Referee report for Hirano et al.: Oleamide as a novel insoluble organic marker for reconstructing Arctic wildfire history in the ice core from southeastern Greenland

I have read the manuscript “Oleamide as a novel insoluble organic marker for reconstructing Arctic wildfire history in the ice core from southeastern Greenland” with interest. The authors investigate the SE-Dome II ice core from South Greenland by applying different methods to derive the mineralogy and composition of microparticles. They identified, among others, the organic aerosol oleamide and discuss its application as a proxy for past wildfires in the boreal regions of the northern hemisphere. I enjoyed reading this manuscript and congratulate the authors on this interesting and sound approach. However, at its current stage, I suggest major revisions. This is mainly due to the manuscript’s unclear structure, which could be greatly improved to better support the interesting scientific findings. Below, I present my general and specific/technical remarks.

General comments

My main concern with this manuscript is structure, which can be confusing and repetitive at times. The Introduction and most of the Methods read well and contain the necessary information. However, the Results section is very short and omits most of the actual results, while including some details that belong in the Methods section (e.g., l.126-129 and l. 146-148). Further, methodological details appear several times in the Discussion, which disrupts the reading flow. Below, I provide some suggestions for restructuring the text to improve readability and understanding.

I would also welcome more details on data processing and analysis. For example, have Raman spectra data been smoothed and calibrated? How much effort/emphasis was placed on identifying dust minerals or unidentified spectra? This is hard to quantify, and identifying spectra can be tedious; it is thus perfectly fine to focus on specific groups of spectra/minerals.

Section 4.3: This first sentence should occur earlier to motivate your tests regarding NPs. The following sentences explain the method and should therefore move to the Methods section. The second and third paragraphs present the results and should therefore move to the Results section. For the Discussion, summarise your findings and put them into context with previous research as you did in the last paragraphs and nicely summarise in the very last sentence.

Lastly, the approach of characterisation and dealing with the “unidentified particles” can be confusing as it mixes results and discussion. In my experience, spectra (including those so far unidentified/not observed) should be mentioned in the Results, aligned with the identification of the respective minerals. The Discussion can then discuss e.g. particle origins, chemical reactions etc. Currently, you try to build a story of identifying these particles, which becomes confusing throughout the manuscript (e.g., figures displaying “unidentified particles” and the identified mineralogy directly below). The Results section is very short; consider framing the identification of these spectra as a Result.

Specific and technical comments

Title: Mention the used ice core or change it to “…history in an ice core from…”

l. 15: To avoid confusion I would place “in ice cores” behind “tracers” or change it to “from ice cores”

l. 16: consider adding something like “…(covering the years 1799-2000)…”

l. 22: Can you specify long-range and long-term?

l. 24: I might have missed something, but I don´t think you can define the geographic location of wildfires with your method. “Arctic wildfire” history might thus be misleading. Further, it would need more elaboration how you explore the fire-climate interaction?

l. 34: Why does the complex chemical structure and environmental impact of OAs make elucidating them essential? I understand the general idea, but this should be rephrased to strengthen the motivation.

l.41: What do you mean with fire-climate interaction? Temporally, fires (hours to weeks) and climate (>decades) work on different scales, please explain.

l. 49: 1 m water equivalent per year, later abbreviated – be consistent.

l. 51-54: These claims need some references.
l. 60: since this is a geochemical study, was it dry or wet drilled?
l. 63: 1.04 m w.e. according to Kawakami et al. (2023)

l.64: is enabled.

l. 65: mention that NH4 data are not available for the deepest depths.

l. 69: How much was roughly removed?

l. 70: no space between number and °C.

l. 74: could be confusing if you refer to ice samples or the particles within, which are samples from hereon. Maybe replace with “particles” to stay consistent with the subsection heading. In the following subsection, you mention aluminium foil samples; try to be consistent.

l. 78: Consider placing table A1 here. Are the optical observations done with the raman set-up or a different microscope? How were the foil samples treated to avoid contamination during the measurement/sample placement.

L. 79: A total of 1139 particles from 15 depths results in an average of 76 spectra per sample or did I miss anything? Please also give some more information regarding the conditions and set-up (e.g. is it located in a clean lab?). Clarify the different gratins, which was used for what? 2 accumulations are comparably few, is there a reason to not use more accumulations but less accumulation time?

l. 88: With optical methods or did you also conduct some geochemical tests?

l. 92: SEM-EDS not explained, avoid the abbreviation

l. 94: Is there a specific reason for the 1908 and 1911 layers?

l. 100: Could you quantify how often “rarely” is? With 30 analysed spots, this could be important.

l. 106: Again, is there a reason for the 1804 layer – why not staying consistent with SEM-EDS and analyse 1908 or 1911? You here also mention for the first time “the unidentified spectra”, which is confusing at this part of the manuscript.

Sect. 2.6: This section should be revised to clearly state the purpose and approach. The title is confusing at first as ice core samples are already frozen and the melting process and the thinking behind it are not displayed. Did you choose a specific part of the sample, or did you melt a random area (or everything) and then took a random droplet)? You also have time-lapse footage, why not show the device and some examples?

l. 150: What is “high”? An absolute value or a relative one in comparison to other samples or the surroundings?

l. 151: replace “present” with “observed”, they might be there but not analysed/identified

l. 152: be more specific about the “specific sample layers”

l. 153: higher absolute frequencies or in relation to the number of identified spectra? You mention it in the last sentence on page 5, but this is hard to put in context without knowing all relative and absolute abundancies.

l. 155: This feels a bit out of place, and I am not sure if it is statistically sound considering the missing NH4 data in the deepest 5 samples and the varying numbers of analysed/identified spectra per sample.

Section 4.1: The paragraphs need refining and restructuring as they currently mix different aspects (e.g. Raman spectra and particle size and shape from SEM-EDS). Further, I would move this section up into the Result and restructure the Results sections into 1) Raman spectra (known spectra/minerals and newly observed ones), 2) SEM-EDS results, 3) FT-IR, and 4) ice nucleating (mentioned in the Methods but not in the Results?).
A perk of Raman spectroscopy is the possibility to identify minerals, not just classes. “Mineral dust” has thus to be explained more by e.g. identifying typical minerals (quartz, feldspar, mica, etc) and then group them for the purpose of this paper as mineral dust.

l. 164: Raman spectroscopy enables the identification of the unique mineral (structure) (if Raman-active) and thus only indirectly the chemical composition, which can be highly complex for certain minerals.

l. 165: BB is defined several times; define it here and delete the rest.

l. 169: Would be good to include studies from ice cores here. BC was identified in Greenland by e.g. Eichler et al., 2017, Stoll et al., 2022, 2023 and in Antarctica by e,g, Eichler et al., 2019.

l. 184: switch the sentence about acid peaks with the sentence above it or clarify “these acid standards” again.

Sect. 4.2: This is arguably the most interesting section of the manuscript and should thus lead the discussion (4.1 and shift current 4.1 to Results). Similarly, l. 214-215 are also results (see comments above about absolute and relative counts). I would further be interested in discussing your method in regard to established methods using e.g. NH4 and if it could also be applied to Antarctica.

l. 207: Repetition from Results section, combine with the following sentence a la “the observed correlation may be attributed…”

l. 211: what do you mean with “structurally ordered”?

l. 232: citations for stable long-range transport and low reactivity within ice matrix or clarify that this is an assumption? The following sentences are good and an important finding; consider restructuring to give it more emphasis.

l. 237-239: Repetitive and should not be the first sentence, consider starting this paragraph with your second sentence.

l. 245: Is it really limited to Arctic wildfires or could they also be from lower latitudes? Occurs throughout the text, change accordingly.

l. 295: combine with first one-sentence paragraph

l. 308: are these suggestions realistic for ice cores?

l. 314: Do you really characterise the morphology in detail? OAs and FT-IR abbreviations not needed as not used in the conclusion.

l. 324: I would be careful with these claims. Your single particle data only goes back to 1908 or 1804 and there is a growing amount of evidence of chemical reactions taking place in (old/deep) ice. In my opinion, it remains to be shown if Oas are stable in deep ice, but this would be a great follow-up study on longer ice cores.

l. 332: Elaborate on the feedback with the warming polar climate? How can past wildfires help here?

Fig.1: I suggest removing the (i)-(o) labels and add two headers, i.e. Raman spectra and microscopic images, combining the rows. Thus, the last sentence in the caption could be deleted. The red dots in (i) and (j) prohibits to see the analysed particle, maybe you can come up with a better idea. As mentioned above, having “unidentified particle X” and the identified particle in brackets below does not make sense.
(h) could be an indication of fluorescence as also seen in other Greenlandic ice cores, e.g. EGRIP (Stoll et al., 2022).

Fig. 2: Consider putting this figure in the appendix and focusing only on the identified particles. It´s good to get an impression of unidentified spectra, but the main information discussed here are the known spectra.
Is there a specific reason for the comparably high number of analysed particles in the 1804 and 1908 layers? Was this on purpose or just random? The green “Mineral” part in the legend is unclear, do you refer to “mineral dust (e.g. mica, quartz, feldspar)” here?
It can be tricky to identify Raman spectra, it would be good to explain how much work was spent to identify particles. This is not the focus of this study, but it might draw a biased image if efforts to identify particles differed.

Fig.3 Caption: You can delete the SEM-EDS abbreviation. Consider adding “Al” in (b) to the prominent peak described.

Fig.4 Caption: Please explain why the red- and green bands and the respective wavenumber ranges matter.

Fig. 5 Caption: Please mention where the provided spectra are from, did you measure them yourself or used a database such as RRUFF?

Fig. A1: As far as I see it, the 1799 layer is only partly covered by data. The available/visible data do not seem enough to assess if this is a “strong” layer as the NO3 concentration does not exceed 100 ug/l, which is roughly the average seasonal peak concentration. I might have missed it, but is there are other data supporting the analysis of this specific layer? It´s the deepest/oldest data, which is a fine reason to analyse it, but this should be mentioned. Maybe also mention where the dating comes from.

Fig. A2: Consider a clearer heading of the three panels with the fitting heading on the left or in the middle of the panel. Currently, it is a bit tricky to distinguish the second and third panel.

Table A1: Can you really date the ice layers to fractions of individual years? Based on the referenced paper, I assume the age is calculated but this should be applied with caution on this scale. From taking samples to cutting them into different sections, it is highly unlikely to date a layer to e.g. 1804.2-1804.5 CE.
Is there a specific reason why there is no NH4 data below 114.6 m?
To distinguish high concentrations/layers, it might be useful to include a (running, yearly, 10 year) average concentration or something similar.

References

l. 420: x+375 pp; is this a typo?

Looking forward to reading the revised version.

Best,

Nicolas Stoll