Response to referee #2

The paper by Bohleber et al. presents the first attempt at two-dimensional mapping of S and Cl in EDC and EGRIP deep ice cores using LA-ICP-MS. Although both elements are relatively abundant in these cores, due to analytical challenges with ICP-MS, they have not been previously targeted by LA-ICP-MS studies. This paper shows that signals of S and Cl can be detected even in samples that do not contain elevated concentrations of volcanic S and Cl. Since both S and Cl are important for understanding mechanisms and extents of impurity diffusion in ice—crucial for interpreting the chemical signatures of "Oldest Ice"—the new methods developed in this study have great potential for future ice core research. The paper also demonstrates that not only the most abundant isotope of S, but also less abundant isotopes can be detected. This would contribute to investigating sources of S. Therefore, I strongly support the publication of the fascinating new results presented in this paper.

We thank the reviewer for the appreciation of this work and the constructive comments, that helped us to improve and expand in particular the presentation of the results and the discussion part of the manuscript.

However, I have a question or concern regarding the conclusion about the localization of S. The authors find a high level of localization of S at grain boundaries, with only minor occurrences within grain interiors even in glacial ice. Previous studies using Raman spectroscopy (Ohno et al., 2006; Sakurai et al., 2011; Stoll et al., 2021) reported numerous S-containing salts or minerals such as Na_2SO_4 and $CaSO_4$. I wonder why the samples used in this study did not contain many of these S-containing particles in grain interiors. Although there may be differences between Dome Fuji (Ohno et al., 2006; Sakurai et al., 2011) and EDC samples (this study), Stoll et al. (2021) used EGRIP samples, as in this study. I wonder if this discrepancy is due to a sample-to-sample (or layer-to-layer) difference, or if it might be an artifact of the analytical methods used here. I would like to see some explanations about the difference between the findings of this study and those of previous studies.

This is a very good point which we have now addressed in more detail in the discussion. First and foremost, we note that the EGRIP sample does show some isolated clusters of high intensity pixels in grain interior locations for Na and S – some co-localised and some with only S. Also in EDC, e.g in sample EDC1819-2, we find high intensity spots in the grain interior. We have highlighted this better in the Figures, and also stress this finding more in the discussion.
In general, we find that comparing the data generated by two different methods is extremely difficult. In two earlier papers (Stoll et al., 2023; Bohleber et al., 2023) we crossed this inter-method bridge between Raman spectroscopy and LA-ICP-MS by analysing the same very dust-rich samples of Greenland cloudy bands with both methods resulting in comparable results. Here, the dust is so abundant and often clustered (larger size) which greatly aids its detection in LA-ICP-MS mapping. Some results showed promising consistencies, e.g. the relative fraction of particles at grain boundaries being very similar seen in both techniques (Bohleber et al., 2023).
We do not believe that differences are related to artefacts. It should be emphasized that LA-ICP-MS and single particle Raman spectroscopy have very different analytical figures of merit which provide insights into different aspects of insoluble particles and soluble species. Raman spectroscopy is applicable to look at a limited number of large particles (diameter of 1 micrometer or above) but cannot resolve smaller particles or ionic (dissolved) fractions

(see Stoll et al. 2021, 2022, 2023). LA-ICP-MS detects both fractions but does not allow a differentiation between ionic and particulate element species. We have spotted several instances of isolated hotspots within the crystal structure, which we suspect to be associated with discrete insoluble particles. However, grain boundaries are composed in a more complex fashion and a definite differentiation was not possible. As such, Raman spectroscopy and LA-ICP-MS are not expected to directly validate each other but rather to grant complementary insights.
Notably, the same situation applies to the comparison with the pioneering works investigating S in ice with SEM-EDS (e.g. Mulvaney et al., 1988). Although in this case we have consistent findings with LA-ICP-MS regarding the presence of S at triple junctions. As explained in the text we suspect that limits of detection may not have been sufficient to detect S at grain boundaries with SEM-EDS.

The paper states that the new impurity maps support a view of diffusive transport not only through ice veins but also along grain boundaries, yet do not show clear differences between samples from the Holocene and the last glacial period in the EDC core. Based on these findings, the authors seem to reject the hypothesis by Rhode et al. (2024) that the diffusion mechanism changed between the Holocene and the last glacial period due to changes in localization. However, if the amount of S in grain interiors changed between the Holocene and the last glacial period but was not detected by the methods used in this study or not observed in the specific samples analyzed by chance, the authors cannot completely deny the hypothesis. Therefore, I would like the authors to confirm that the very low amount of S detected in grain interiors in glacial EDC ice is robust and not an artifact caused by analytical issues.

We can confirm that the low amount of S in the grain interiors is robust and consistent with other data generated on EDC samples before and after this study. To be fully clear: Small amounts of S may be present in the interior (see comment above). Regarding the implications for the hypothesis by Rhodes et al. (2024), we have rephrased the respective text in the discussion to make clear we are not completely discarding this hypothesis based on our, admittedly, limited “snapshots”. We would also like to point out that our data is consistent with a recently formulated view that the majority of the diffusion is triggered at shallow depths and that only minor differences occur after (Ng et al., 2025).

Ng, F. S. L., Rhodes, R. H., Fudge, T. J., and Wolff, E. W.: Doomed descent? How fast sulphate signals diffuse in the EPICA Dome C ice column, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2025-1566, 2025.

Additionally, I have some minor editorial comments, which are listed in the “Detailed comments” below.

Detailed comments:

1. **Section 2.1** – This section needs more details on how this study succeeded in detecting S and Cl using LA-ICP-TOFMS. I recommend moving a major part of Lines 223–251 to Section 2.1, as this part is more appropriate in the Methods section rather than the Discussion.
   Changed accordingly, also to address comments by reviewer #1.

2. **Line 145, pre-ablation** – Please explain more about pre-ablation. If this involves sublimation of the sample surface, I have a concern that grain boundaries might be preferentially sublimated compared to grain interiors, which could lead to concentrated impurities at grain boundaries. Please confirm that this is not the case.
   This is an important issue which we have taken seriously from the beginning starting with LA-ICP-MS mapping on ice. So far, we have concluded that the grain boundary localization is not an artifact caused by sublimation, although we do not feel comfortable with a giving an ultimate answer (if there is ever such a thing in science). Notably, already in the first study (Bohleber et al., 2020) we experimented with various consecutive maps taken on top of each other, each exposing a new surface- and including further experiments with preparing fresh surfaces for sequential mapping of the same area. The purpose of pre-ablation is to remove the surface layer immediately before analysis, providing an additional decontamination step. How thick this layer is, is hard to estimate, but visible ablation is traceable in general, especially with larger spots.
   We have also investigated the effects of repeated ablation on the same ice core area to investigate to what extent elemental maps can be obtained repeatably. These experiments have shown qualitatively the same elemental distributions, which is a clear indication that sublimation and the artefact generation as suggested is not a driving mechanism.
   We further would like to emphasize again that intra-grain intensities do occur, so the grain boundary localization is not the full story. Moreover, not all impurities are found at grain boundaries by LA-ICP-MS mapping. Impurities with a significant insoluble fraction like Al, Si and Fe can also lack the grain boundary association (e.g. for the cloudy band sample in Bohleber et al., 2023), or show it much less pronounced.
   Recent calibration experiments provided an additional route for cross-checking the LA-ICP-MS maps: we found that the concentrated impurity values at the grain boundaries are consistent with (lower) bulk concentration levels measured on the same sample after melting. We further found that the comparison with meltwater analysis revealed that the LA-ICP-MS maps correctly predicted which samples had a substantial contribution from insoluble particles (Bohleber et al., 2024).
   In summary, we have found no evidence for the grain boundary localization being an artefact. Especially no evidence of a time-dependent effect changing the impurity distribution on the ice surface was found, which would arguably be the case if sublimation was the dominant cause of the grain boundary signal.
3. **Table 2** – Please add concentrations of S (or SO_4^{2-} would be fine), Cl, and Na for the samples used in this study. If the data from exactly the same depths are unavailable, concentrations from similar depths would be helpful to better understand the differences among samples.
   For the exact depths we unfortunately do not have any data. We intend to keep the samples used for this study available for further analysis, thus did not melt them for analysing liquid concentrations (since not in focus here). The EGRIP CFA chemical record is work in progress and, so far, no data on S or SO4 concentrations is available.
4. **Figures 1, 2, 4, and S2** – It is difficult to see grain boundaries and air bubbles in the optical mosaic images. Please add optical mosaic images with marked grain boundaries and air bubbles for each figure. Figure S1 also needs an optical mosaic image to show grain boundaries.
   Changed accordingly.

5. **Lines 166–167, "In EGRIP 2286…… (Fig. 2)"** – It is hard to identify the isolated pixels within the grain interior showing high S values. Please mark these pixels clearly.
   Changed accordingly. Note these pixels in relation to the first comment above about detecting mineral dust (and salt) particles.
6. **Lines 167–169, "The EGRIP cloudy…… (40 µm EDC)"** – It is hard to see the intensity difference between EGRIP and EDC. To confirm this, the authors need to show the intensity data.
   We are not sure we fully understand this request, as the intensity is already shown as the scale on the color map of figures 1 and 2, and the color-coded maps provide arguably the best representation of our 2D data. However, considering carefully this comment and the following 7. & 8., we made an attempt for an alternative quantitative overview, trying to address the comments 6,7 and 8 here.
7. **Lines 169–170, "Both maps show…… a few mm"** – Please show the intensity data for the grain boundaries.
   We would like to point out that with this part of the text we referred to the spatial variability in the grain boundary intensities – something you can only show with the 2D maps. We tried to illustrate that with a concrete example in lines 171-173.
   In the context of comments 6, 7, 8: We understand this as a request to separate out the intensities at the grain boundaries from our data, and have come up with the following solution: First, to show the entire dataset we calculated the histogram of the intensity values of the entire map (shown exemplarily in the Figure below – to be included in the manuscript or the Supplementary Material). Here we typically observe a bimodal distribution with one mode corresponding to the low intensity grain interiors and another mode matching the high intensities at grain boundaries. To confirm this, we segmented out the pixels belonging to the grain boundaries using a watershed algorithm (as in Bohleber et al., 2023). The red dot and line indicate the median and its interquartile range of the grain boundary pixels, respectively.

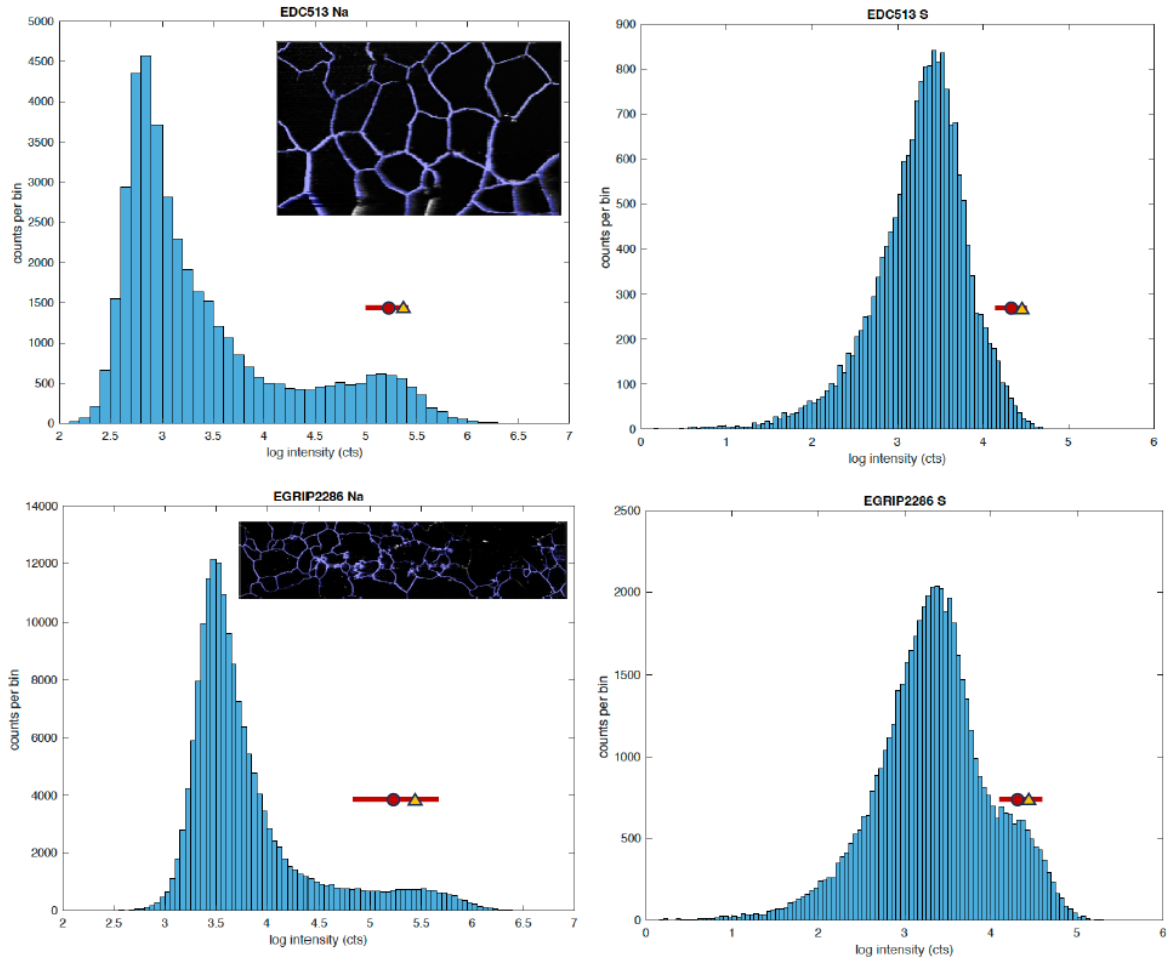

Figure xy: Intensity distributions shown as histograms for Na & S of Figure 1 and 2 in the main manuscript. Note the bimodal distribution, especially visible for Na, which correspond to high intensity foreground (e.g. grain boundaries) and low intensity background (grain interiors) of the image. The inserts in the Na histograms show the grain boundary segmentation. Red dots denote the median of the thereby segmented grain boundary pixels, the red line extends within the 25-75% interquartile range. Yellow triangles denote the median intensity of pixels at the triple junctions (segmented manually).

8. **Lines 173–174, "At 40 µm and …… at triple junctions"** – I'm not convinced by this sentence. Some triple junctions appear to show strong intensities. The authors need to provide more quantitative discussion here, as I wrote in comments 6 and 7. It is indeed hard to assess intensity variability just from visual images.
   Our main point here was that we believe this to be a (partial) matter of resolution, as only very high resolution (1 µm) may be able to resolve the concentration differences between the triple junction and its adjacent grain boundary due to the very small size of theses microstructural features. To further substantiate the sentence referred to here we now include an exemplary investigation into the triple junctions of Figures 1 and 2. We manually segmented the pixels belonging to triple junctions in both maps, and calculated the respective median value, which is shown as a yellow triangle in the Figure above. It becomes clear that, albeit slightly elevated with respect to the median of the grain boundaries, the triple junction value in all cases still falls within the interquartile range. We thus regard this as no clear evidence for a clear

enhancement at the triple junction – but again, we stress that this is likely connected to the spatial resolution of 40 and 20 µm not being sufficiently high.

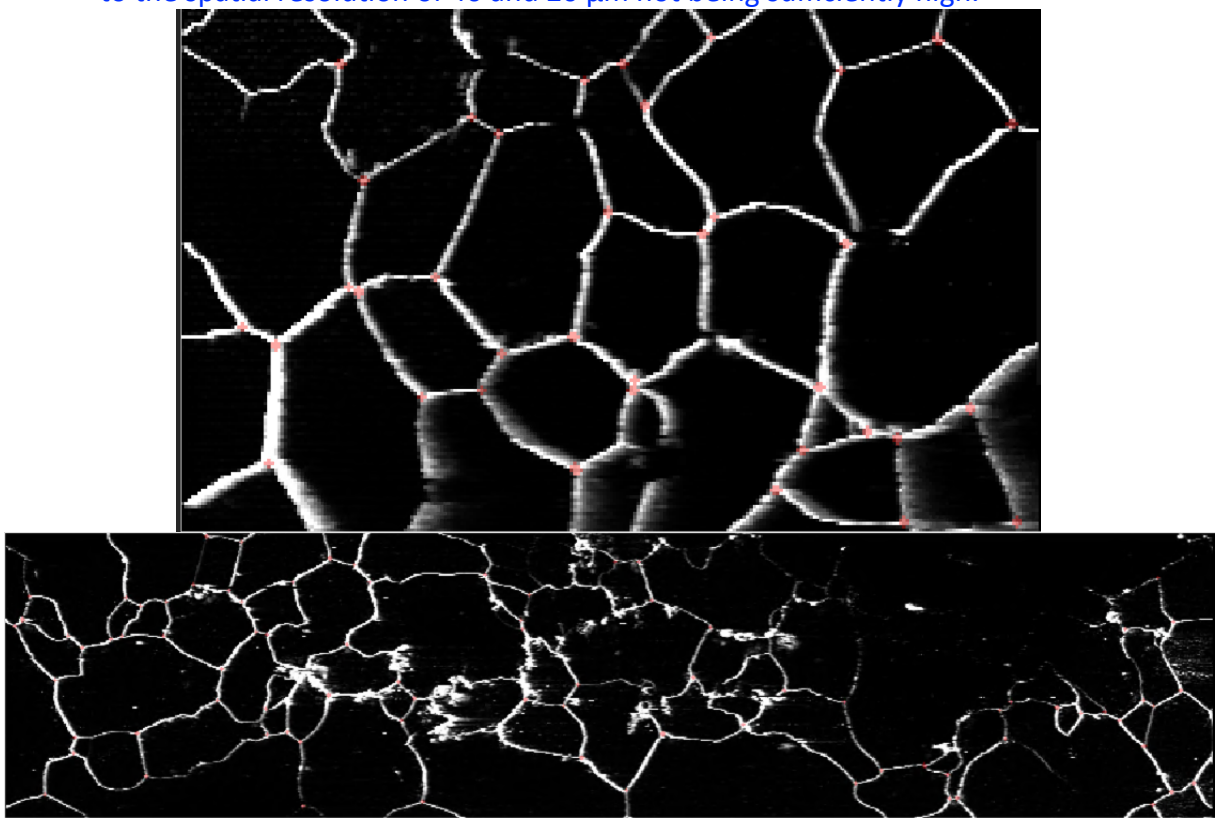

Figure xy: Manual segmentation of the pixels belonging to triple junctions in Figure 1 and 2, shown on top and bottom, respectively. Red crosses show the segmented pixels at triple junction. Their median values are shown in the Figure above as yellow triangles.

9. **Figures 3 and 4** – Please add the spot size in the figure captions. Although it is mentioned in the text, including it in the captions would make it easier to follow.
   Changed accordingly.
10. **Figures 1, 3, 4, 5, 6, S1, S2, S3** – Please use larger fonts in the diagrams.
    Changed accordingly.
11. **Line 226, "Fig. 1–7"** – This should be "Fig. 1–6." There is no Fig. 7.
    Changed accordingly.
12. **Line 250, "It is likely that also ^{37}Cl is mass-shifted and detected at ^{39}K instead."** – If this is the case, please explain why the authors can still distinguish between K and Cl signals. Why can we be sure that the signals in the maps represent Cl?
    We can clearly distinguish Cl and K by taking the isotopic abundance of Cl into account. The mass shifting of Cl is an element-specific feature, which happens to Cl alone. As such, ^{35}Cl and ^{37}Cl are mass shifted to $^{35}Cl^{1}H_2^+$ and $^{37}Cl^{1}H_2^+$, respectively. The latter has a spectral overlap with K and on its own, it cannot be differentiated from ^{39}K. However, the former ($^{35}Cl^{1}H_2^+$) does not show any overlap with other elements and can selectively be detected as proxy for the Cl distribution.
13. **Lines 286–288** – Why do the intensities at grain boundaries depend on scan direction? Why does this dependence only appear for the 1 µm spot size? Unless a clear explanation is given, I'm concerned about the authors' discussion on differences in signal intensities.
    We do not have an explanation for this effect yet as LAICPMS analyses at 1 µm are novel to ice core research and we are investigating it further. While refraining from

speculation we still wanted to point it out, however, for full transparency. We did not observe this dependency on scan direction at coarser spot sizes (e.g. 10 µm), and thus the vast majority of the data. Investigating this issue further is beyond the scope of this study and could be the main topic of discussion in a future study.

14. **Lines 313–322** – Considering previous studies, I would expect higher concentrations of Na in grain interiors. However, this is hard to see in Figures 2, 3, or 4. Please mark Na in grain interiors more clearly.
    Changed accordingly. We also note again, that the EGRIP map (Figure 2) is consistent with what we have previously observed in cloudy band samples from Greenland (Bohleber et al., 2023, Stoll et al., 2023).
15. **Lines 332–334, "At least for sections… bulk S concentration."** – I agree that it is difficult to see systematic differences between the data presented here. However, if the ratio of S at grain boundaries to grain interiors changes (but not detected by the methods used in this study), it could affect the apparent diffusivity. To draw a conclusion, I think more quantitative analysis is needed.
    To be clear: We can observe intra-grain concentrations – the primary challenge is not the localization but the detectability. If individual minerals / salts are much smaller than the spot size, the resulting intensity contrast becomes weaker and harder to detect. This means that, even if present, the relative fraction of the grain interior contributions to the bulk concentration is small for Na, Cl and S – hence also their expected contribution to alterations via diffusion. Within these limitations, there is no systematic difference in the impurity localization, providing valuable constraint for discussion potential impurity diffusion mechanisms.
16. **Lines 346–349** – From Figures 3 and 4, it is difficult to see partially interrupted impurity populations at grain boundaries and air bubbles in glacial maps. Please show these features more clearly.
    Changed accordingly.
17. **Lines 357–365** – If S/Na and Cl/Na at grain boundaries are similar for Holocene and glacial samples, I don't think this necessarily argues against a relative difference. Changes in the amounts of these elements in grain interiors—possibly not observed by the methods used—could result in apparently different diffusivity.
    See our reply to comment 15. One of the primary merits of the maps shown here is that they can constrain the contributions by grain boundaries and interiors. From the limited snapshots that we can provide so far, in-grain concentrations should not be drastically different, or they would have been rising to detectable limits. We would also like to stress that, in the previous direct comparison with liquid ICP-MS analysis (Bohleber et al., 2024) we found no evidence for a systematic underestimation of concentrations by LA-ICP-MS, which would indicate that we are systematically missing some fraction due to limits of detection. This is not the case.
18. **Lines 384–385, "but do not show any …. EDC ice core."** – If impurity localization at grain boundaries and veins shows no clear differences, differences in grain size would change the ratio of grain boundaries and veins in a unit volume, potentially affecting diffusivity. However, smaller grain sizes in glacial ice would give larger ratios of grain boundaries and veins, leading to faster diffusion, correct? I think grain size data are also important for considering diffusion mechanisms.
    We agree that grain size variability and/or rate of grain growth *may* be important determinants on diffusion rate, depending on the mechanism(s) acting. Barnes et al., 2003 provide two different sulfate diffusion mechanisms that both imply increased

diffusivity with increased grain growth rate. However, this relationship was not observed for EDC sulfate by Rhodes et al., 2024 or Fudge et al., 2024. But, it would be most recognizable in deeper EDC ice than investigated by those studies (or here) where temperatures exceed -10C and migration recrystallisation (rather than normal grain growth) occurs.

Ng's 2021 proposed diffusion mechanism within veins is 'independent of grain growth and occurs in the absence of grain-size variations'. Ng (2021) also defines 'residual diffusion' resulting from vein motion due grain boundary migration (normal grain growth assumed). Ng concludes that diffusivity is independent of grain diameter even in this case because "smaller grains lead to faster grain boundary migration but proportionally shorter mean free path for the vein motion" (see his Appendix B). Smaller grain sizes and therefore greater area of veins and/or grain boundaries per unit volume will not automatically cause faster diffusion. Diffusivity is not reported per unit volume (unit: m2yr-1). The level of interconnectedness between veins and grain boundaries, which may be impeded by bubbles or particles, will also play a role.

References

- Barnes, P. R. F., Wolff, E. W., Mader, H. M., Udisti, R., Castellano, E., & Röthlisberger, R. (2003). Evolution of chemical peak shapes in the Dome C, Antarctica, ice core. Journal of Geophysical Research: Atmospheres, 108(D3).
- Bohleber, P., Larkman, P., Stoll, N., Clases, D., Gonzalez de Vega, R., Šala, M., ... & Barbante, C. (2024). Quantitative insights on impurities in ice cores at the micro-scale from calibrated LA-ICP-MS imaging. Geochemistry, Geophysics, Geosystems, 25(4), e2023GC011425.
- Bohleber, P., Stoll, N., Rittner, M., Roman, M., Weikusat, I., & Barbante, C. (2023). Geochemical Characterization of Insoluble Particle Clusters in Ice Cores Using Two-dimensional Impurity Imaging. Geochemistry, Geophysics, Geosystems, 24(2), e2022GC010595.
- Bohleber, P., Roman, M., Šala, M., & Barbante, C. (2020). Imaging the impurity distribution in glacier ice cores with LA-ICP-MS. Journal of Analytical Atomic Spectrometry, 35(10), 2204–2212.
- Fudge, T. J., Sauvage, R., Vu, L., Hills, B. H., Severi, M., & Waddington, E. D. (2024). Effective diffusivity of sulfuric acid in Antarctic ice cores. Climate of the Past, 20(2), 297-312.
- Mulvaney R, Wolff EW and Oates K (1988) Sulphuric acid at grain boundaries in Antarctic ice. Nature, 331(6153), 247–249 (doi: 10.1038/331247a0)
- Ng, F. S. (2021). Pervasive diffusion of climate signals recorded in ice-vein ionic impurities. The Cryosphere, 15(4), 1787-1810.
- Rhodes, R. H., Bollet-Quivogne, Y., Barnes, P., Severi, M., & Wolff, E. W. (2024). New estimates of sulfate diffusion rates in the EPICA Dome C ice core. Climate of the Past, 20(9), 2031-2043.
- Stoll, Nicolas, Eichler, J., Hörhold, M., Shigeyama, W., & Weikusat, I. (2021). A review of the microstructural location of impurities in polar ice and their impacts on deformation. Frontiers in Earth Science, 8, 658
- Stoll, N., Hörhold, M., Erhardt, T., Eichler, J., Jensen, C., & Weikusat, I. (2022). Microstructure, micro-inclusions, and mineralogy along the EGRIP (East Greenland Ice Core Project) ice core–Part 2: Implications for palaeo-mineralogy. The Cryosphere, 16(2), 667-688.
- Stoll, N., Westhoff, J., Bohleber, P., Svensson, A., Dahl-Jensen, D., Barbante, C., and Weikusat, I. (2023). Chemical and visual characterisation of EGRIP glacial ice and cloudy bands within, The Cryosphere, 17, 2021–2043, https://doi.org/10.5194/tc-17-2021-2023.