Review of Bohleber et al. manuscript #egusphere-2025-355

"New evidence on the microstructural localization of sulfur, chlorine & sodium in polar ice cores with implications for impurity diffusion"

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.

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

- **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?

- **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.

- **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?

- **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.

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¡ Y¡ 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.

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.

- **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.

- **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.

- **Line 49:** "For the upper 350 m in the EDC ice core drilled in central Antarctica"

  Should read "upper 350 m of the"

- **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.

- **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.

- **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?

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 cyrostage.

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?

- **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.

- **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?

- **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 ZrO2 blade (American Cutting Edge, USA) immediately before inserting the samples into the ablation chamber."

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

- **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-ablaiton?

- **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?

- **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?

- **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.

- **Line 155:** 250 000 particles/ml

  Typo: 250,000 particles/mL

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.

Specific comments by line number:

- **Line 162-163:** "Figures 1 and 2 show examples for the large size ^{32}S intensity maps alongside ^{37}Cl and ^{23}Na 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.

- **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.

- **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.

- **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 µm EGRIP vs 40 µm 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?

- **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?

- **Line 189-190:** "The map for ^{35}Cl contains only noise in all maps recorded (hence not shown), but strong signal in ^{37}Cl, 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.

- **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?

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.

- **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?

- **Line 228-260:** "The main hurdle for detecting S is the mass interference by ... collision-reaction cell gases, such as Xe or CH_4 (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.

- **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.

- **Line 291:** "Consequently, we only investigated this exemplarily in this work."

  There appears to be some missing text in this sentence.

- **Line 294-295:** "While at 10 µm spot size, grain boundaries are typically mapped with 2-3 high intensity pixels, for 5 µm 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.

- **Line 298-299:** "The 1 µm 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?

- **Line 299-300:** "In previous studies a comparable spatial resolution around 1x1 µm was used."

  Citations needed.

- **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.

- **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 availibility problem? How do you know that your method will still work on deeper ice core samples?

- **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.

References

Many of the citations are incomplete, lacking dois 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.

- **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

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.

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".

Specific Comments:

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

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.

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

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