

## Response to referee #1 Hanna Brooks

### Overall quality of the preprint manuscript

This preprint manuscript presents new findings on the spatial distribution of sulfur (S), chlorine (Cl), and sodium (Na) in polar ice using high-resolution laser ablation inductively coupled plasma mass spectrometry (LA-ICP-TOFMS). The study focuses on samples from the EPICA Dome C (EDC) core in Antarctica and the EGRIP core in Greenland, aiming to understand impurity localization and its impact on post-depositional diffusion. The results show that S, Cl, and Na are predominantly localized along grain boundaries, with limited evidence for accumulation at triple junctions or within grain interiors, except in dust-rich ice. These findings suggest that diffusion may occur primarily along grain boundaries rather than through interconnected veins, challenging assumptions that post-depositional mobility varies significantly with climatic periods. The study highlights the need to integrate impurity mapping with modeling efforts to better constrain diffusion processes that affect paleoclimate records preserved in deep ice cores.

While the fundamental science discussed in the preprint is a significant contribution to the field and is clearly within the scope of The Cryosphere, the manuscript text requires substantial reworking before it is suitable for publication. In particular, the framework established in the introduction and methods sections lacks clarity and cohesion, making the central aims and motivations of the study difficult to follow. This undermines the accessibility of the results and their implications, even for readers familiar with ice core and/or LA-ICP-MS science. Once the manuscript has undergone major revision, it will be a lovely addition to The Cryosphere.

We thank the referee for her effort in providing help in making the manuscript more accessible to the readers of TC. We generally followed these suggestions and believe it has significantly increased the clarity of the text.

### Individual scientific questions/issues/comments

For ease of reading, specific comments, questions, and issues have been broken into sections. Generally for each section, a list of small, specific comments by line number follows the more general comments.

### Abstract

The abstract does a great job of summarizing the work presented. There are just a few comments to help readers as they are introduced to the presented work.

### Specific comments by line number:

- Line 12: “Na, S and Cl are among the relatively abundant impurity ... precise physical mechanisms remain unclear.”

Does one expect that similar post depositional effects are seen in Na and Cl?

Very generally, each chemical impurity could be affected differently by post-depositional movement. Differences may arise based on ionic radius and charge (cations and anions) as well as localization within the ice. This is a highly simplified answer, of course. The second sentence quoted here refers to diffusion, which may affect not exclusively S (or sulfate) – and for this the physical mechanism remains to be fully identified. This is where we hope to make a contribution with the manuscript – complementary to modelling and data-based

efforts investigating peak-broadening. Due to the brevity of the abstract, not much has been added but this aspect is picked up on in the revised introduction.

Do we know enough about the system to know that there is an element that does not suffer post-depositional changes?

The short answer: No. The application of LA-ICP-MS is an entirely new paradigm to study the distribution of elements at the microscale and it ultimately might contribute to an enhanced understanding how elements behave during post-depositional changes. However, we are only at the beginning and further investigations are required.

- Line 15: "Mapping the two-dimensional impurity distribution ... S and Cl have not been targeted thus far."

Can you give us an example of what elements work well?

S and Cl are traditionally elements which are difficult to analyse in ICP-MS due to spectral interferences. The here developed methods provides new options to study these elements in ice and allows correlative studies to other elements. Typically, metals are significantly easier to analyse in ICP-MS and consequently, elements such as Na, Mg, Sr can be resolved easily. We have added this to the manuscript as "e.g. for Na, Mg, Sr, ...",

- Line 17: "We show here that signals of S and Cl can be detected in ... exemplarily even 1µm."

The grammar at the end of the sentence ("exemplarily even 1µm.") is really awkward. Please rewrite for clarity.

Changed accordingly.

- Line 19-20: "We find a high level of localization of S and Cl (and Na) at grain boundaries but also some dispersed occurrence within grain interiors in dust-rich ice."

Why is Na pulled out into parentheses? Is this a paper about S, Cl and Na? Or about S and Cl?

The paper is primarily about Cl and S, being the new analytes. Na provides an important reference, e.g. to previous LA-ICP-MS maps. Hence the parentheses. After more consideration, we will remove Na from the title of the manuscript to make it clearer that the novelty of the paper comes through the investigation of Cl and S, while Na serves as a reference element.

- Line 20-23: "The new maps support a view on diffusive transport not only through ice veins but also along grain boundaries, but do not show any clear differences in this regard between samples from the Holocene and last glacial period in the EDC ice core."

This sentence is long and bulky. Consider splitting it into two. Also you have not defined EDC yet, please do so here. The casual reader, even someone who works in the field will likely not know what you are talking about.

Changed accordingly.

## Introduction

While the introduction does introduce concepts relevant to the manuscript and science, the structure of the introduction is disjointed and the message muddled. The majority of the introduction is dedicated to understanding a single element, S. Small interjections mention Cl and Na as well, but the reader is left confused as to why we are looking at three elements,

if only one is of importance. There are also large leaps in text, rather than presenting a cohesive narrative.

It seems best to take a step back and outline the key information that needs to be conveyed. Once a clear flow of information has been outlined, the narrative will quickly come together. Most of the pieces are already there. Perhaps something like this?

- First, talk about the fact that we work with a fundamental assumption that there is no post-depositional migration of species. However, we know that this assumption is a simplification.

Here are some post-depositional effects that we are really concerned about. Critically, ice cores that have much to tell us about the very distant past are at the highest risk of experiencing these migrations. Specifically, the community knows that species X<sub>i</sub> Y<sub>j</sub> Z are of particular concern. There is a high level of concern about S because we know that it migrates at depth and is one of the underpinning species for age/depth scale determination.

- Using LAICPMS, we can begin to assess the distribution of species within ice grains, along grain boundaries, and in veins. To date, we have looked at this list of species because they occur in relatively high abundance.

- Now, we are continuing this work to examine Na, S, and Cl to determine more about the post-depositional effects on these species. To gather a complete picture, we look at both clean and dusty ice from a range of ages.

We are grateful for the comments (including the ones to follow) that helped to restructure the introduction. The point is that while the original study by Barnes et al. (2003) also considered Na, Cl, and S – in most of the following studies the study of diffusion is connected to S/sulfate. In the introduction we need to discuss the state of knowledge regarding the diffusion mechanism and where it is coming from (modelling vs data, analytical techniques). Thus, a natural focus on S/sulfate develops in the introduction. However, we emphasize now that, in this work, all three elements are important. We have tried to integrate better Na and Cl, while also emphasizing the role of Na as a reference element.

#### **Specific comments by line number:**

- Line 26-33: Seems like this paragraph could be expanded to include more about the oldest ice and the challenges it poses, but also why it is scientifically important. In addition to work on extremely old ice, does the research presented here have any potential ability to help understand current changes in post-depositional effects on ice cores in a warming climate? If so, that would be important to mention.

We generally tried to keep the introduction as concise as possible but are now including a reference to the “Mid-Pleistocene Transition”, which is driving the current Oldest Ice efforts (Fischer et al., 2013, Wolff et al., 2022). The suggestion about a connection to ice in a warming climate is very interesting, but this would likely concern mostly the uppermost layers in the ice sheet – if not being as dramatic as leading to temperate conditions and impurity elution, but this would be a different mechanism requiring a separate study.

- Line 34-35: “One very important process in this framework ... (e.g., Severi et al., 2007; Svensson et al., 2013; Fujita et al., 2015; Sigl et al., 2022).”

It is unclear what framework we are talking about here. Post-deposition framework? In the

following paragraph, there is no mention of a framework.

We removed the word “framework” and clarified this paragraph.

- Line 45-59: Are you looking at S, Cl, and Na because they all can (or cannot) be influenced by effective diffusivity? Why these three only? The prose is unclear, leaving the reader guessing. Clarify why your study is focused on these elements.

S and Cl are difficult to resolve in LA-ICP-MS and with the here presented method, it becomes possible to study their distribution at micrometer resolution. The focus on S and Cl is related to their relevance in post-depositional changes. However, Na can be seen as a reference element, which can be found more easily, and which allows comparison of the distribution of the respective elements. The extent to which these elements are affected by post-depositional processes may vary depending on species and process – e.g. this is not just connected to diffusion, but also other processes, such as salt-formation and displacement by grain growth. Another reason is related to the original study by Barnes et al. (2003) providing an important reference for Na, Cl and S. Furthermore, we focus on only three (not 30) elements to enable a concise analysis (due to the analytical limitations and challenges mentioned below) and interpretation. We clarified this motivation in the text.

- Line 49: “For the upper 350 m in the EDC ice core drilled in central Antarctica”  
Should read “upper 350 m of the”

Changed accordingly.

- Line 85: “Exploring the localization of impurities thoroughly over larger numbers of grains has so far been limited primarily due to methodological limitations, in particular high detection limits, hampering the collection of statistically significant large datasets that allow to draw generalized conclusions.”

This sentence is really awkward and hard to read. Consider splitting into two.

Changed accordingly.

- Line 90-101: This entire paragraph is confusing. Are S and Cl mostly soluble like Na? How does increasing Na concentration lead to increased detection potential for S and Cl? It is not clear what you are trying to convey about the increase in Na concentration and its relationship to other elements. Is Na increasing as a post-depositional process? Or is that a depositional thing for Na to be on the boundaries and that causes S and Cl to migrate as well?

This information needs to come earlier so that the reader is not reading for 4 pages wondering why we are looking at these specific elements.

The main point concerns the fact that localization at grain boundaries entails a local concentration increase with respect to what is measured in bulk liquid samples; several orders of magnitude are possible. We observed this already for Na (and other elements) (Bohleber et al., 2024) and this “high concentration at grain boundaries” effect may help us to detect Cl and S with LA-ICP-MS mapping, in spite of the analytical challenges connected to Cl and S.

We have clarified this further and moved it up in the introduction.

- Line 111-112: We thus focus on delivering information on the localization in the ice matrix over obtaining quantitative information on concentrations, which adds considerable complexity and uncertainty (Bohleber et al., 2024).

This concept comes out of nowhere. It would be helpful to add a sentence or two earlier in the introduction that presents this concept with more context. Why is it okay to just provide the spatial localization information? Do we need concentration data to successfully comment on the post-depositional diffusion hypotheses?

As observational microstructural impurity data, especially regarding S, remains scarce, we can already gain significant new insight on the diffusion mechanism from the localization of the impurities, hence concentrations are not needed (in this context, for now). We now mention this connection earlier in the introduction.

## Methods

The methods section does not adequately explain how the study was conducted or why certain choices were made. This section needs to be revised to ensure that the methods are well explained.

First tell us about the samples you are going to work on. How you decided what to work on? Where are they from? What preparation steps did you have to go through to get the ice ready? Then, introduce the LAICPMS system(s) on which the samples were run. Tell us about how you ran them! Why did certain samples get run on one instrument vs. the other? Was there any post-processing of the data. If so, what steps did the data have to pass through? For the LA-ICP-MS section (currently 2.1), the authors need to clarify why they ran samples at two different labs. It is unclear to the reader if the authors were attempting to have an inter-lab comparison. If so, the results and discussions are confusing because they lack a section discussing the similarities or differences observed between the two runs for the one piece of ice – sample EDC 513 – run on both machines. Section 2.2 “sample selection” should be greatly expanded to help the reader understand where the ice is from, why specific intervals were chosen, and what preparation had to happen before the samples were inserted into the cryostage.

We agree with the referee that additional explanation will help the reader to understand the sample selection and combined use of two instruments at different laboratories. The data of the Graz laboratory came out of a previous investigation that was, initially, not primarily focused on sulfur. Yet this is where it first became clear that Cl and S can be mapped with LA-ICP-TOFMS. After the recent installation of the new LA-ICP-TOFMS at AWI, we have added further maps at higher resolution – and were again able to use a sample of EDC bag 513 (not the identical sample as in Graz, however). We have added text at the beginning of the method section and in “sample selection” to make this clearer.

We would further like to stress that this study was not designed as an inter-lab comparison, and have clarified on this. However, the fact that two labs generate qualitatively consistent data provides some form of validation. The combined use of data generated by different systems is not uncommon and we have done so previously for different purposes (Larkman et al., 2024), generally trying to exploit the individual strengths of each system.

The technical details have been described elsewhere already, namely concerning a) the LA-ICP-MS mapping method, map construction and decontamination protocol (Bohleber et al., 2020, 2021, 2023, 2024), b) the Graz LA-ICP-TOFMS system (Niehaus et al., 2024; Lockwood et al., 2024). Recently, we have added a respective publication on the new LA-ICP-TOFMS system at AWI (Bohleber et al., 2025). For the sake of brevity and readability of the manuscript, we are including a digest of the experimental steps involved. The interested reader can then consult the above referenced publications for more detail.

### Specific comments by line number:

- Line 124: “Using a NIST612 glass standard ... distance between cell and sample surface.”  
Why not tune with a matrix matched ice standard?

The NIST glass has a homogenous distribution of elements, which facilitates tuning and methods development significantly. Using ice standards is here difficult as they will also form grain and boundaries with varying concentrations. Ablating these ice standards, we would not be able to benchmark instrument performance. We refer to Bohleber et al. (2024) for more details on the challenges of solid ice standards for LA-ICP-MS analyses and mention this now also in the text.

- Line 133: “The latter comprises an Analyte G2 laser ablation system (Teledyne Photon Machines, USA) equipped with a HelEx II ablation chamber compatible with the Venice cryostage.”

You either need a citation for the Venice cryostage or a description here.

Added accordingly (Bohleber et al., 2020).

- Line 137-140: “Since using an identical ICP-TOFMS, the two systems are complementary through the differences in the laser ablation instrument.”

Sentence is unclear – incorrect word choice with “through”? Why are you using two systems? An interlab comparison? Some other reason? How did you make the decision that one lab would run large spot sizes and large areas, and that the other lab would run small, high resolution maps? If I were to attempt to replicate your method, how would I know what spatial or resolution I should map at?

As explained above (and now in the text), the Graz analyses came first. Based on these results, we have been able to further advance the method with the system located at AWI providing higher resolution analysis with small spots. This new system enabled us to increase spatial resolution by conducting 10 and 1 micron spot analyses. The choice of resolution will always depend on the scientific question and the capabilities of the instrument, so no general answer is possible here. The chosen approach shows what you can expect from using two different systems - that the investigation of triple junctions greatly benefits from spot sizes as small as 1 micron which could be crucial for further analyses.

- Line 142: “Following our previously established approach for impurity mapping (Bohleber et al., 2020), the ice surface was decontaminated by scraping with a major-element free ceramic ZrO<sub>2</sub> blade (American Cutting Edge, USA) immediately before inserting the samples into the ablation chamber.”

This belongs in the sample selection and preparation sub-section.

Moved accordingly.

- Line 145: What were your pre-ablation methods? How many passes did you make? Did you record the optical mosaics before or after the pre-ablation?

As indicated by the reference in the text, this is already described in detail elsewhere (Bohleber et al., 2020) and has not changed. At least one preablation run is done with a larger spot size and low fluence. Optical mosaics are recorded after the measurement run.

- Line 146: “The maps were generated using HDIP (Teledyne Photon Machines).”

What is HDIP? Why do you need to use it to generate the maps? Is it something that is

done during or following the data collection?

Laser ablation set-ups don't automatically produce chemical maps, but the laser position and chemical data have to be compiled into an "impurity map". For this crucial purpose, many commercial and open-source solutions exist. We are using the commercial HDIP software for final map generation after the data acquisition as explained in Bohleber et al. (2020). With the ICP-TOFMS you can also check the maps during data acquisition but post-measurement map processing is needed still.

- Line 151-156: "We chose a set of ice core samples both from the Holocene and the last glacial ... to provide a realistic subsample of typical polar ice conditions."

Can you give us more details about the cores when you introduce them here. Where exactly was it drilled. When was it drilled? Provide us with citations of other work that has been done on these cores. What time frame did you sample from? What parameters did you use to inform your sample selections? Was it purely limited by sample availability? Why did you choose these intervals of all the ice that exists? Explain not just that it is glacial, but why was \*this\* glacial sample selected? Are the samples from the inner part of the core? From the outer part of the core? What had to happen to the sample once you selected it? Did it have to be cut down to size? What was the cleaning procedure? Additionally, please explain why was only one sample run at both facilities? How was it determined which samples would be run where?

Referring to what is already explained above, we have added further detail to explain how the samples were chosen and prepared for analysis. The main motivation was in fact to look at samples with different chemical compositions, and therefore samples from the Holocene and the last glacial were selected. Numerous publications exist on the analysed ice cores and we thus refrain from adding basic information on them as it is not crucial to this manuscript dealing with specific analytes.

These samples were prepared similarly, with inner sections of the core cut specifically for LA-ICP-MS analysis, thus ensuring suitable dimensions for measurement (a cross section of 10 by 17 mm, with lengths between 5 cm and 9 cm, depending on core quality/breaks). These cuts were made in a cold room, with samples being placed immediately into clean vials after cutting, with pre-ablation in the LA-ICP-MS system providing suitable further decontamination.

- Line 153-154: "The glacial EGRIP sample contains a dust-rich cloudy band from the Younger Dryas and thus represents contrasting conditions to the low impurity samples from EDC." You later refer to the samples with their sample number (i.e. EGRIP 2286). This system should be used throughout the manuscript for clarity.

Changed accordingly.

- Line 155: 250 000 particles/ml

Typo: 250,000 particles/mL

Changed accordingly.

## Results

As currently written, the results and discussion sections are difficult to follow. Since The Cryosphere has no strict section requirements, consider if blending the results and discussion sections into a single section would help readability. Framing the section as: To examine XXXX we made this map on this sample. We find XXXX. To better

understand XXXX, we analyzed the sample again higher resolution (?). To examine this other hypothesis, we made a map of this sample XXXX, and found XXXX.

This would allow you to form a cohesive narrative that would benefit the reader's comprehension of the science.

We understand why a single narrative might seem easier to follow first, but the manuscript offers two different aspects of insight: a) the analytical challenge of mapping elements like Cl and S in ice, revealing where they are located in the ice matrix, and b) the implication of these findings for impurity diffusion studies. While there is certainly an element of personal preference involved, we believe that it is clearer to treat Results and Discussion separately under such circumstances. This allows us to present in detail the results acquired by the different systems, and then to discuss them with respect to the two aspects a) and b). We are optimistic that by addressing the comments from both referee reports, the revised results and discussion sections will be clearer to the reader.

#### **Specific comments by line number:**

- Line 162-163: "Figures 1 and 2 show examples for the large size 32S intensity maps alongside 37Cl and 23Na recorded with the Graz LA-ICP-TOFMS system."

This is the first time you have presented isotopes of elements. Since you will later go on to show maps of multiple isotopes for each element, it would be good to add some text in the methods explaining what isotopes you gathered and why it is helpful to look at more than one.

Changed accordingly.

- Line 163: "Additional maps are included in the Supplementary Material"

Which maps are you referring to here? All of the supplementary material. There are no other references to Figure S1 and Figure S3. Are they needed? If they are adding something important, they should be discussed in further detail somewhere in the manuscript.

They are needed for the sake of showing all relevant data, but provide no added new insight with respect to the main figures in the manuscript. Thus, we used the Supplementary Material to display them.

- Line 163-165: "Na serves as a reference element showing the high degree of localization at grain boundaries, analogous to previous observations in EDC and EGRIP (Bohleber et al., 2020; Bohleber et al., 2023; Stoll et al., 2023).

This is a super important sentence and needs to be clearly stated in the introduction.

We agree on this as discussed above and have changed the text accordingly.

- Line 167-170: "The EGRIP cloudy band sample likely has significantly higher impurity content compared to the EDC Holocene sample, reflected in the higher signal amplitude in spite of the smaller spot size used (20  $\mu\text{m}$  EGRIP vs 40  $\mu\text{m}$  EDC)."

What is the sample number of the EDC sample? Why were the samples run at different spot sizes? This needs to be explained with more clarity because it is not clear that comparing different spot sizes is a good idea. Are you comparing apples and oranges, or is it okay to compare like this?

It is the "EDC Holocene sample", hence EDC513 (added in the text). Different spot sizes were used, especially in Graz, as they allow you to make a compromise between map area covered and spatial resolution achieved in the same amount of time. The spot size also affects the limits of detection (which is what is referred to here), and the impurity-rich EGRIP

sample showed clear signals of Cl and S even at 20 microns. For the comparatively lower impurity content in Antarctic Holocene ice, we chose a 40 micron spot. Arguably, an apples vs oranges situation would arise from a quantitative comparison, but here we are just noting that, in spite of using a smaller spot (less material ablated), the EGRIP sample still has higher intensities, consistent with the higher impurity concentration in Greenland glacial ice vs Antarctic interglacial ice. We have clarified this in the text.

- Line 183-187: “Using the AWI setup, maps were recorded on two subsamples ... the map on EDC513-1 (shown in the Supplementary Material).”

This should not be the first time that we are learning that EDC 1819 and EDC 513 were subsampled. This information should be provided in the “Sample Selection” portion of the methods. It should also be included in Table 2. It is unclear why it matters what order the samples were mapped in. If it is important, then the order of mapping should be included in the methods section. It would be helpful if you expanded the discussion of Figures 3-5. A brief description of each figure, including the sample, pixel size, and notable features, is warranted. What supplemental figure is EDC 513-1?

We agree that this detail was missing and have added information about the subsampling. Please note that this also has potential for further confusion (which we clear up in the revised text): 1819-1 and 1819-2 refer to two individual subsamples at adjacent depths, not an order of analysis (which does not matter).

- Line 189-190: “The map for 35Cl contains only noise in all maps recorded (hence not shown), but strong signal in 37Cl, which indicates the potential formation of Chlor- hydrogen adducts (see Sect. 4.1).”

It may be helpful to show both isotopes as a figure in the supplement. That way the reader doesn't have to trust you at your word. The discussion about Chlor-hydrogen adducts would be helpful to have right after you introduce this so the reader can follow easier.

We added one exemplary figure in the Supplement.

- Line 190: “As shown in Fig. 3 – 5 for S”

If you are not going to discuss each figure in detail, it is strange to have all three. Why show them if they are not noteworthy?

We are later referring to these Figures in the Discussion.

## Discussion

### Specific comments by line number:

- Line 223-225: “Although Na, S and Cl belong to the most abundant elements in polar ice (albeit generally at low ppb bulk concentrations)(Legrand & Mayewski, 1997), initial studies in LA-ICP-MS ice core analysis and in particular impurity mapping have focused on analytically more easily accessible elements such as Na, Mg, Al, Ca, Fe, Sr”

This idea is so crucial to the understanding of your research. This needs to be said \*way\* earlier, like in the introduction!! The text would also benefit from an additional prose about why Na, Mg, Al, Ca, Fe, and Sr are more accessible.

We have added text in the introduction in this regard. “More accessible” is meant here especially by comparison to S (interference) and Cl (low ionization).

- Line 226: “As demonstrated by the results shown in Fig. 1 – 7”

There are only six figures in the main text. Where is figure 7?

Well spotted. Should be Fig 1-6. Changed accordingly.

- Line 228-260: “The main hurdle for detecting S is the mass interference by ... collision-reaction cell gases, such as Xe or CH<sub>4</sub> (Guillong et al., 2008; Singh et al., 2025).”

Both of these paragraphs need to be moved into the methods section when you talk about LA-ICP-TOFMS setup and analysis methodology.

Since this was not our method, or anything we have tried, we do not see this information in the method section but have included mentioning this in the introduction. Our rationale was to discuss the analytical challenge of measuring S and Cl in the discussion and to compare our technique to other approaches, like the ones mentioned here for S. Future studies may want to try these reaction gases for measuring S in ice with LA-ICP-MS if their ICP-MS allows it.

- Line 290: “the higher amount of resources consumed”

What kinds of resources? Ice? Or analytical resources (time, energy, gases)? You make a reference of 200k shots for the map in Figure 6, but the reader has no idea how many shots were needed for other maps. Therefore, it is hard to understand the increase in resources. Primarily time, which also translates into consumption of resources like gases (Ar, He) and hence, not surprisingly, costs. Recent developments may help to find alternative strategies to the compromise between map size and spatial resolution (Larkman et al., 2025). We have reworded this sentence to make it clearer.

- Line 291: “Consequently, we only investigated this exemplarily in this work.” There appears to be some missing text in this sentence.

Reworded.

- Line 294-295: “While at 10  $\mu\text{m}$  spot size, grain boundaries are typically mapped with 2-3 high intensity pixels, for 5  $\mu\text{m}$  this reduces to 1-2 pixels, with the same dosage 10 for all maps.”

It is unclear how the number of high intensity pixels translates into data quality.

Not data quality per se but physical/chemical extent (width) of the grain boundaries is the point here. We have reworded the statement to point this out better.

- Line 298-299: “The 1  $\mu\text{m}$  spot size may be more capable of resolving the fine-scale impurity variability around triple junctions, and shows that some enhancement at triple junctions relative to grain boundaries may exist at that spatial scale”

Enhancement of what? High intensity pixels?

Enhancement of Na at triple junctions relative to grain boundaries, shown as higher intensity pixels.

- Line 299-300: “In previous studies a comparable spatial resolution around 1x1  $\mu\text{m}$  was used.”

Citations needed.

Added accordingly.

- Line 324-327: “Accordingly, the physical reality likely is a mix between the two scenarios described in Ng (2021), with a highly localized nature of impurities in ice but variable

contributions from ice veins, grain boundaries and grain interiors depending on conditions, such as climate period and insoluble particle content, and uncharacterized microstructural processes.”

This sentence is hard to understand. It would benefit from being split up into multiple sentences and more detail added.

Changed accordingly.

- Line 329-331: “Notably, the situation in deep ice sections, with larger grains and more time spent at higher temperatures, may deviate from the snapshots from relatively shallow depths presented here and remains to be explored, in particular regarding the influence of geochemical reactions leading to dissolution at grain boundaries (Baccolo et al., 2021).”

Why has this research been done at relatively shallow depth intervals, if developed methodology is supposed to be used on ultra-deep ice? Is it an ice availability problem? How do you know that your method will still work on deeper ice core samples?

Two reasons: First, the diffusion studies also primarily focus so far on the last glacial cycle – as explained above. Second, the complex conditions in deep ice warrant a separate investigation – concerning large grains challenging the mapping from a practical point of view but more interesting, the suspected chemical reactions happening in deep ice. That said, there is no principal reason why this mapping should not work in deep ice, and deeper sections have been successfully mapped with LA-ICP-MS before (Bohleber et al., 2021; Stoll et al. 2023).

- Line 331-332: “Technically, the same is true for sections with high S-peaks from volcanic eruptions, which have not been measured here.”

Please add citations to papers where the high S peaks have been measured, so the reader can learn more and see how your data compares.

This is likely a misunderstanding and needs to be clarified: To our knowledge, no studies on using LA-ICP-MS on ice containing volcanic S peaks have so far been published, but of course plenty of data from liquid analysis exists. We clarified this accordingly.

## References

Many of the citations are incomplete, lacking doi and other information. In addition, your citations do not follow the format required by the journal. A complete list of reference requirements can be found at <https://www.the-cryosphere.net/submission.html>. Note that the year is at the end of the citation and that no part of the citation includes italicized text. Please work through the citations, fixing formatting and adding information where possible.

Changed accordingly.

- Here is the style for journal articles: Porter, J. G., De Bruyn, W., and Saltzman, E. S.: Eddy flux measurements of sulfur dioxide deposition to the sea surface, *Atmos. Chem. Phys.*, 18, 15291–15305, <https://doi.org/10.5194/acp-18-15291-2018>, 2018.

- And the style for books: Singh, O. N. and Fabian, P. (Eds.): *Atmospheric Ozone: a Millennium Issue*, Copernicus Publications, Katlenburg-Lindau, Germany, 147 pp., ISBN 393658608X, 2003.

## Tables

Table 1:

Consider reformatting this table so that it is easier to compare the laboratories with each other. This could be achieved in three columns: setting, value for AWI, and value for Graza. Why are the TOF settings not the same in the two labs? Is it because of the different lasers? What dictated changes to the rep rate?

The authors should have an expanded version of this table, either here or in the supplement, that lists all of the settings that were used. Note that these lists were generated for sample analysis on a Thermo Element 2, Thermo Element XR, and an Agilent 8900. Potentially, some settings are listed that are not appropriate for ICP-TOFMS or settings that need to be added to the list for ICP-TOFMS.

For the laser ablation system:

- Instrument Make/Model
- Software
- Ablation Cell
- Laser Wavelength
- Pulse Width
- RF Power
- RF Matching
- Sample Depth
- Gas Flow Setup (i.e. Direct connection)
- Carrier Gas Flow
- Energy Density
- Repetition Rate
- Spot Size
- Sampling Pattern (i.e. Single hole drilling or raster)
- Ablation Duration • Signal Smoother

For the ICP-TOFMS system:

- Instrument Make/Model
- Software
- Sample numbers measured
- RF Power
- Plasma Gas Flow
- Auxiliary Gas Flow
- Nebulizer Gas Flow
- Makeup Gas Flow
- Reaction Gas
- Reaction Gas Flow
- Analyzer Pressure
- Sample Inlet
- ARIS rapid aerosol introduction system settings
- Nebulizer make/model
- Sample uptake rate
- Sample Cone make/model
- Skimmer Cone make/model
- Torch Z position
- Sensitivity
- Scan Type

- Mass Window
- Integration Time or Window
- Detection Mode
- Isotopes Measured

We would rather present a concise overview of the two systems in Table 1 in the main text. The values are actually quite similar between the two systems and relevant differences are easily spottable and pointed out in the text (e.g. spot sizes). We also believe all relevant technical information – what is requested above- is already either in the table, the text or in the cited references. The scope of *The Cryosphere* is further not comparable to a methodological journal and these technical details would hamper readability without scientific value added.

Table 2:

This table should be expanded to include the laser spot size(s) used to help the reader understand what ice was measured with what settings. This is especially important because this information cannot easily be gleaned from Table 1. For audiences with broad backgrounds, consider adding a column noting if the sample is Holocene or Last Glacial. We have modified the table accordingly and point out the climatic period. We also decided to add further detail to the Figure caption directly (as also requested) and include detail on the mapping there, avoiding redundancies.

## Figures

### General comments:

Consider moving the element labels to the left y axis. This would allow you to stack the maps close together for ease of visual comparison. The scale bars would benefit from a white box behind it or to be moved off of the map. It is very difficult to read. Consider adding a scale bar to each image/map if you choose to leave them as is (not closely stacked). Does cts = counts per second (cps)? Cts should be explained. Consider adding more details to the figure caption. Talk about the sample time frame that we are looking at and any notable features that the reader should focus on. Please reference the specific figures in the supplement instead of just saying “Supplementary Material”.

We expanded the figure caption as requested. Explained now that “cts” is counts, not counts per second – albeit this differs only by a constant factor.

### Specific Comments:

Figure 2: Make sure that your optical mosaic is cropped to the same extent as the LA-ICP-TOFMS elemental maps.

This is a marginal cut caused by a different spatial resolution of the camera compared to the laser spot size, but done anyway.

Figure 6: It seems that this figure would work better as a 3 panel strip; in each row – optical, 10um, 5um, 1um for a different element/isotope. If you keep it as is, please add an element/isotope label to the 5 um and 10 um spot size panels.

Changed accordingly

Figure S2: Is it possible to adjust the contrast on the mosaic image to improve the visibility of the grain boundaries?

It remains challenging, but we have tried to further improve the contrast as can be seen in the modified manuscript.

Figure S3: The intensity is now in au. Why the shift from cts? What is au?

We changed this to cts to be consistent.

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