Bold: Reviewer comments
Regular: Author comments
Italic: Revised text

Reviewer 1

R1 General comment:
The manuscript, "Mixing states and composition of fine aerosol particles in the 2023 Canadian wildfire plumes detected in southern Greenland" reports the mixing states and chemical composition of ambient aerosol particles in southern Greenland and compares particle properties under wildfire-influenced and background conditions. Overall, the manuscript is generally well organized and provides valuable observations. However, the following issues should be addressed before publication. I recommend minor revision.

A1 Author comment:
We appreciate the reviewer's supportive comments to improve our manuscript.

R1-1:
Line 149: The statement that large soot particles were "externally mixed with sea salt and sulfate-dominated samples" appears unclear. External mixing generally means that different chemical components are present in separate particles. If soot, sea salt, and sulfate were detected within the same individual particles, this should instead be described as internal mixing. Please check this statement and clarify the intended meaning.

A1-1: We have revised the unclear sentence as follows:
Section 3.1:
Nevertheless, we occasionally observed large uncoated soot particles, possibly originating from local sources such as traffic and domestic activities, that were externally mixed with (i.e., present as particles separate from) sea salt and sulfate particles in the sea salt- and sulfate-dominated samples.

R1-2:
Section 3.2: Since the carbonaceous category includes both organic carbon and elemental carbon, please clarify whether the high fraction in background air mass was mainly associated with organic material or black carbon. Wildfires can emit substantial amounts of both organic carbon and black carbon; therefore, further discussion or evidence is needed to distinguish their respective contributions and explain the high carbonaceous particle fraction under

background conditions.

A1-2: Organic material dominated the carbonaceous particles in both background and wildfire samples. Although STEM-EDS alone cannot clearly distinguish between organic carbon and soot, soot particles can still be identified based on their characteristic aggregate morphology and graphitic structures in TEM images. The TEM image observation indicates that soot particles accounted for only a small fraction of the carbonaceous particles, i.e., uncoated soot particles accounted for <~1% of carbonaceous particles by number, and most soot particles were coated with organic materials. Therefore, the high carbonaceous particle fraction under background conditions is attributed mainly to organic material rather than soot (black carbon). We have added this clarification to the revised manuscript as follows:

Section 2.2:

Their predominant chemical forms are 1) aluminosilicate, 2) sodium chloride/sulfate, 3) potassium sulfate, 4) ammonium sulfate, and 5) organic material.

Based on TEM observations of particle morphology, the carbonaceous particle category was primarily composed of organic materials, while soot particles with varying degrees of organic coating accounted for only a small fraction.

In Section 3.4.2:

These aerosol particles predominantly consist of carbonaceous materials, mainly organic materials, and appear gray due to their amorphous structure and the relatively low atomic numbers of their constituent elements, which are primarily C, N, and O.

We have explained the high carbonaceous fraction under background conditions as follows:

Section 3.4.1:

Considerable amounts of carbonaceous and K-bearing particles were also present in the background air samples (Fig. 4). We hypothesize that these particles mainly originated from aged and diluted smoke from the Canadian wildfires (Fig. S3), although other sources, such as marine biogenic organic matter and local emissions, may also have contributed. This hypothesis is supported by the observation of thin organic coatings on sea salt particles (Fig. 7a) and sulfate particles (Fig. 8a), as well as by high fractions of carbonaceous particles in the small particle size ranges of background air samples (Fig. 4c).

R1-3:

Could the authors compare the characteristics and mixing states of wildfire-derived black carbon with those of black carbon from anthropogenic sources? (e.g. https://doi.org/10.1021/acs.est.6c03343; https://doi.org/10.5194/acp-19-10433-2019)

A1-3: The references are certainly interesting to compare. We have discussed those results as follows:

Section 3.4.1: *Teng et al. (2026) showed that small, uncoated soot particles with a peak size of around 141 nm were prevalent in samples collected near the Greenland coast in the early summer of 2022. As our samples were collected in a town, our large soot particles had a much shorter transport time from their emission sources (e.g., several hours), which may explain their larger particle sizes compared with those reported by Teng et al. (2026).*

Section 3.4.2: *Similar soot mixing states, in which multiple small soot particles are embedded within organic material, have also been observed in samples influenced by biomass burning plumes (Adachi et al., 2025a, 2025b) and in long-range transported samples in the Arctic (Yu et al., 2019). In contrast, samples collected without biomass burning influence did not show such soot mixing states (e.g., Teng et al., 2026). These results suggest that this soot mixing state may be characteristic of long-range transported biomass burning plumes.*

Reviewer 2

R2 General comment:

This study utilizes transmission electron microscopy to conduct a comprehensive single-particle analysis of fine particulate matter in southern Greenland during the summer of 2023. It provides a highly valuable microscopic perspective on the aging processes and mixing states of Canadian wildfire smoke after long-range transport. The record-breaking wildfire events of 2023 undoubtedly provided an unfortunate but excellent "natural laboratory" for atmospheric scientists. The manuscript is logically structured, and the comparative analysis between background air (dominated by sea salt and sulfate) and wildfire plumes (dominated by carbonaceous and potassium-bearing particles) is well presented. To further enhance the rigor and academic impact of this manuscript, I offer the following suggestions.

A2: We thank the reviewer for the constructive comments. We have addressed the suggestions as fully as possible, and we believe that they have substantially improved the manuscript. However, we could not fully address some suggestions because our dataset did not provide sufficient evidence. In such cases, we kept our interpretations conservative and maintained the focus of the paper on single-particle measurements rather than broadening its scope. Our point-by-point responses are provided below.

R2 Major comments

R2-1:

In Section 2.3, the authors estimate PM1 mass concentration by combining the volume distribution measured by FIDAS with TEM compositional analysis. This calculation relies on a strong assumption that the number fraction of aerosols measured by STEM-EDS directly represents the mass fraction of PM1 during the same period. Given the significant density differences among various particle types (e.g., mineral dust at 2.7 g cm -3 vs. carbonaceous particles at 1.4 g cm -3), a direct conversion from number to mass fractions will inevitably introduce non-linear biases. I suggest the authors add an uncertainty analysis regarding this assumption, or provide a basic discussion of the error margins in the methodology section to enhance data reliability.

A2-1: We agree. In our calculation, we assumed that the number fractions of particle types measured by STEM-EDS were equivalent to their mass fractions when estimating the average particle density, and this assumption introduces uncertainty. To evaluate a range of this uncertainty, we considered two extreme cases in which all particles were assumed to be either carbonaceous (1.4 g cm^{-3}; the minimum case) or mineral dust (2.7 g cm^{-3}; the maximum case). The actual values should lie between these two extremes. The estimated uncertainty ranges are between -25% and +50% of the estimated $PM_{1.0}$ values. We revised the text as follows:

Section 2.3: *This estimation assumes that the aerosol number fractions measured by STEM-EDS represent the mass fractions of the $PM_{1.0}$ measured at the same time. Assuming that all particles are either carbonaceous particles (1.4 g cm^{-3}; the minimum case) or mineral dust particles (2.7 g cm^{-3}; the maximum case), the estimated density and $PM_{1.0}$ values have an uncertainty range of -25% to +50%, which represents an upper bound because the actual aerosol density is expected to fall between these two extreme cases.*

R2-2:

In Section 3.1, this manuscript identifies three wildfire plume periods based on CO concentrations, estimated PM1 concentrations, backward trajectories, MASINGAR simulations, and particle composition. While the first two plume events appear convincing, the evidence supporting the third plume is substantially weaker. For Plume 3, the PM1 enhancement is relatively modest, and the modeled organic carbon transport shown in the supplementary material is much weaker than during Plumes 1 and 2. Consequently, the criteria used to classify this period as wildfire influenced are not sufficiently clear. I suggest the author provide a more objective and quantitative definition of wildfire plume periods.

Specifically: (1) What thresholds were used for CO enhancement? (2) What PM1 enhancement was considered significant? (3) Were MASINGAR organic carbon concentrations quantitatively evaluated? (4) How sensitive are the conclusions to the definition of the plume periods? If possible, additional independent evidence (e.g., CAMS aerosol analyses, MERRA-2 smoke products) would considerably strengthen the plume identification.

A2-2: As the reviewer pointed out, “Plume 3” was influenced by diluted smoke from the Canadian wildfires rather than by an intense plume such as Plumes 1 and 2. We changed the term “plume” to “period” throughout the manuscript, as the air mass during Period 3 was associated with a diluted wildfire pollution period. Nevertheless, the backward trajectories and particle compositions indicate that Period 3 was still influenced by the Canadian wildfires. Other accessible model products (e.g., SPRINTARS) also indicated a diluted smoke distribution.

Regarding the reviewer's specific questions: (1) we used a CO concentration of 0.15 ppm as a threshold (a baseline CO concentration was ~0.1 ppm), and (2) $PM_{1.0}$ concentrations > 2 μg m^{-3} were regarded as an enhancement (Section 3.1). (3) The MASINGAR organic carbon concentrations were not evaluated quantitatively; they were used qualitatively to examine the spatial distribution of the smoke. (4) Because compositions and mixing states changed gradually before, during, and after each period, our conclusions are not highly sensitive to the exact definition of these periods.

In summary, wildfire-influenced periods were identified using the following criteria: (1) CO mixing ratios exceeding 0.15 ppm, corresponding to an enhancement of at least 0.05 ppm above the campaign background of 0.1 ppm as shown in Figure 2; (2) $PM_{1.0}$ concentrations exceeding 2 μg m^{-3}; (3) backward trajectories passing over active fire regions in Canada, identified from MODIS fire detections, within 7 days before arrival; and (4) MASINGAR organic carbon concentrations evaluated qualitatively through examination of the spatial distribution of smoke. Period 3 met all criteria, although its $PM_{1.0}$ enhancements (2 μg m^{-3}) were smaller than those of Periods 1 and 2 (> 3 μg m^{-3}). This is consistent with more diluted smoke, as also indicated by MASINGAR simulations showing weaker organic carbon transport. We have revised the text accordingly.

Section 3.1: *Additionally, the period from July 23 to 25 showed a broad increase in CO concentrations (>0.15 ppm) with a modest enhancement in $PM_{1.0}$ concentration (~2 μg m^{-3}). Based on the elevated CO concentrations, aerosol composition, and model results, which will be discussed later, we also considered this period to be influenced by the Canadian wildfires that are the focus of this study (Period 3; from July 23, 14:00 to July 25, 02:00 in UTC).*

Section 3.1: *On July 24 (Period 3), a diluted plume from the Canadian wildfires was transported to the sampling site, although it was less distinct than in Periods 1 and 2. We consider Period 3 to be an airmass regionally influenced by the diluted plume from the Canadian wildfire, with some*

aerosols potentially being removed from the atmosphere during the transport.

In summary, wildfire-influenced periods were identified using the following criteria: (1) CO mixing ratios exceeding 0.15 ppm, corresponding to an enhancement of at least 0.05 ppm above the campaign background of 0.1 ppm; (2) $PM_{1.0}$ concentrations exceeding 2 μg m^{-3}; (3) backward trajectories passing over active fire regions in Canada, identified from MODIS fire detections, within 7 days before arrival; and (4) MASINGAR organic carbon concentrations evaluated qualitatively through examination of the spatial distribution of smoke.

R2-3:

In Section 3.4.2, the manuscript notes that unlike fresh wildfire samples typically found in the western US, tarballs were rarely detected in these long-range transported samples. The authors propose three hypotheses: minimal tarball production from Canadian wildfires, physical/chemical removal during transport, or high-altitude transport (1-5 km) missing the ground stations. While the authors frankly admit these hypotheses cannot currently be verified by their observational data, I suggest attempting to introduce third-party remote sensing data (such as CALIOP lidar vertical profiles, if it is available) to partially corroborate the "high-altitude transport" hypothesis, which would make the inference much more robust.

A2-3: We thank the reviewer for this helpful suggestion. Unfortunately, CALIOP lidar data were not available for our campaign period (starting from July, 2023) because the CALIPSO mission was being terminated at the end of June 2023.
https://asdc.larc.nasa.gov/calipso-imagery/lidar/browse_images/std_v500_index.php
Instead, Alden et al. (2026) reported vertically resolved aerosol observations, including ceilometer measurements, during the same campaign. These observations showed that the main wildfire plumes (Periods 1 and 2) were transported at altitudes > 1 km above ground level. We describe this information in the revised manuscript as follows (Section 3.4.2): *tarballs may have been transported primarily at higher altitudes—specifically, the main plumes were observed to be located at 1–5 km during Period 1 and 1–2 km during Period 2 by ceilometer observations during the campaign (Alden et al., 2026).*

R2-4:

In Section 3.4.2, The observation of numerous small soot particles internally embedded within organics is fascinating, and the authors correctly point out that the DEMA (Dynamic Effective Medium Approximation) model is more suitable than the core-shell model for describing the optical absorption properties of such mixed states. However, no optical calculations were performed in this study. Accordingly, the manuscript should clearly state that this is only a

hypothesis based on particle morphology and previous literature. Statements implying improved estimates of light absorption should be softened unless supported by optical simulations. In addition, to make this microscopic finding more directly applicable to future climate radiative forcing models, I suggest discussing whether it is possible to roughly estimate the average area or volume fraction of soot within these mixed particles based on the existing 2D TEM images.

A2-4: We thank the reviewer for these helpful suggestions. We agree that no optical calculations were performed in this study, and we have revised the relevant statements to clarify that the possible effects on light absorption are hypotheses based on particle morphology and previous studies. Performing optical calculations based on the TEM measurements would provide an advancement beyond the findings presented in this study. However, in the current manuscript, we prefer to focus on concisely reporting the findings obtained from the TEM measurements and briefly introducing their possible implications. Although it is possible to roughly estimate the soot volume fraction within the observed coatings by counting individual soot monomers, we do not believe it is realistic to obtain robust quantitative values for the entire sample set, because overlapping monomers are difficult to count accurately. Instead, we prefer to focus on demonstrating the fundamental occurrence and spatial distribution of soot particles within individual particles, such as their two-dimensional configurations revealed by TEM observations. Nevertheless, exploring the optical properties of soot based on observed configurations would be a valuable topic for a future study. We revised the text as follows:

Section 3.4.2:

A possible implication of the observation is that such soot mixing states may influence their light absorption properties (Tuccella et al., 2025).

The mixing of small soot particles within coating materials may be better represented by the Dynamic Effective Medium Approximation (DEMA) with Mie theory than by a core-shell model, as suggested by Chen et al. (2025).

Future studies based on optical calculations of these soot configurations are needed to quantitatively evaluate the effects of these mixing states on the radiative forcing caused by black carbon.

R2-5:

Supplementary Text 1 highlights the occasional observation of V-containing particles during background air periods, noting they are primarily mixed with sea salt (52%) and sulfate (28%), likely originating from anthropogenic sources like ship emissions or coal combustion. I suggest linking this independent finding to the discussion of the backward trajectories in Figure 3 (July 16), which clearly shows some air masses passing through anthropogenic

emission source regions in North America. This will significantly enhance the scientific coherence between the main text and supplementary materials.

A2-5: We agree that the detection of V-bearing particles is an interesting finding. Although they were relatively abundant during the background periods as well as the period 1, they were not detected in the samples collected on July 16, when the air mass originated from North America. Furthermore, the back-trajectory analysis did not clearly identify their source regions. We speculate that these particles may have originated from more local sources, such as ship emissions and/or other fuel combustion sources. However, despite investigating this observation during manuscript preparation, we were unable to draw definitive conclusions regarding their occurrence based on the available dataset. Therefore, we decided to briefly present this finding in the Supplementary Text rather than include an extensive discussion. We have revised the SI text as follows:
SI text 1: *The back-trajectory analysis did not clearly identify their source regions. We speculate that they can be sourced from local ship emissions or long-range transport.*

R2 Minor comments:

R2-6:
Please include a map indicating the sampling locations in the supplementary materials.

A2-6: Maps showing the location of the sampling point have been added in Supplementary figure 1.

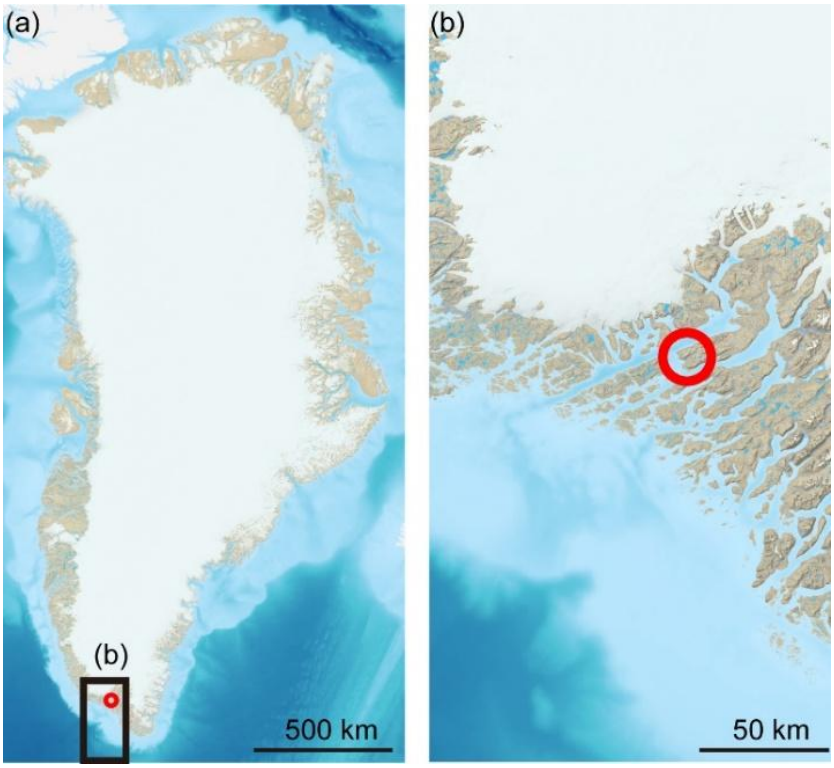


Figure S1. Sampling location at Narsaq, shown on (a) a map of Greenland and (b) a zoomed-in view of the surrounding area. Red circles indicate the sampling location. Map data were obtained from Geological Survey of Denmark and Greenland (GEUS). (2026). GEUS Map Server (Greenmin) [Interactive map]. https://maps.greenmin.gl/geusmap/ (Last accessed: September 17, 2026).

R2-7:

Line 169: The citation "(Jian et al., 2024)" is missing from the reference list and may be a typographical error for "(Jain et al., 2024)." Please verify this and carefully double-check all citations throughout the manuscript.

A2-7: We thank you for noticing this error and have corrected it accordingly.

R2-8:

Lines 241–243: Please provide a brief discussion regarding the variability of the sulfate and dust particles.

A2-8: We have added a brief discussion of the variability of sulfate and dust particles to Section 3.3 as follows:

Section 3.3:

Sulfate fractions were relatively higher during the first half of the campaign (July 4–19) than during the second half (July 20–August 4), possibly reflecting the larger burned areas in the source regions during the first half (Jain et al., 2024). The number fractions of dust particles were relatively low and showed no apparent peak period in the sampled fine-mode size range, suggesting that these particles would be less influenced by long-range transport of the wildfire smoke.

R2-9:

Line 262: Could the authors elaborate on the potential reasons for the observation that, "Although sulfate and chloride crystals can occur in the same particle, they tend to consist of different grains (Figs. 7a and 7b)"? The manuscript attributes this to replacement by sulfate and acidic species, but the discussion remains rather brief. The authors should discuss possible chemical mechanisms in greater detail, including: sulfuric acid displacement, nitric acid displacement, organic acid reactions, heterogeneous oxidation within wildfire plumes. This result has broader implications for aerosol aging and deserves a more comprehensive discussion.

A2-9: We have added a brief discussion of the possible reasons to the revised manuscript. The chemical processes suggested by the reviewer may indeed have occurred in our samples. However, because our observations were based on ambient particles, multiple processes may have operated simultaneously, with varying contributions among individual particles and heterogeneous reactions occurring both on particle surfaces and within particles. While we can speculate on these potential mechanisms, we have refrained from discussing them in greater detail because our current observations do not provide sufficient evidence to support specific reaction pathways. We agree that these processes are important and warrant further investigation. We therefore hope to address them in future studies that are specifically designed to observe and constrain such mechanisms. We have revised the manuscript as follows:

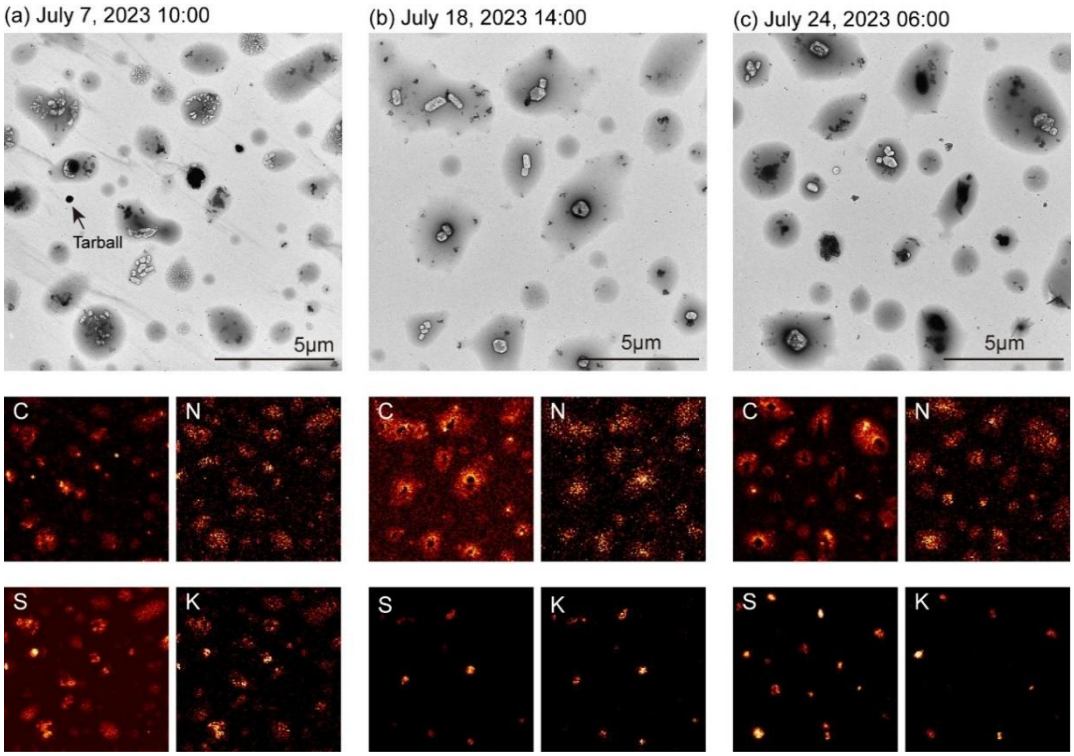
Section 3.4.1: *Although sulfate and chloride crystals can occur in the same particle, they tend to consist of different grains (Figs. 7a and 7b), possibly due to differences in the reaction rates with acidic gases and/or in the efflorescence relative humidity of each salt.*

Section 3.4.1: *This result suggests that wildfire plumes modify the sea salt composition by replacing Cl with sulfate and other acidic species (e.g., nitric and organic acids) and releasing HCl to the gas phase and indicates significant chemical processing during wildfire plume transport.*

R2-10:

Figure 9 (a): Please change the color of the arrow pointing to the tarball to improve visibility.

A2-10: The arrow has been revised.



R2-11:

Please add the time series of the meteorological conditions in the main text or supplementary information, including (1) relative humidity and temperature, (2) wind speed and wind direction, (3) precipitation, and (4) boundary layer height. This information would help interpret aerosol variability.

A2-11: We have added data on temperature, relative humidity (RH), precipitation, wind direction and wind speed in Supplementary Figure 2, obtained from an open dataset (Alden et al., 2025). Unfortunately, boundary layer height data was unavailable, so we do not discuss it in the current manuscript. These meteorological conditions have been discussed by Alden et al. (2026), and we have referred to their summary in our main text (Section 2.1).

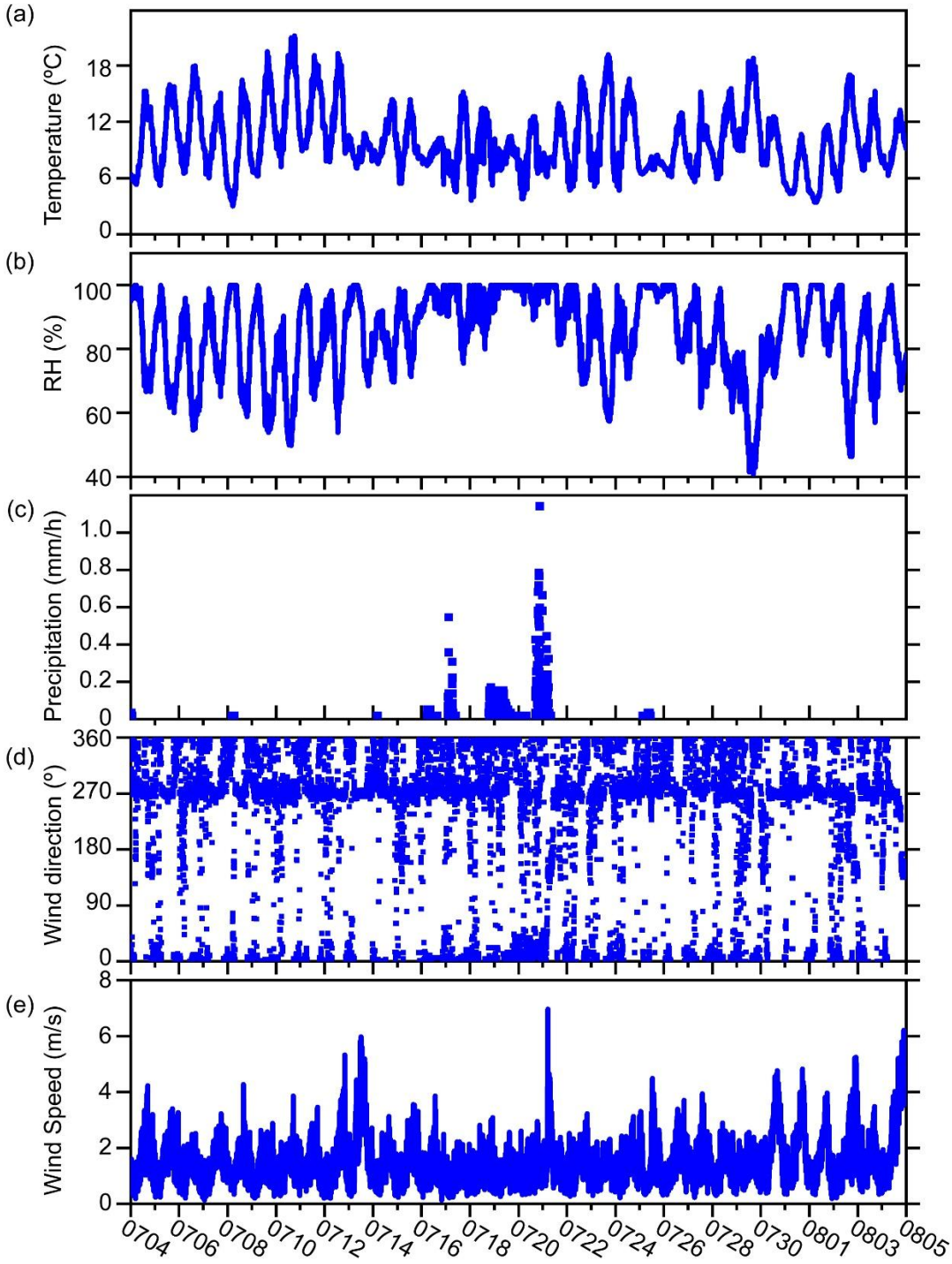


Figure S2. Meteorological parameters observed at the sampling site. (a) Temperature, (b) relative humidity (RH), (c) precipitation, (d) wind direction, and (e) wind speed are shown. Data were obtained from Alden et al. (2025, 2026).

R2-12:

Figure 7 could quantify the degree of chloride depletion (e.g., average Cl/Na ratio) rather than showing only scatter plots.

A2-12: We have replaced the plots from the sample average values to individual particle values to discuss the Cl/Na ratio on an individual particle basis. The average Cl/Na ratios for individual sea salt particles with Cl > 1.0 wt% from background samples are 1.5 on a weight basis and ~1.0 on a molar basis. This result indicates that they are fresh sea salt particles. In addition, the correlation between Cl and Na is relatively strong ($R^2 = 0.66$), indicating a linear relationship when the samples contain appreciable amounts of Cl for background samples. On the other hand, almost no Cl was detected in sea salt particles from wildfire-influenced plume samples. Based on these results, we infer that the background samples experienced little chloride loss, whereas the wildfire-influenced samples underwent substantial chloride depletion. In other words, the degree of chloride depletion is inferred to be close to 0% in the fresh (background) samples and nearly complete in the wildfire-influenced samples. We have discussed this interpretation in the revised manuscript as follows: Section 3.4.1: *In addition, these background sea-salt particles showed a correlation between Na and Cl (Cl/Na = 1.5 on a weight % basis and 1.0 on a molar basis) (Fig. 7d), suggesting that they consisted predominantly of fresh sea salt. Conversely, almost no Cl was detected in sea salt particles from wildfire-influenced samples. This result suggests that wildfire plumes modify the sea salt composition by replacing Cl with sulfate and other acidic species (e.g., nitric and organic acids) and releasing HCl to the gas phase and indicates significant chemical processing during wildfire plume transport.*

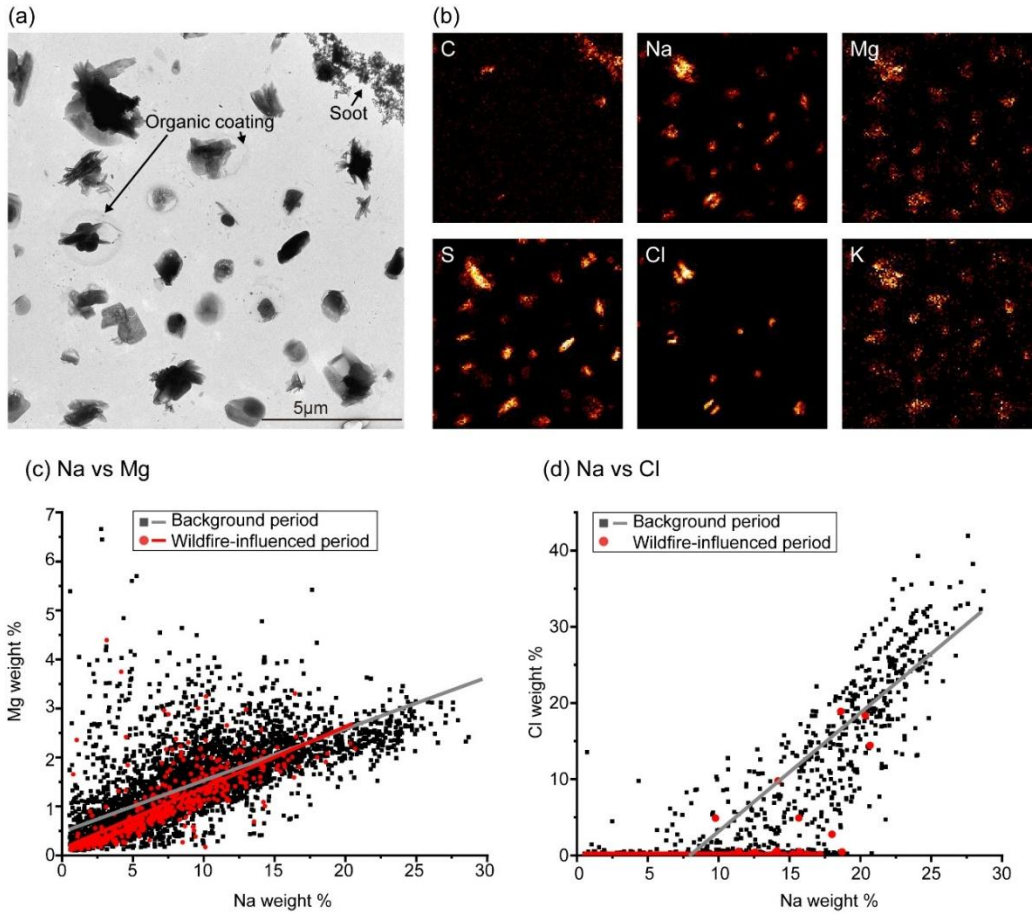


Figure 7. A representative image of sea salt dominant sample and sea salt composition. (a): A transmission electron microscopy image of a sample from the sea salt-dominated background period on July 4 2:00 (UTC). (b): Elemental mapping images of C, Na, Mg, S, Cl, and K in the area shown in the TEM image. (c): Relationship between Na and Mg weight percentages and (d) Na and Cl weight percentages for all individual sea-salt particles. Regression lines for sea-salt particles from both periods are shown in (c). A regression line for individual sea-salt particles with Cl > 1.0 wt.% during the background period is shown in (d).

References:

Alden, J., Bergner, N., Heutte, B., Farinotti, D., Favre, L., and Schmale, J.: Meteorological data from multiple weather stations in Narsarsuaq and Narsaq, South Greenland during Greenfjord 2023, Zenodo [data set], https://doi.org/10.5281/zenodo.15388080, 2025.

Alden, J., Bergner, N., Heutte, B., Favre, L., Surdu, M., Weng, J., Augugliaro, M., Winiger, P., Dönmez, B., Pohorsky, R., Calmer, R., Chatterjee, C., Violaki, K., Nenes, A., Gregor, L., Henning, S., and Schmale, J.: Vertically-resolved source contributions to climate-relevant aerosol properties in Southern Greenlandic fjord systems, Atmospheric Chemistry and Physics, 26, 7165–7191, 10.5194/acp-26-7165-2026, 2026.