Pankhurst et al., 2022) but also, more recently in clinopyroxene (CPx) cores and in magnetites (Andujar et al., 2025). These droplets separated from the silicate melt upon reaching the sulfide saturation during a pre-eruptive crystallization episode (Day et al., 2022), as confirmed by our own saturation calculations using the O’Neil (2021) SCSS model (see Appendix B2). Importantly for the sulfur budget, although part of the primitive magma S content, as recorded in MI, the sulfur they contain is not included in matrix glass analyses (since it is physically segregated) and is not released as gas during eruption. The sulfide abundance could range between 0.03 vol.% (QEMSCAN quantification in Pankhurst et al., 2022) and 0.066 vol.% (0.001 mass fraction in the crystallizing assemblage in the models of Day et al., 2022). Assuming a density of 4500 kg·m⁻³ (Saumur et al., 2015) and an average sulfur content of ~35% in the analyzed sulfides (Fig. B1), this range of abundance would represent a potential sulfide cargo in the erupted lava until day 20 (Day et al., 2022) of ~30 to 60 kt of non-degassed sulfur (equivalent to ~60 to 120 kt of SO₂). Accounting for this contribution would further improve the agreement between the petrologic budget (1.81-1.87 Mt of SO₂) and satellite-based estimates (1.81 ± 0.18 Mt of SO₂).”

We present hereafter in Figure R3 the S vs FeO contents (corrected for post-entrapment crystallization) in published melt inclusions (hollow circles for Burton et al., 2023; grey dots for Dayton et al. 2024). Note that Dayton et al. (2024) state:

“Our analyzed melt inclusions do not record evidence of sulfur saturation, identified by the presence of sulfide blebs (Hartley et al., 2017), except in two heterogeneously entrapped inclusions with anomalously

low H_2O (~ 0.5 wt%) and high chlorine contents ($\sim 1,000$ ppm).” We remark the difference between both datasets, which we attribute to the PEC correction procedure (most probably FeO^*_{i}) used by the different authors.

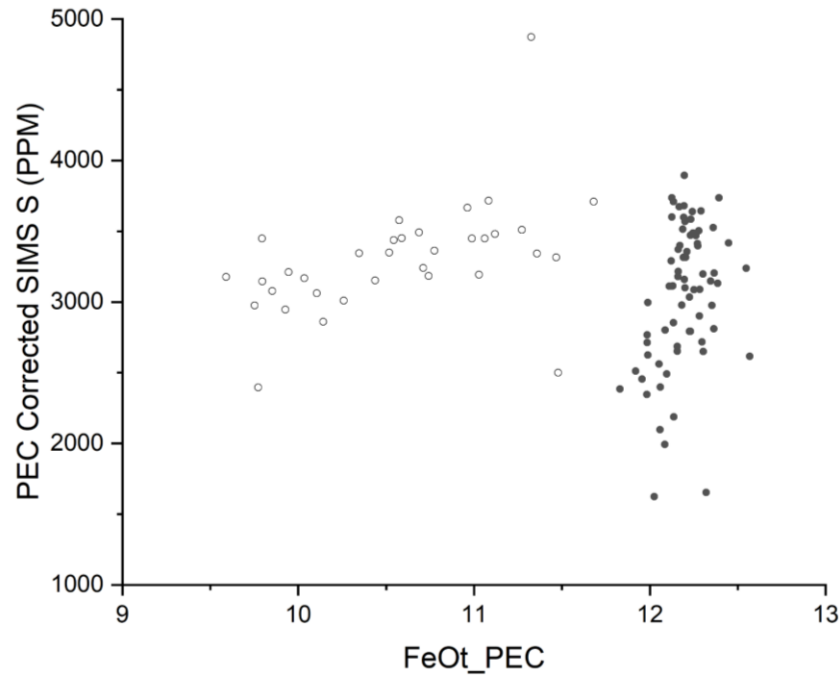


Figure R3: Correlation plot between S and FeO contents measured in the melt inclusions from literature data (Burton et al., 2023 and Dayton et al., 2024).

The MgO content is less affected by this effect and its relationship with S shows a clear increase from 2500 to >3500 ppm between 8.5 and ~ 6.5 wt% MgO, then slightly decreasing down to a maximum S content of 3500 ppm at 4.5 wt% MgO, suggesting possible precipitation of sulfide, S being exsolved only in subsurface (Burton et al. 2023).

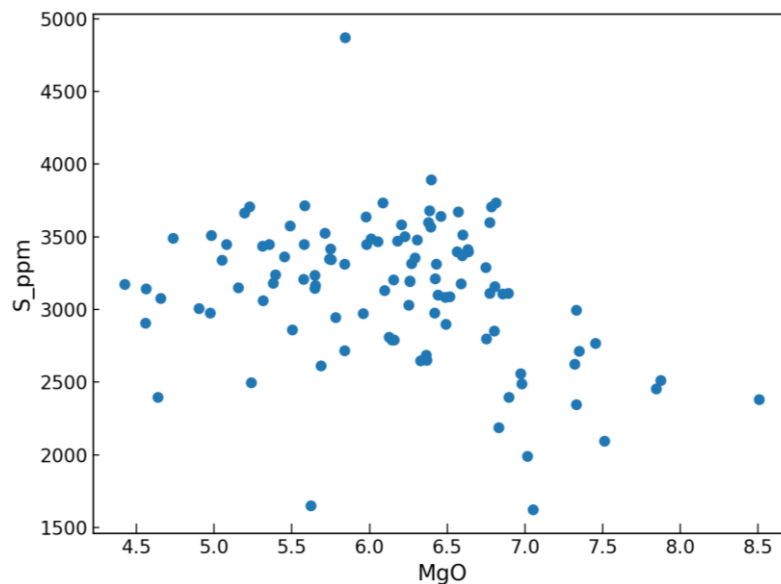


Figure R4: S vs. MgO diagram for the published MI showing an increasing trend between 8.5 and ~ 6.5 wt.% MgO that stabilizes at lower MgO contents.

To confirm this hypothesis, we further calculated the sulfur content at sulfide saturation using the PySulfSat tool (Wieser and Gleeson 2023) and added the following figure and description in the Appendix B.

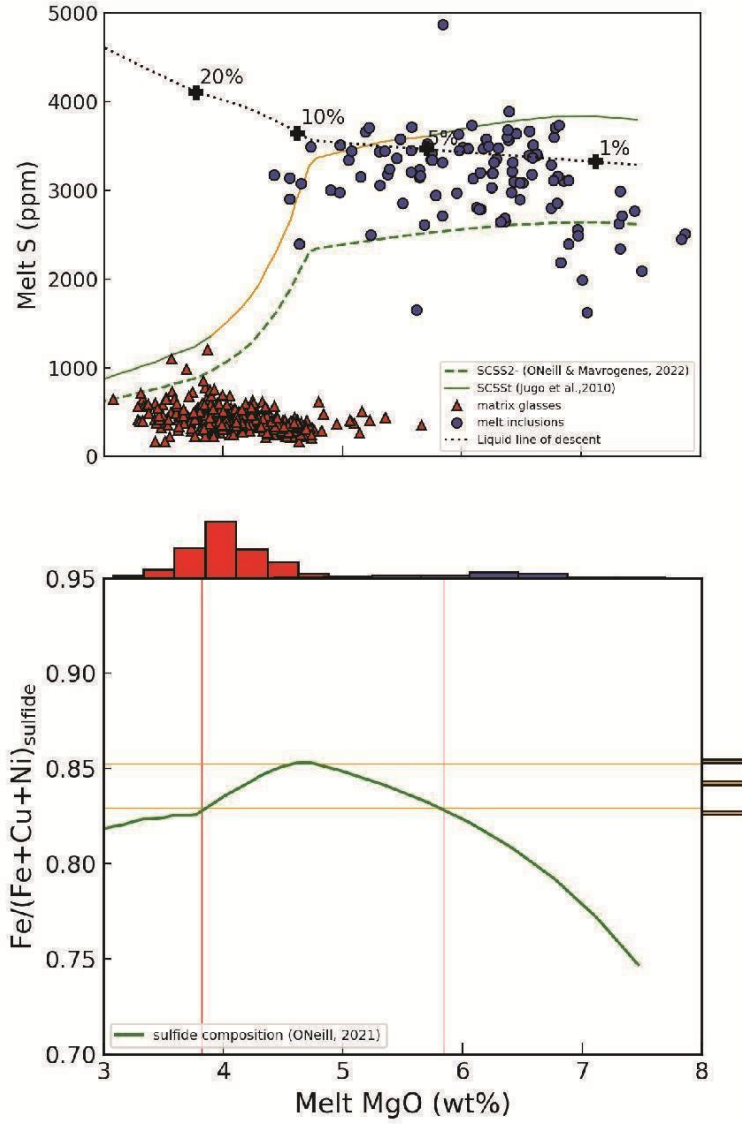


Figure R5: The upper panel shows the results of the sulfur content at sulfide saturation (SCSS) calculations performed using the model of ONeill (2021) implemented in the open-source Python3 tool PySulfSat (Wieser and Gleeson, 2023). The starting composition is one of the most primitive MI of the literature dataset for the eruption (LM0 G29 Dayton et al. 2024), to which a Petrolog3 (Danyushevsky and Plechov, 2011) crystallization model (with olivine±clinopyroxene + spinel as crystallizing phase, following Day et al. 2022) is applied at a magma stalling at 3.5 kbars and a fO_2 buffer of NNO+0.4, following Andujar et al. (2025). Given these conditions, the melt is expected to contain a significant proportion of sulfur as sulfate (S^{6+}), rather than sulfide (S^{2-}). Therefore, we used the SCSS1 model of Jugo et al. (2010), which accounts for mixed sulfur speciation, to evaluate saturation. Only a few inclusions slightly exceed the SCSS1 curve, consistent with the rarity of sulfide globules in the eruptive products and with the interpretation that sulfide saturation was only reached locally or after some crystallization (Day et al., 2022). The bottom panel shows the modeled composition ($Fe/Fe+Ni+Cu$) of the sulfide phase precipitating along the liquid line of descent, which is matching the measured compositions between ~4

and 5.8 wt% MgO (after 5-15% crystallization). This range is reported as the orange section of the liquid line of descent in the upper panel.

Figure B2: Please specify the sample types (tephra vs flow).

We checked over again the original publications to be sure, but the full dataset represented in this figure arises from tephra. For clarity, we added a line in the caption of figure B3: “*Matrix glasses have been measured on tephra samples and are from this study, Burton et al. (2023), Ubide et al., 2023, Dayton et al. (2024), Longpré et al. (2025).*”

Figure D1: The data from Asensio-Ramos et al. (2025) could be added to your Figure 4 also.

Done: We added the data from Asensio-Ramos et al. (2025) as shaded areas to the Figure 4 of the new version of the manuscript, for consistency with Figure 3, and updated the legend accordingly. In addition, following Reviewer 2’s comment, we removed the literature data from Figure D1 to clarify the message of the figure.