

This manuscript investigates the variability of impurity signals at the microscale by comparing high-resolution 2D impurity signals to modeled 1D CFA measurements. The authors seek to improve understanding of a significant issue within LA-ICP-MS analyses, namely that localized impurities, cause significant variation in 1D signals due to their uneven distribution across the ice matrix.

The model addresses a key challenge in interpreting impurity signals and offers a method to quantify the impact of impurity localization on 2D LA-ICP-MS signals. The manuscript is well written and offers guidance on the number of profiles and level of smoothing required to generate representative signatures. This information is critical for designing LA-ICP-MS experiments. However, while the manuscript provides a step forward in the experimental design, I have concerns regarding the level to which the modelled data accurately represents the climate signal and its applications.

We thank the referee for their encouraging comments and critical assessment of this manuscript. We appreciate the note that the model is useful for experimental design for LA-ICP-MS. The revised manuscript addresses the concerns regarding climate signal interpretation. The reviewer's comments are addressed below in blue, alongside the original review text.

The authors describe in the introduction that LA-ICP-MS analyses are necessary to reconstruct climate records in deep ice and use this as a primary reason for this study. However, the authors use the most basic structure of ice in this model. This is understandable given the continued questions around methodologies for LA-ICP-MS, however, as the work currently stands there are limited implications for deep ice studies.

This manuscript aims to step towards using LA-ICP-MS for high-resolution climate signal acquisition, such as that likely required for deep ice samples. It aims to demonstrate the presented model's applicability in a better-understood shallow ice regime before future work to model deep ice. We agree that the basic ice structure utilised does not reflect deep ice conditions and outline considerations to extend the discussion to deep ice.

The limitations of the current approach with regard to deep ice applications and potential additions for future work have been clarified in the introduction of the amended manuscript.

Additionally, while there is an attempt to quantify the CFA results using modeled results, no actual experimental data is provided to ground truth the model's ability to reconstruct CFA results. Additionally, as no concentrations are provided and no calibration was conducted, it is difficult to see whether the modeled data that this project hinges on are realistic or comparable. As a result I recommend the manuscript be reconsidered after major revisions.

Matrix-matched calibration is a widespread challenge in LA-ICP-MS, and only recently has significant progress been made in this regard for high-resolution studies on ice (Bohleber et al., 2024). In the future, we will target collecting and analysing additional calibrated LA-ICP-MS data. The presented modelling framework can be easily adapted to accept calibrated data. A comparison with experimental CFA data will also be targeted, as this will further test the model, as noted by the reviewer. Given that many studies using LA-ICP-MS to measure ice core samples use uncalibrated data (e.g. Della Lunga et al., 2014, Spaulding et al., 2017, Bohleber et al., 2021, Bohleber et al., 2022, Stoll et al., 2023), the present modelling discussion aims to contribute to the interpretation of analysis conducted on such signals. The routine use of calibrated data represents an exciting future development to extend both experimental and modelling studies.

Given the evident additional value calibrated data contributes to this topic, a discussion of recently-published calibrated ice LA-ICP-MS data that has a calibrated bulk data counterpart has been included to provide a ground-truth reference in the revised manuscript, as noted concerning the reviewer's comment on L222 below.

Specific comments:

L188: The statement "These modelled signals show the same general features as experimentally measured signals, with large spikes in intensity where profiles intersect grain boundaries." is not proven as the experimental signals are not shown for comparison.

This statement has been clarified to note that it refers to only the LA-ICP-MS profile data, plotted in figure 5, and not to modelled CFA, which does not have an experimental counterpart.

Figure 6: greater contrast is needed to see grain boundaries in a) and c). It is also very difficult to see the blue and red lines. Please make these thicker or choose different colors.

The colours used in the figure have been revised to make the features clearer.

Figure 7: There is no explanation I can find for why 7d and 7e show opposite profiles. Please provide more information. This is particularly important for the author's claim that this model can be used to compare between LA-ICP-MS and CFA results.

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).

Line 222: I'm unclear why no calibration is used here. Particularly for comparing LA-ICP-MS to CFA signals or comparing between analyses, and ground truthing the model, this is important to understand how well the parameterized model works.

As noted above, we agree that calibration provides valuable insight. Based on the limited calibrated data available in the manuscript by Bohleber et al., 2024, a ground truth example in comparison to bulk data has been included in the revised manuscript's discussion section 4.3.3. This discussion presents ice modelled based on calibrated LA-ICP-MS data and compares the results to calibrated bulk analysis. These results and the reviewer's comments encourage future analysis to be carried out in comparison with CFA.

Line 254: "In this context, the framework presented here can allow improved comparison between the outputs of different experimental setups and can form an essential foundation for inter-technique comparisons, first and foremost with CFA." This has not been proven. The authors themselves mention that day-to-day comparisons are not comparable, and as no calibration or concentration data is provided this remains conceptual.

This statement has been revised to highlight the link is conceptual.

Line 264: “Furthermore, the simulation of a CFA signal allows a direct comparison of LA-ICP-MS and CFA signals which is only possible as this is a 3D model” This has not been shown in this paper as no comparison to experimental CFA data is provided to show these are comparable.

This statement has been revised to highlight this work provides the framework for such a comparison and that further (ongoing) work is required with calibrated data collected using both techniques to satisfy a link.

Line 264: What does “This facilitates a direct comparison that is not currently possible for physical ice samples as the outer portion of ice measured using CFA is not measured to avoid contamination (Dallmayr et al., 2016).” Mean? I’m unclear how direct comparison is only possible with a 3D model here and why contamination control procedures impede this.

This statement was intended to illustrate the fact that typical surface LA-ICP-MS and bulk CFA analyses can not be carried out on the same part of a sample and that there will be spatial offsets in their measurement. As the outer portion of a CFA stick’s cross-section is usually fed to waste, and LA-ICP-MS measures a surface, they do not measure the same part of a sample. This has been clarified in the revised manuscript.

References

Bohleber, P., Larkman, P., Stoll, N., Clases, D., Gonzalez de Vega, R., Šala, M., Roman, M., and Barbante, C.: Quantitative insights on impurities in ice cores at the micro-scale from calibrated LA-ICP-MS imaging, *Geochem. Geophys. Geosyst.*, 25, <https://doi.org/10.1029/2023GC011425>, 2024.

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>, 2023.

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.

Spaulding, N., Sneed, S., Handley, M., Bohleber, P., Kurbatov, A., Pearce, N., Erhardt, T., and Mayewski, P.: A new multielement method for LA-ICP-MS data acquisition from glacier ice cores, *Environ. Sci. Technol.*, 51, 13 282–13 287, <https://doi.org/10.1021/acs.est.7b03950>, 2017.

Della Lunga D., Müller W., Rasmussen S.O., Svensson A.: Location of cation impurities in NGRIP deep ice revealed by cryo-cell UV-laser-ablation ICPMS. *Journal of Glaciology*. 60(223):970-988, <https://doi.org/10.3189/2014JoG13J199>, 2014.