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"Two-dimensional impurity imaging in deep Antarctic ice cores: Snapshots of three climatic periods and implications for high-resolution signal interpretation"

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- Response to reviews -

Please note:

- ***All line numbers in "Changes to manuscript" refer to the new revised version (if not noted otherwise)***
- ***Changes in the revised pdf are highlighted in red***
- ***Author's responses to the referee's comments are in blue***

Overview on manuscript revision

We thank both referees for their positive and helpful reviews of our manuscript. The revision comprised the following main changes:

- The presentation of the imaging method was clarified regarding the connection between fast washout and high repetition rate (Section 2).
- The assessment of the spatial significance of line profiles (Section 3.4) was clarified in more simple terms to improve readability.
- The discussion on impurity localization was re-organized to better separate the discussion of the chemical images and aspects regarding the imaging method (Section 4.1).
- Figure 7,8,9 were changed to include the correlation matrix as a square plot. The Figures in the Supplementary Material were changed accordingly.

We believe that these changes have substantially improved the manuscript. The responses to the specific comments and technical corrections are detailed below (in blue) together with the track changes in the original manuscript (in red) which is at the end of this document.

Response to referee #1 David M. Chew

Dear editor,

This is an interesting study employing LA-ICP-MS mapping of ice cores from Antarctica. The glaciology/climatology aspects are not my area of expertise, so my substantive comments below mainly concern the methodology. The paper is generally easy to follow, but there are many instances of awkward phrasing. I have a list of suggested typographical improvements below, but the paper should have a quick edit by a native English speaker. I recommend minor revisions.

We thank the referee for the comments, which especially helped to present the methodology more clearly. We have addressed all comments as described below and have also tried to improve the readability of the text with the help of a native English speaker.

A washout of 34 ms is quoted (i.e. the system is capable of returning to baseline with a repletion rate of 29Hz). Yet it says in the paper L70-71 "With washout times in the tens of ms range, the recording of baseline-separated single pulses at high repetition rates becomes possible; 294 Hz and a dosage of 10 were used here". There is no way with a washout of 34 ms that that you would see baseline-separated single pulses, so some rewording is needed here. Additionally, the term "dosage" is not used all that commonly in the LA-ICP-MS literature. I would define it in one sentence, and the recent JAAS article by Šala et al. could be cited.

We now realize that the two sentences can be misunderstood. With a dosage of 10 we improve the image quality but do not separate individual pulses anymore. To avoid this misunderstanding, we decided to separate the general statement regarding the benefit of fast washout and the specific statement regarding our acquisition settings. The general statement is now moved to the introduction, where the use of fast washout technology was already mentioned (line 31). This way, we are focusing in the method section solely on the description of our acquisition settings. We are also including the suggested reference by Šala et al. and give an explicit explanation of the term "dosage" (line 74).

> employing dedicated ablation cells with fast washout as well as optimizing the lasing and ICP-MS settings have introduced a new state-of-the-art in imaging techniques with LA-ICP-MS (Wang et al., 2013; van Elteren et al., 2019). The term "washout time" refers to the time needed to transfer the ablated sample aerosol plume to the ICP-MS. It is principally determined by the extraction efficiency from the ablation cell and any subsequent dispersion in the transfer line. With washout times in the tens of ms range, the recording of baseline-separated single pulses at high repetition rates becomes possible (Van Malderen et al., 2015). Recently, this new imaging approach was transferred to ice core analysis with LA-ICP-MS, offering the opportunity

> ARIS, a rapid aerosol transfer line, was used, resulting in a washout times of ~34 ms. A repetition rate of 294 Hz and a dosage of 10 was used here. In contrast to single pulse analysis, a dosage greater than 1 implies that each pixel is generated by multiple partially overlapping laser shots, which leads to an improved signal-to-noise ratio and better image quality (Šala et al., 2021). The fast washout combined with a high repetition rate allows scanning of the surface at around one millimeter per second, which is roughly 10 times faster than previous studies on ice cores (Della Lunga et al., 2017; Spaulding et al., 2017). As a

The isotopes 23Na, 25Mg and 88Sr were measured, with dwell times of 4, 4.6 and 10 ms respectively. What was the total sweep time (i.e. including settling) and the duty cycle?

The total sweep time was set to 34 ms, matching the washout time in order to avoid image artefacts. We routinely acquired four analytes, including Na, Mg, Sr and the additional mass 55Mn, the latter with a dwell time of 10 ms. This results into a total duty cycle of ~84%. We added this information to the text. (line 86).

> precise synchronization of data acquisition required to avoid image artifacts, the number of analytes/isotopes was restricted. Four elements were routinely recorded per image: ^{23}Na, ^{25}Mg, ^{55}Mn and ^{88}Sr with respective ICP-MS dwell times of 4, 4.6, 10 and 10 ms. (Bohleber et al., 2020). The total sweep time was 34 ms, specifically set to match the washout time, resulting in a total duty cycle of 84%. Considered in the following are Na, Mg and Sr, due to their significance as paleoclimate proxies in polar ice cores (Legrand and Mayewski, 1997): Na being related mostly to sea-salt, Mg with both marine and terrestrial sources

L138-140 "The relative higher background level seen in Na has been observed before in LA-ICP-MS ice core analysis and was suggested to be related to the use of NIST glasses as reference materials (Della Lunga et al., 2017)." Same would probably apply to any soda-lime glass. But my main query here were the signal intensity maps not background-corrected? And if not, why?

Following the referees' comments, we find that we have to clarify here the fact that the higher levels observed for Na are mainly due a higher (absolute) instrumental sensitivity for the element, but we cannot exclude some memory effect due to the contextual ablation of glasses for tuning, drift correction and quantification, as hypothesized by Della Lunga et al. 2017. We decided to reword this paragraph to avoid this potential misunderstanding (line 147). To answer the question: Yes, the signal intensity maps were in fact background and drift corrected, this is already explicitly stated in Lines 84-85 of the original manuscript.

> For further comparison of the degree of co-localization, the matrices of intensity values that underlie the images shown in Figure 2, 3 and 4 were used to make scatter plots for each pair of elements. As becomes evident from Figure 5, the intensities for Mg and Sr are generally similar, while Na intensities can be higher by several orders of magnitude. This difference can be explained by higher Na concentrations paired with a higher (absolute) instrumental sensitivity for the element. The scatter plots also indicate the almost absent co-localization in the TD Holocene image, showing signs of mutual exclusions (values

Typographical improvements

All suggested changes were made accordingly.

L54 "In presence of a variable signal" – reword start of sentence.

Changed accordingly. The respective sentence was reworded.

various depth sections were selected, that were representative of distinct climatic periods. The samples were analyzed, aiming to include a broad spectrum of ice properties, such as age and mean grain size. These snapshots of the 2D impurity distribution taken by LA-ICP-MS elemental imaging, provide important details on the location of impurities in relation to the grain boundary network. The imprint of the grain boundaries may vary between different impurity species and climatic periods. Consequently, the spatial significance of a single line profile along the main core axis has to be carefully assessed. These 2D images provide new and improved information for this purpose. It has also been shown how measurement settings can be adapted so LA-ICP-MS line profiles can be used when investigating climate proxy signals in highly thinned deep polar ice.

L56 delete "on this ground"

Changed accordingly.

L63 "keeps the ice samples surface temperature durably at" – change to "keeps the surface temperature of the ice samples consistently at"

Changed accordingly.

L91 "Sample selection was guided to consider ice of" change to "Sample selection targeted ice at"

Changed accordingly.

L93 change to "calls for mapping large areas"

Changed accordingly.

L99 change to "local maximum in grain radius at around 3.5 mm"

Changed accordingly.

L106 use of "sections" is confusing in this sentence. Are we talking about different samples, or area / domains within a sample.

We are actually referring to certain parts of the image. We clarified this sentence accordingly.

The elemental intensity distribution maps obtained are shown in Figures 2, 3 and 4, together with the optical images of the corresponding sample surface. All three analytes generally show sufficiently high signal/noise ratios. The three sets of maps show clear differences but are composed of similarly basic features. If sorted by increasing spatial extent, the basic features are: i) individual bright spots, typically comprising of just a few clustered bright pixels, ii) a network of lines, especially dominant for the Na maps, iii) mm-scale differences in the intensity, with some parts of the images being distinctly lower in intensity compared to the others. Comparison with the optical images clearly shows that the network of high-intensity lines

L109 delete 'their'

Changed accordingly.

L121 "In-grain intensities of Mg and Sr" is not clear.

Reworded to clarify.

> – **EPICA Dome C, MIS 5.5** (Figure 4): This sample stands out by showing a high degree of localization at grain boundaries for all elements. In the grain interiors, Mg and Sr occasionally show elevated intensities at locations close to the grain boundaries. Bright spots are almost completely absent.

L129 change to "in the Mg and Sr signal distribution"

Changed accordingly.

L133 delete "the image of"

Changed accordingly.

L146 change to "since they are superior in such cases"

Changed accordingly.

L159-160 change to "allows image segmentation based solely on the LA-ICP-MS images to be performed"

Changed accordingly.

L174 change to "between 3-6 times higher than for"

Changed accordingly.

L176 and 177. I do not follow either of these two sentences" "Both effects translate into an analogue situation for the ratios, with the exception of the Mg/Sr ratio. In grain boundaries, the latter shows only comparatively a small difference between MIS 2 and MIS 5.5."

We have reworded both sentences in order to clarify.

> The ratios reveal that the relative enrichment at grain boundaries is generally highest for Na, between 3-6 times higher than for Mg and around 10 times higher than for Sr. Next, the relative enrichment at grain boundaries is 3-5 times higher in MIS 5.5 compared to MIS 2. The relative higher enrichment of Na at grain boundaries translates into corresponding high values of Na/Mg and Na/Sr. The Mg/Sr ratio is also increased at grain boundaries, although to a lesser extent than the ratios including Na.

L186-7 delete "It is important to note that this analysis assumes the continued presence of optimized instrumental settings, thus no further artifacts are introduced."

Changed accordingly.

L188 what is the "transversal dimension"? Do not follow.

We have rephrased the respective section in order to clarify what was done.

> In order to simulate how the spatial impurity distribution would appear in coarser resolution LA-ICP-MS elemental imaging, the 35 μm resolution images are sub-sampled in longitudinal (along the scan, i.e. left to right) and transversal (perpendicular to the scan) direction. The transversal sub-sampling is primarily simulating using a larger spot size whereas the decrease in longitudinal direction additionally corresponds to longer washout times. The rows of the original images are averaged stepwise

L192 change to "since it features"

Changed accordingly.

L197 change to "while comparatively smaller grains"

Changed accordingly.

L200 change to "only a small influence". I do not follow "the relative transversal position" part of the sentence.

Rephrased to clarify.

> scale of 700 μm, the TD Holocene and EDC MIS 2 images resemble mostly the large-scale intensity gradients. At this point, a high degree of spatial significance of a single line is achieved. This means that the obtained signal is largely independent of the positioning of the line profile perpendicular to the scan direction. Notably, this situation is different for the EDC MIS 5.5 images, comprised by comparatively large grains. Regarding Mg, a comparable degree of homogeneity as for Na is achieved at the steps shown here, indicated by similar relative standard deviation (RSD) values (Supplementary Material).

L202 delete "at the steps shown here"

Changed accordingly.

L210 change to "but extend approach to samples from core sections"

Changed accordingly.

L217 replace "analyzing" with "of"

Changed accordingly.

L218-9 reword to "However, prior to the advent of the LA-ICP-MS imaging technique, elemental maps had to be acquired using arrays (grids) of laser spots with spot sizes larger than 100 µm, followed by spatial interpolation"

Changed accordingly.

L231 change "may have fractions" to "may be"

Changed accordingly.

L237 I do not follow 'may show "pinning of" or "dragging with"

Rephrased to clarify.

Considering the Na enrichment at the grain boundaries in a simplified view would mean that, with grains growing over time, the comparatively mobile (e.g. soluble Na) species are more easily collected at the grain boundaries as opposed to the less mobile species such as the insoluble particulate fraction. This is simplified because particulate inclusions may also inhibit grain boundary growth (e.g. through "pinning of" or "dragging with" grain boundaries). This process could also result in localization of particulate impurities at boundaries (Faria et al., 2014b; Stoll et al., 2021). It is evident that only limited generalized conclusions can be drawn from the small-sized images. Accordingly, it is not intended here to discuss in detail the different behavior of chemical impurities in relation to their mobility and insoluble fractions.

L244 delete "exemplarily" (this word is used incorrectly in all instances in the paper

Changed accordingly (and revised throughout the paper).

L254 delete "here analyzed"

Changed accordingly.

L257 delete "already investigate"

Changed accordingly.

L262-3 "image analysis applied to investigating the chemical images is advantageous"

Changed accordingly.

L269 delete "signal of"

Changed accordingly.

L272 replace "task" with "goal"

Changed accordingly.

L296 change to "not a generally applicable value, however as the larger grains"

Changed accordingly.

L305 change "recording" to "imaging"

Changed accordingly.

L311 change "regarding" to "for"

Changed accordingly.

L321-2 "are more distributed" is not clear

Rephrased to clarify.

differences among glacial and interglacial samples of the Talos Dome and EPICA Dome C ice cores from central Antarctica. The images reveal that grain boundaries coincide with high intensities of Na for all samples. In the Talos Dome Holocene sample and the glacial sample from EPICA Dome C, Mg and Sr are presented also in the grain interiors. The interglacial

L324-6 change to “Simulations of coarser resolution experiments shows that the spatial significance of a single line profile increases as the imprint of grain-boundaries weakens at coarser resolution.”

Changed accordingly.

L326 change to “This allows settings to be adapted specifically fit-for-purpose”

Changed accordingly.

Figure 5 caption. Change second sentence to “A linear regression (red dashed line) is shown purely as a visual aid.”

Changed accordingly.

Figure 7 caption. Change first sentence to “Example images illustrating the effect of decreasing the spatial resolution of the original image (a) in 35 μm steps in the vertical and horizontal direction (see text).

Changed accordingly.

Table 2 caption. Delete “Overview on results from”

Changed accordingly.