Review of manuscript entitled “What does the impurity variability at the microscale represent in ice cores? Insights from a conceptual approach” submitted to EGUsphere (TC) by Piers Larkman.

General comments:

This manuscript investigates the impact of measurement scale by comparing high-resolution 2D data from LA-ICP-MS with smoothed and converted 1D profiles aligned with the CFA measurement scale. High-resolution measurements are crucial for extracting climate signals from extremely thin layers of deep ice. Results from LA-ICP-MS analysis revealed that impurities, particularly sodium, are preferentially concentrated at grain boundaries rather than within the grain interiors. This indicates that impurity distribution becomes more heterogeneous as grain size increases. Consequently, signal deviation in 1D profiles (quantified as mean absolute deviation, MAD) increases with larger grain samples.

For most glaciologists, the CFA technique offers sufficiently high resolution; however, the resolution of tens of microns provided by LA-ICP-MS is an impressive advancement. Identifying the precise location of impurities is essential for understanding microstructures and deformation mechanisms.

The manuscript is well-written, well-organized, and could make a valuable contribution to the chemical analysis of ice cores and the oldest ice core project. Therefore, I recommend that the manuscript be accepted after minor revisions. I have some questions, comments, and suggestions regarding the results and their interpretation, which may require further explanation. Additionally, some figures need to be redesigned and modified to ensure they are easily understood by the readers.

We thank the referee for their insightful review, the reviewer’s comments are addressed below in blue, alongside the original review text.

Specific comments:

The present manuscript focuses on sodium, which tends to accumulate at grain boundaries. In contrast, certain ions, such as chloride, dissolve and substitute for H_2O molecules within the grain interior. In these cases, I suspect that the impact of grain size on measurement resolution (or the difference between 1D profiles and CFA) may not be as pronounced compared to impurities that accumulate at grain boundaries.

We agree that considering the specific microstructural location of different species in isolation is important. Based on existing data so far, we find that many elemental impurities are located at the grain boundaries, for which we take Na as an archetypical example case. Other, primarily insoluble and dust-related impurities, can also be found in the grain interiors, and these species are so far not considered in this approach. With ongoing developments to LA-ICP-MS allowing the measurement of more chemical channels, we plan to extend this work in more detail in the future.

We refer to the archetypical nature of Na in the introduction and this is stressed in section 4.1 of the revised manuscript. Furthermore, we have stressed that insoluble impurities in grain interiors are not directly targeted in this approach so far in sections 1 and 4.1 of the revised manuscript.

In Figure 4, impurities appear to be distributed within the grain interiors in both EDC and RECAP LGP samples. (In Figure 3, sodium distribution does not seem to extend into the grain interiors.) While this may not be the primary focus of the current paper, the differences in impurity distribution between glacial and interglacial ice samples are intriguing.

The authors concluded that signal deviation increases with larger grain sizes. I wonder whether this deviation is influenced solely by grain size. It seems likely that impurity type (whether substituted within the grain interior or concentrated at grain boundaries) and climate period (glacial or interglacial ice) could also play a role in signal deviation. If the authors have insights on these factors, I suggest them to share their perspectives, as it would be beneficial for readers.

We agree that multiple factors must be considered when attempting to explain the observed impurity localisation at grain boundaries and that these factors may vary in their relative magnitude among different climatic periods. A growing body of work (e.g. Della Lunga et al., 2017, Stoll et al., 2023, Bohleber et al., 2022) illuminates the impurity localisation in the microstructure for different climate periods featuring different grain sizes (Holocene, Younger Dryas, Glacial Stadials and Interstadials). An explanation and improved understanding of the origin of the impurity localisation remains an ultimate target. Here, we are focusing on exploring the implication of localisation for interpreting LA-ICP-MS line profiles and CFA profiles. Figure 4 primarily shows that grain boundaries consistently feature higher intensities with respect to the grain interiors – again using Na as an example case for a specific (but large) subset of impurities. As the implemented framework considers both changes in grain size and the specific impurity localisation, modelled signal deviation captures at least these two factors.

Additional factors influencing signal deviation have been expanded on in the discussion in section 4.3.1 of the revised manuscript. The topic of different impurity types has also been included in the revised manuscript's introduction.

The discussion in Section 4.4 *Potential extensions* is particularly significant. As the authors mentioned, one of the key future goals of this study is to accurately extract climate signals from deep, thin ice. The deepest ice layers are subject to dynamic recrystallization due to the high-temperature environment, leading to a grain volume distribution that deviates from a gamma distribution. Moreover, migration recrystallization introduces small grains and creates complex grain boundaries, resulting in non-isometric grain shapes. Such complexities in grain boundaries and size distribution are observed not only in deep ice but also in ice samples deformed under high temperature and stress, such as those from the EastGRIP ice core. Replicating these intricate microstructures within an ice matrix model presents significant challenges.

We again agree with both the value and challenge of modelling complex microstructures, including in deep ice and sites such as EastGRIP. This manuscript introduces the modelling approach, providing a basis for further in-depth studies. We take this comment as further encouragement to explore how this model can be extended in this and other regards in the future.

A note has been included in section 4.4 on cores (specifically EGRIP) originating from sites where high deformation is present.

Although it may be considered future work, the manuscript's discussion and practical implications could be greatly enhanced by including results and assessments from ice samples

with complex microstructures, such as those containing small grains and complicated grain boundaries formed by migration recrystallization. In my view, even without 3D ice matrix modeling, simply comparing LA-ICP-MS data with smoothed and combined 1D profiles (like Figure 5), and grain size (distribution) offers substantial value.

In principle, this is an excellent idea, and we hope to extend this work accordingly in the future. We must emphasize the substantial experimental effort in capturing the 2D impurity maps, although the technique is still rapidly evolving to measure more data faster. At present, the limited availability of LA-ICP-MS data prevents the inclusion of such a discussion in this manuscript. We take the suggestion as encouragement for future work, as noted.

L7 in the abstract: What does "high-frequency component of signals" mean?

This phrase was used to refer to the variations in 1D signals that change rapidly (in the case of the 1D signals discussed in the paper, the 'high-frequency' component arises due to the grain-boundary imprint causing rapid changes in intensity. By contrast, the 'low-frequency' component would be the slower changes due to e.g. a climate signal).

Given that the paper does not discuss variations in terms of frequency elsewhere, this sentence has been rewritten.

L15 in the abstract: *This approach guides collecting layer-representative signals from LA-ICP-MS line profiles and may help to bridge the scale gap between LA-ICP-MS data and data collected from meltwater analysis*.

As mentioned, this approach could assess the scale gap. On one hand, how does this approach specifically bridge the scale gap? I think this is the most interesting for general glaciologist.

The scale gap concerns the different spatial resolutions of the data generated by CFA and LA-ICP-MS, centimetres and micrometres, respectively. In the presence of a regularly cm-spaced stratigraphy encoding climate variability, there is a question of how this signal manifests in micron-resolution LA-ICP-MS data, which is highly influenced by the impurity-localisation at grain boundaries and thus a second factor, grain size. We try to elucidate this question in the present work, specifically for different grain size conditions and climatic periods. Before, the scale gap was mainly addressed heuristically by smoothing LA-ICP-MS data until they resemble existing CFA profiles (e.g. Della Lunga et al., 2017, Bohleber et al 2021). Assistance from the model allows the scale gap to be bridged independently of comparison to CFA. It allows us to determine how different LA-ICP-MS profiles can capture cm-scale variability. The model allows studies that are not (easily) possible with empirical measurements, such as the generation of spatially coherent measurements with different experimental techniques and parameters, the isolation of components contributing to measured signals (e.g. due to impurity localisation or grain size).

The above discussion has been captured in the introduction of the revised manuscript.

L79 (Table 1) In the EDC ice samples, mean grain size in LGP is larger than that in Holocene? In Figure 3, grains in EDC LGP ice sample look small.

The area illustrated in figure 3 for LGP does indeed contain small grains; this is just a small snapshot of the surface measured using LA-ICP-MS. The optical/microstructure measurements of the grain sizes reported in table 1 are taken from and are collected over larger areas. This has been clarified in figure 3's caption. This example shows how important it is to obtain high-

resolution microstructural and laser ablation data to exploit the potential of the presented approach fully.

L63: What does "The computational representation uses the arguably most simple manifestation of a climate signal, a constant signal" mean? How does the climate signal mode affect the results and discussion of the present study such as experimental measurements and ice structure generation? Please provide brief explanation for general cryosphere's readers.

We realize that this needs further clarification. The main idea is that based on the cm-resolution of CFA, a CFA profile can be regarded as a sequence of discrete constant values spaced at the resolution of the system, 1 cm or up to 0.5 cm (the exact value may vary according to climatic period and local variation). This computational representation simplifies this signal to a discrete constant value, and we investigate under which conditions we can reliably extract this discrete constant value. Measuring an empirical signal under the conditions that extract a constant value from the model would arguably detect the cm-scale climate variability present in an ice sample if the (parallel) LA-ICP-MS profiles are extended along the main core axis.

We have clarified this point accordingly in section 2.1 where it was first mentioned.

L103: I understand that the modelling of 3D ice structure is useful. However, I didn't see how 3D ice structure helped the verification of results and discussion. Figures 4 to 8 indicate 1D or 2D results. 2D ice matrix model is not sufficient?

The 3D model is critical for the simulation of CFA signals. Based on additional feedback from reviewer 2, a discussion has been added regarding comparisons to bulk analysis, which also requires modelling a 3D structure. Points regarding the applicability of the 3D model have been stressed in the discussion.

L160: *A comparison of the optical images and intensity maps in Fig. 3 shows sodium is concentrated preferentially at the grain boundaries compared with grain interiors for all measured samples*.

Even shallow EDC sample (Holocene ice), sodium is concentrated grain boundaries. Does this mean that impurities are already concentrated at the grain boundaries during deposition?

This is a very interesting question, referring again to the physical cause(s) of the observed localisation. Due to the limited amount of data, we are not confident in attempting to answer this (yet). However, we can say that based on the data acquired thus far, the localisation of impurities such as Na appears to be already significant in upper ice sections. First results were shown by Stoll et al. (2023a) displaying that localisation in the NEEM ice core already occurs in the upper 50 m. Measuring firn with LA-ICP-MS remains challenging, but more research will be conducted to better assess the localisation process.

L188: *These modelled signals show the same general features as experimentally measured signals, with large spikes in intensity where profiles intersect grain boundaries*.

It is difficult to determine whether experimental and modelled profiles signals have similar behaviors. Replication of experimental results by means of a model is, in my view, important in the present study. Please provide a comparative figure between the experimental and modelled results.

The plots in figure 5 (a) and figure 6 (a) are equivalent for experimental and modelled results, this link has been highlighted in the results and stressed in the discussion.

Figure and table:

Table 1: Please provide explanation for “Profile lateral separation (mm)”.

This value has been illustrated in figure 6 (in addition to the redesign suggested by both reviewers). The table 1 caption directs the reader to this illustration.

Figure 3: Redesign is required.

Three images (optical image grain boundary segmentation, and chemical map) are not identical at RECAP ice samples. For example, in Holocene sample, grains in the middle and right images are elongated vertically. In LGP sample, grains in the left image are elongated vertically. Please modify.

The optical image of EDC Holocene sample is low resolution, it is difficult to distinguish grain boundaries.

Size of EDC LGP samples is too small. Image sizes should be the same for all samples.

Figure 6: (a and c) It is difficult to see grain boundaries, please make contrast clearer.

(b and d) What do the color difference of grains mean?

Thank you for the suggestions, the figures have been redesigned accordingly. In fig. 6 b and d, the colour difference is arbitrary and holds no special meaning, the colour scheme has been updated and clarified in the figure caption.

Figure 7: Why do the smoothed profiles (d) and (e) appear to be different? (It doesn’t even look similar to panels a to c)

This is also the case in Figures S6 and S9.

This phenomenon has been clarified in the revised manuscript in the figure’s caption and in section 3.2. The deviations are very small from the modelled un-changing climate signal, on the order of 2% for LA-ICP-MS (7d) and 1% for CFA (7e), both modelled LA-ICP-MS and CFA signals collected from slightly different spatial locations can show varying trends in signals showing such small-amplitude variability. In this case, the modelling shows opposite trends greatly highlighting this effect. However, the modelled LA-ICP-MS and CFA signals are similar in that they only demonstrate minor deviation from the underlying signal. (This response is replicated in response to similar comments by both reviewers 1 and 2).

Figure 8: Bottom two panels are labeled with (a) and (b). Please modify. Additionally, the spot size in panel b and caption is shown as 280 um, but the main text explain 260 um. Please correct value.

The figure label and spot size disparity have been corrected (updated to 280 in the text).

References

Della Lunga, D., Müller, W., Rasmussen, S. O., Svensson, A., and Vallelonga, P.: Calibrated cryo-cell UV-LA-ICPMS elemental concentrations from the NGRIP ice core reveal abrupt, sub-annual variability in dust across the GI-21.2 interstadial period, The Cryosphere, 11, 1297–1309, https://doi.org/10.5194/tc-11-1297-2017, 2017

Stoll, N., Westhoff, J., Bohleber, P., Svensson, A., Dahl-Jensen, D., Barbante, C., and Weikusat, I.: 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, 2023a.

Stoll N., Bohleber P., Dallmayr R., Wilhelms F., Barbante C., Weikusat I.: The new frontier of microstructural impurity research in polar ice. Annals of Glaciology 1–4. https://doi.org/10.1017/aog.2023.61, 2023b.

Bohleber, P., Stoll, N., Rittner, M., Roman, M., Weikusat, I., & Barbante, C.: Geochemical characterization of insoluble particle clusters in ice cores using two-dimensional impurity imaging. Geochemistry, Geophysics, Geosystems, 24, e2022GC010595. https://doi.org/10.1029/2022GC010595, 2022.

Bohleber, P., Roman, M., Šala, M., Delmonte, B., Stenni, B., and Barbante, C.: Two-dimensional impurity imaging in deep Antarctic ice cores: snapshots of three climatic periods and implications for high-resolution signal interpretation, The Cryosphere, 15, 3523–3538, https://doi.org/10.5194/tc-15-3523-2021, 2021.