Stoll and co-authors present results from single particle time-of-flight (SP TOF) ICP-MS analysis on EGRIP (Greenland) ice core samples that have already been analysed by Raman spectroscopy and laser ablation (LA)ICP-MS. Overall, I find the subject very interesting and would like to see publication. Before this, I recommend that the authors consider significant revision to ensure the case they attempt to present for this new method is a compelling one, based on robust interpretation of the data, accounting for assumptions and uncertainties.

A: We thank the referee for their helpful comments which will improve the manuscript significantly. We are happy to include more details and the suggested changes in a revised version. Below, we will answer the raised issues in blue.

I found the manuscript difficult to read. After reading the abstract, introduction, and conclusions (what many readers initially do) I was no wiser as to the specific focus of the study. The abstract includes several nebulous claims of 'complimentary perspectives' and 'new possibilities' but it is not clear what these are. From reading the manuscript through, the only advantage of including SP TOF analysis in the chain of particle-related analytical methods presented by manuscript is the chance to estimate particle size distribution from the SP TOF results. It would be better if the abstract, conclusions, and likely also the title, focused on this aspect, rather than claiming any benefits that are not demonstrated in this study.

A: We will tighten the writing to provide a more streamlined reading experience. As described in the manuscript, the SP technique is so far hardly used in ice core sciences despite its benefits. These go far beyond the aspects mentioned in the above comment and we will highlight critical advantages within the revision. In brief, with SP ICP-TOFMS, it is possible to gain single particle resolution from an elemental perspective. Especially the TOF mechanism is a game changer as it enables non-target screenings for particulate elements without a priori information. Found particle signals carry convoluted information which enables us to calibrate number concentrations for selectable particle populations, to determine mass distributions and estimate sizes, as well as to carry out an in-depth composition analysis which provides opportunities to identify geochemical signatures. As such, several critical parameters for particle analysis can be retrieved, which is not possible with current techniques. However, it is fair to point out that the purely "elemental" perspective is limited and single particle Raman spectroscopy provides a unique complementary vision enabling to withdraw mineral data enabling a much better modelling of particle composition and adding information which otherwise remain hidden. We will highlight these advantages with more emphasis in our revision. This emphasis was weaved into the manuscript in a way, which also makes the aims and objectives easier to identify.
The presented approach is a potential systematic analysis tool for the future especially for very rare samples from the "Oldest Ice" quest, such as Beyond EPICA, Dome Fuji or Blue Ice samples.

Why develop a new method for particle sizing at all? Why not stick with CFA-based Abakus, SPES or Coulter counter methods? It would be great to see some justification of the need for the method development proposed here. L285-288 could be moved from the Discussion for example.

A: We mention that the commonly applied techniques (Coulter Counter and Abakus) have limitations, such as the measurable particle size range (usually above 1 micron, l. 160). SPES is indeed exciting progress for nanoparticle size measurements (particle minimum size of 0.2 micron in Zeppenfeld et al. 2024) and we will include SPES in the revised text. However, SP ICP-TOFMS provides much deeper insights into ice cores and accesses several particulate parameters simultaneously at single particle resolution. It becomes possible to detect one particle and determine mass/size as well as its elemental composition. Importantly, we may detect particles as small as 30-50 nm, which goes far beyond the capabilities of the aforementioned techniques. Through the counting of thousands of particles per minute, we gain the ability to distinguish between different (small!) particle populations which have different significance regarding their presence in ice and through clustering methods, we may estimate their identity. Through the consideration of cluster-specific numbers, mass/size distributions as well as faint chemical impurities, we gain insights, which remain hidden when only using established methods.
Thus, we believe that it is advantageous to explore such new approaches enabling a more holistic view into particle characteristics. Particle size is important for e.g. climate modelling while both, chemical composition and particle size, are important to explore the role of dust during the Mid-Pleistocene Transition (Wolff et al., 2022). We will focus more strongly on these aspects in the revised version and move important information to the introduction as suggested.

A couple of technical queries:

- Could more information be provided on the conversion from measured ‘intensity’ (Fig. 1) to a ‘detection’ (is this the same unit as intensity, minus the threshold value?), to ‘normalised detection’ (normalised to what?).
  A: The exact workflow has been published previously, and detailed information on raw data streamlining is available in Lockwood et al. (2021, 2024).
  In brief: We use compound Poisson statistics to establish a threshold over which a signal is identified as a particle event with a certainty of 99.999%. Each signal is usually resolved across 3-10 data points, which are summed up as “detection” (or one particle event) and the same time, we automatically check for coinciding signals from other elements, which will be associated as “present within the same detection/particle event”. The mean signal is subsequently subtracted and processed data is saved as an array for subsequent calibration, in which the elemental response and the transport efficiency is used to determine masses and sizes. Subsequently, we use hierarchical agglomerative clustering to suggest common particle populations. As described in the text and the answer to referee 1, different background thresholds have to be applied depending on the data analysis approach and the measured samples. To compare samples with highly different dust concentrations, we applied the same background threshold thus influencing the number of detections. Normalised detections are relative values referring to the percentage of a certain element found in the analysed sample. This enables a qualitative comparison between samples with highly varying particle concentrations, as is the case for our samples, ranging from the Holocene to the Younger Dryas and Last Glacial.

- L43 “if suitable standards are analysed concurrently”. What are the standards referred to here? Are these the “calibration standards” mentioned at L107? How do you calibrate for ionic species and insoluble (particulate) elements? Or (related to above point) does a true calibration not actually occur?
  A: There are two critical parameters in SP ICPMS, which need to be calibrated with a set of two standards: 1) A particle standard containing a particle with known composition, size and density (or alternatively with a known number concentration), which is analysed to determine the transport efficiency (see answer below). 2) An ionic standard (as well as a blank for background subtraction) containing all elements to be calibrated at a known concentration, which is analysed to determine elemental responses and to calibrate raw intensities into masses. If mineralogy data is available (which is the case if Raman spectroscopy is carried out in tandem), we can further translate single particle masses into sizes considering phase density and elemental mass fractions. The streamlined and automated process is explained in much detail in our previous (and cited) publications: Lockwood et al. (2021) and Lockwood (2024).
- How representative do you expect the Au nanoparticle recovery result to be of particulate matter within these ice core samples?
  A: The Au nanoparticles are not used as internal standard. They are used to determine the transport efficiency in SP ICP-MS (see answer above). This efficiency describes the fraction of liquid nebulized and transported into the plasma. Using conventional set-ups, this efficiency is only around 5%, which means that from 100 particles, we only see 5. When attempting for example calibrations of number concentrations, this parameter is applied to consider the remaining 95%.

How well is the efficacy of the proposed SP TOF method for particle sizing demonstrated…?
A: SP ICP-TOFMS is a mass sensitive technique. As such we can accurately determine elemental masses within a single particle, which typically are within the ag to pg range. The sizing efficacy is dependent on complementary knowledge and also on some assumptions. On the one hand, we require some information on mineralogy to estimate particle density and mass fraction to translate mass into size. Especially in environmental studies, mineralogy is usually based on a sophisticated guess. However here, instead of guessing mineralogy, we determined mineral composition using Raman spectroscopy, which enables us to have more accurate models of size distributions making our study innovative. On the other hand, no knowledge on particle shape is available and SP ICP-TOFMS is used to project masses into a spherical shape. Admittingly, this does not reflect reality well but provides an estimate on the size scale of particles. Similar assumptions and limitations are present in other particle size analysis devices (e.g. Simonsen et al. 2018).

The authors state “Estimating particle sizes is possible if specific crystal phases are chosen for each element to obtain phase density and element mass fractions.” In section 2.5 they describe how each element measured is assigned a mineral, based on previously published Raman spectroscopy work. This assumes, for example, that all Si is sourced from SiO2, all Al from potassium feldspar, and that the mineralogy present in the nanoscale particles matches that of the microscale particles

measured. These both seem like huge assumptions. The authors state the mineralogy assignment is a “simplification”. I don’t see that the implications of these assumptions are tested, i.e., to what extent do they influence the particle size results obtained? Si and Al are, by definition, present in all aluminosilicate minerals, which have different densities and elemental fractions.

A: It is right, that sizing is based on various assumptions as outlined in the previous answer. SP ICP-TOFMS is more applicable to detect element masses within a particle. However, this data is difficult to interpret and size information (e.g., 50 nm), provides a better understanding than mass data (Fe mass: 50 fg). As such, it is common to give a size estimate and admittingly, this sizing is subject to various assumptions and errors. In the past, environmental studies entirely guess mineralogy and while out approach is not flawless, we have some understanding of common mineral phases based on hundreds of previously characterized particles in the same samples. However, we admit that this still provides inaccuracies, because not all Al and Si are present as feldspar and a significant fraction is likely to consist of aluminosilicates. Nevertheless, our approach is still more evidence based than the current state of the art. Overall, we still think that our approach is a sensitive compromise of assumptions and available data. This could change if a coupled SP-Raman system trapping particles could be used (Neuper et al. 2024) providing direct in-situ data, but this has not been achieved yet for cryogenic analysis.
We will emphasize in the revised manuscript that our size estimation is prone to several assumption and simplifications, and point out that the aim is to provide a general understanding of potential size distributions without claiming they are absolute.

In section 3.2.1, Figure 4, each element (or isotope) has been assigned to a mineral, and each mineral is assumed to have a certain density. Are these provided anywhere? – this choice seems absolutely critical to the particle size estimate, if I understand correctly. Overall, the conversion from mass to size and the potential uncertainty is not clear – the reader is referred back to Section 2.5, which provides little help.

A: This is true, the chosen values are currently only indirectly mentioned via the mineral phases. We will provide the used densities in the revised text. See answers above for the mass-size approach as well as the mentioned references describing the conversion.

Figure 5 displays the calculated particle size distributions for the five chosen elements/mineralogy assumptions for three of the samples only. The axes labels are impossible to read so it is difficult to begin to judge how these distributions might compare to existing particle size data.

A: *TC* only allows a figure maximum width of 12 cm limiting the number of displayed examples without making the plots completely unreadable. Thus, mean and median values are displayed separately. We will enlarge the labels and update the plot to enhance readability.

Only samples H1, H2 and YD3 have insoluble particle data available (and only H1 is plotted on Fig 5). There doesn’t appear to be any comparison with these existing

data within the manuscript. Unless I missed it, there is no attempt to verify the results of the SP TOF particle sizing method using independent means.

A: Unfortunately, insoluble particle data for the EGRIP ice core is limited as it is primarily motivated to gain a better understanding of ice flow and deformation. Thus, only specific depth regimes of the core have been analysed with CFA and large parts of the core are not planned to be analysed at the moment. Insoluble particle concentrations for the upper ~1300 m are displayed in Stoll et al. (2022). However, no particle size or chemical data has been published yet, hampering comparisons. This fact, and that SP data from ice cores is so scarce, make it very challenging to discuss this further as mentioned in the text.
Additionally, it is challenging to interrogate data obtained with other methods. At the current state, there is very limited knowledge of the number of nanoparticles within ice, and established methods focus either on the upper nanoscale or microscale. As such, we navigate within an uncharted territory. Furthermore, the number of particles, as well as data on mean sizes and composition, are massively biased by the lower detection limit. As such, our data and study should be regarded as a tentative approach to chart the nanoscale of particles found in polar ice cores. We will emphasise that we still have many blind spots, but aim to expand the accessible range of particles. As such, there are discrepancies, which, however, are negligible given the explorative approach suggested here.

Finally, a quick note to say I do not share Reviewer 1's concerns on contamination potential. Significant contamination from drill fluid or human handling would have shown up in the previous analyses. Drill fluid needs micro-cracks to penetrate into the ice core and these were not visualised. A clearer description of decontamination procedures and maybe a brief justification for their choice would be valuable. The second point highlighted by Reviewer 1, on the threshold setting, needs clarification before publication.

A: We will improve the text on sample preparation and decontamination procedures. We will further explain the threshold procedures better as mentioned in our answer to the first referee report.

Minor suggestions:

The Introduction needs re-writing to streamline the information and argument presented. Many of the paragraphs reiterate arguments previously made.
A: We agree and will streamline the introduction to avoid repetitions.

L21: Is there not a more up-to-date reference than this 1997 one? The excellent Encyclopaedia of Quaternary Sciences by Koffman springs to mind (although I appreciate it is not OA).
A: Agreed, we will add more recent publications on the matter.

L32: please more be specific on the 'particular material characteristics of ice'!
A: This refers to the challenges provided by ice in solid form, such as the need for e.g. ice laboratories and specific cryo-sample holders as well as the logistical difficulties in obtaining and transporting samples. These challenges hamper the

straight-forward transfer of state-of-the-art analytical chemistry approaches to ice core samples. We will elaborate on this in the text.

L55: please explain what a “competitive trace element analysis” is.
A: This states that not only quadrupole MS, but also TOFMS can be used for trace elements analysis. We will edit this sentence.

L56-57: Please explain, for the average ‘ice core’ reader, the terms ‘non-target particle screening’ and ‘the internal and external mixing state of particles’ (if these advantages are actually relevant to this study).
A: Non-target screening enables rapid definition of a decision limit for all recorded m/z making it possible to choose specific elements with concentrations above a certain ppm-level for further analysis and without a priori knowledge. This reduces the processing time for TOF data by e.g. enabling to rapidly pinpoint relevant particulate elements beforehand. The exact workflow is described in Gonzalez de Vega et al (2023).
In atmospheric science, the **mixing state** of particles describes how different chemical components are distributed among individual aerosol particles. An **externally mixed** aerosol population consists of distinct particles, each composed of a single chemical species; thus, the particle population is chemically diverse at the single-particle level. In contrast, an **internally mixed** population contains particles that each comprise multiple chemical components, resulting in a more homogeneous chemical composition across the entire population. The mixing state significantly influences particle properties such as hygroscopicity, optical behaviour, and reactivity, and is therefore critical for understanding aerosol-climate and aerosol-health interactions. These states can vary a lot and are of importance in e.g. climate-relevant aerosol physical properties such as optical scattering/absorption and cloud condensation nuclei activity. This will be elaborated on in the revised manuscript.

Paragraph from L58: Isn’t there some SP TOF work coming out of Ohio State (Stanislav Kutuzov)?
A: There is work being done at Ohio State, which has been presented at conferences over the last years. Unfortunately, it has not been published in peer-reviewed journals yet.

L103: Acid-cleaned vials?
A: No, we however used novel vials and checked blank levels to confirm the absence of contamination.

L125, 147: 24Mg etc are isotopes not elements. This occurs throughout the manuscript!
A: This is true and might appear slightly confusing. SPTOF analysis measures isotopic data, it is thus important to clarify which isotope is referred to. However, isotopic abundances are considered during calibration, which means that the Mg levels are determined over the 24Mg isotope. We will address this more clearly in the revised version.

L187: Again, isotopes are listed not elements. 43Ca in G7 is low on Figure 2 but 44Ca is not – surely the relative abundance of isotopes of the same element should be corrected for? Why not describe elements as elements? Why persist in using

isotopes? Hopefully Table 3 is not actually listing 56Fe/27Al (ditto for Figure 6)?
A: See answer above.

Figure 2: Last sentence of caption needs adjusting for clarity.
A: Changed.

L249: 23Mg should be 24 Mg.
A: Changed.

References

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