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"Tw	o-dimensional impurity imaging in deep Antarctic ice cores: Snapshots of three climatic
	periods and implications for high-resolution signal interpretation"
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	Barbante
	- Response to reviews -
Please	e 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 tha	ank both referees for their positive and helpful reviews of our manuscript. The revision
compr	ised 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.
٠	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 bel	lieve that these changes have substantially improved the manuscript. The responses to the
specifi	c 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.	

29	Response to anonymous referee #2
30	This paper shows some of the first images produced with a new laser ablation – ICPMS system that is
31	configured to produce two dimensional maps at high resolution. The paper shows maps from 3
32	cores, representing the Holocene at Talos Dome, MIS2 and MIS 5.5 at dome C. In fact the method
33	itself and the results from the Talos Dome Holocene core have already been presented (in the
34	authors' JAAS paper). However this paper is definitely an advance in that it shows the wide
35	applicability and potential of the method, displays some beautiful images for the glaciological
36	community, and considers some issues related to how such a method should be used, processed and
37	imaged.
38	The highlight of the paper is certainly the lovely images we see in Figs 2-4. These really are a fine
39	technical achievement and a joy to look at and think about. The paper considers the differences
40	between elements (Na, Mg and Sr), and the differences between climate periods. The second of
41	these is indicative but difficult to pursue: with only one example from each climate period, can we be
42	sure that the findings are typical? I accept that it is unreasonable to expect more at this stage, and I
43	am willing to ignore this problem this time. However in the future it will be necessary to see enough
44	different sections in each climate period to really understand the rules.
45	The discussion of how to average the records in order to use the method to its best effect is
46	important, but is not very well-explained. I think I got it in the end, and the result is worth discussing,
47	but I will suggest some better explanation of what was done. I like the thinking in this section though
48	- until now it seems to have been assumed that better resolution is always good. Here the authors
49	show clearly that better resolution helps with understanding microstructure, but will have to be
50	sacrificed to understand large-scale layering.
51	Overall, I do see some ways in which the explanations in the paper could be improved. But as a well-
52	illustrated proof of concept this is an excellent paper and should be published.
53	
54	We thank the referee for the encouraging comments, which we were able to address fully in our
55	revision. We have clarified our approach to assessing the spatial significance of single line profiles by
56	spatial averaging, aiming to improve readability and to present it in a clearer way. Details are
57	presented below. We fully agree with the referee regarding the need for further data in order to
58	better assess the significance of the results. This reasoning is also behind the framing of the title,
59	where we refer to the datasets as "snapshots". At the present point we believe it was important to
60	demonstrate that images from different climatic periods do show distinct differences, and to discuss

- 61 how, on this ground, the interpretation of LA-ICP-MS datasets can be improved.

- 64 Detailed comments:
- 65
- 66 Page 1, line 11 "it is demonstrated how instrumental settings can be adapted specifically fit-for-
- 67 purpose". This doesn't quite make sense, I suggest "it is demonstrated how instrumental settings can
- 68 be adapted to be fit-for-purpose".
- 69 Changed accordingly.
- 70
- 71 Line 41. I suspect this became available after the paper was prepared but the authors may wish to
- 72 reference Ng et al 2021 here as well as Rempel et al.
- 73 Changed accordingly.
- 74
- Line 68-71. Like the other reviewer, I didn't understand how one could reach 294 Hz if the washout
- 76 time is 34 ms. Please explain this further.
- 77 We see this potential misunderstanding. We followed state-of-the-art imaging techniques and used a
- 78 dosage of 10 (10 overlapping laser shots per pixel) to improve image quality but did not resolve
- 79 individual pulses this way. We rephrased this in order to separate clearly the general statement
- 80 about the importance of achieving fast washout (line 31) and the specific statement referring to our
- 81 image acquisition (line 74).
 - 30 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.,
- 82 35 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

- 75 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
- 84 Line 75. I don't think you mean 150 mm square! Maybe 150 um? But anyway please be clear whether
- 85 this means 150 x 150, rather than a size that amounts to an area of 150 um².
- 86 150 x 150. Changed accordingly.
- 87

83

- 88 Figs 2-4. I really like the elemental maps but am a little less clear what I am seeing in the composites
- 89 in part c. Perhaps it's just the colour scale that is confusing me, because superimposing even the
- 90 lightest colours shown there will certainly not give a white. Should the scales run through to very
- 91 light blue/red/green to more correctly characterise what you did?

- 92 The composite images use a standard way of combining chemical channels. We agree with the
- 93 referee that there are some difficulties with this approach, at least as far as using the visual
- 94 inspection for quantitative co-localization investigations. This is a fundamental issue with this way of
- 95 presenting the data, which would not be remedied by using a different color scale. We have referred
- 96 to this in the text already but, following this comment, have added a statement to make it clearer
- 97 (line 144).

where single channel bright spots stand out abundantly. However, the visual overlay has its limitations regarding analyzing colocalizations. Differences in absolute signal intensity and signal/noise ratio can subdue or mask co-localization. The composite
images in Figures 2, 3 and 4 with each element in a separate color channel are thus considered only as a starting point.

- 98
- 99 Line 140. I don't really understand this discussion which leads to the discussion about the use of NIST
- 100 glass reference standards. I can understand that the instrument can be more sensitive to Na, and
- 101 that Na is at higher concentrations so should give higher counts. But I'm not understanding how the
- 102 standards would affect the background or why this is relevant. Do you mean that there is a
- 103 contamination background because of the standard? But then you're clearly seeing a stronger signal
- 104 response as well as a background response for Na. As you can see I am confused so please explain
- 105 what you are suggesting here.
- 106 Following the comments made by both referees, we realize that there was some unintended
- ambiguity in this statement, which we have now rewritten in order to clarify. We only intended to
- 108 refer to the fact that a relatively higher background for Na was observed before in the study by Della
- 109 Lunga et al. (2017) where the NIST glass standards (which we also used) were suggested to be a
- 110 potential cause. As pointed out correctly by the referee, the main issue is however the sensitivity,
- 111 which is also relatively higher for Na, making a clear signal stand out over background. We have
- rewritten this accordingly to clarify it (line 147).

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

- 150 plots also indicate the almost absent co-localization in the TD Holocene image, showing signs of mutual exclusions (values
- Line 170 and Table 3. Are the elemental ratios in Table 3 ratios by weight or molar ratios?
- 115 The elemental ratios are given as mass ratios (weight), which we have clarified in the text.
- 116
- 117 Around lines 170 and 230: You seem to suggest maybe the marine material is at the grain boundaries
- and the crustal dust in the grains. While this makes sense the ratio of Na/Mg in the grain boundaries
- is much higher than that of sea salt. Might be worth discussion.
- 120 Thank you for pointing this out, we now refer to this observation in the discussion. Our main point in
- 121 this context is that for Mg, we cannot easily distinguish potential sea-salt and dust-related fractions
- 122 based on co-localization analysis with Na and Sr, respectively. Including additional elements may help

- in the future to develop a more sophisticated distinction between marine and crustal material in the
- 124 LA-ICP-MS images. Following careful consideration of the referee's comments, we have re-organized
- 125 the respective section of the discussion (line 240). We believe this will increase the readability
- 126 significantly.
 - 240 The fact that the enrichment at grain boundaries is generally highest for Na, followed by Mg and Sr, suggests that on the micron-scale, differences in the interaction with the grain boundary network exist among these elements and among ice from different climatic periods. Mg may be related to sea salt as well as terrestrial dust (Legrand and Mayewski, 1997). However, based on the LA-ICP-MS images, Mg does not show a clear preference for neither Na (related mostly to sea-salt) nor Sr (a tentative substitute for terrestrial dust sources more commonly investigated through Ca). The Na/Mg ratio also shows the sig-
 - 245 nificant enrichment in Na at the grain boundaries (Table 3). However, it seems worth noting that in the grain interior is within a range typical for sea salt (e.g. Mouri et al., 1993), warrating further investigation.
 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
 - 250 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.
 - However, in future multi-elemental images such a type of analysis may become possible. Imaging the localization of impurities
 does not require a fully quantitative method for this purpose. As an additional indicator, the ratio of intensities, either between boundaries and interiors, or among two elemental species, can also be investigated without calibration. Since LA-ICP-MS measures the total impurity amount, and thus cannot directly distinguish soluble and insoluble fractions, a broader spectrum of elements could serve to identify impurities associated with a specific aerosol based on their glacio-chemical signature (Oyabu et al., 2020).
 - 260 Until images comprising a larger number of elements become available, introducing image analysis techniques can provide an alternative to overcome such limitations. This approach was explored here to compare intra-grain vs. in-grain signals. It is worth pointing out that this type of analysis using image segmentation was performed as a post-processing step and did not require a separate experimental design. Experiments aimed at comparison of intra-grain vs. in-grain were previously performed with LA-ICP-MS but required the manual tracking of the grain boundaries with the laser scan (Beers et al., 2020; Kerch,
 - 265 2016). It becomes clear that the new LA-ICP-MS imaging technique can offer important insights into the ice stratigraphy on the micron-scale and that special merit comes from introducing techniques of image analysis applied to investigating the chemical images. Future efforts in combining techniques image analysis in an automated way and for even larger images seem highly intriguing in this context (Bohleber et al., 2021).

The LA-ICP-MS chemical imaging may offer special merit to investigate the conditions in very deep ice, in particular regarding
impurity diffusion and post-depositional chemical reactions. The localization of the impurities at grain boundaries and triple junctions is a prerequisite for their potential migration along the ice vein network (Rempel et al., 2001; Ng, 2021). The imaging

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Page 11. I found it really hard to follow what the correlation matrices in Figs 7-9 are. I think I got it in

- 129 the end but please spell it out. If I have understood correctly you have taken all the parallel vertical
- profiles (ie at 420 um resolution you'd have 10 parallel profiles) and correlated them against all the
- 131 others. This should then lead to a symmetrical pattern where perfect correlations would be white
- across the entire diagram. Please explain it in these kind of simple terms. I think it's harder to grasp
- because you have put the figures as rectangles rather than squares, leading the reader to think they
- 134 might be looking at a map, and also to the plot not looking symmetrical.
- 135 This is correct. However, following this comment we have re-written the respective paragraph to
- 136 clarify it in more simple terms (line 195). We are also now using square plots for the correlation
- 137 coefficient and have also updated the supplementary material.

195 Using a gaussian filter along the scan direction in each line mimics the combined effects of increasing washout time and the moving laser (firing at a fixed repetition rate). This is not needed in the transversal direction since individual lines are essentially independent samples. In order to assess the spatial significance of a single longitudinal line, all lines in the image are correlated against each other. The correlation matrix (using the PCC) between all lines in the image is thus symmetric and should be perfectly white (i.e. equal to unity) in case of identical lines. This ideal case would correspond to perfect spatial significance, because it would be irrelevant at which position the individual line profile is measured. The actual images do not fulfill this ideal case. The relative standard deviation (RSD) of the correlation matrix entries is reported to quantify the degree of inhomogeneity.



Figure 7. Example images illustrating the effect of decreasing the spatial resolution of the original image (a) in 35 μ m steps in the vertical and horizontal direction (see text). The correlation matrix is calculated from all lines in the sub-sampled images, together with its relative standard deviation (RSD). Shown here are results for the TD Holocene Na image, at steps of 210, 420 and 700 μ m, in tile (b), (c), (d), respectively.