

Interactive comment on “On-line differentiation of mineral phase in aerosol particles by ion formation mechanism using a LAAP-ToF single particle mass spectrometer” by Nicholas A. Marsden et al.

Anonymous Referee #3

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General comments

The authors present a technique to analyze chemical composition and structure of air-borne mineral dust particles using a laser ablation aerosol particle time-of-flight mass spectrometer (LAAPTOF), based on measured differences in key marker ion arrival times of chemically similar particle types, but with a variety of crystal structures. This is an interesting idea that merits publication. However, some sections could be written more clearly and/or need more information, the introduction could be somewhat streamlined, and some of the figures need higher resolution.

More specifically, I wonder about the usefulness of the analysis for other LAAPTOF

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users given the difficulties in forming reproducible mass spectra with this instrument from complex atmospheric particles. The results presented here are based on one particular laser setting – are the effects e.g. supposed to scale linearly with laser power? I am aware that the authors might not be able to redo the experiments, but a discussion of the validity and transferability of results to other LAAPTOF (settings) should be added to the manuscript.

Another aspect that should be discussed, even if only in a speculative manner, is the applicability of results to ambient particle types that just contain fractions of dust, or are of more complex mixing state than the laboratory standards. The differentiation of clay mineral standards certainly indicates at least the potential for such studies to be performed with ambient samples, but this should be elaborated upon further.

Specific comments

P. 13, l. 5 – p. 14, l. 18: How was the mass calibration done, specifically? Was it performed on each raw spectrum individually, with resulting time series of parameters, which were subsequently averaged? Or were spectra averaged first, and then the calibration was performed? Also, have the authors explored a mass calibration with a 3-parameter fit, i.e. a power law fit where the exponent is not kept at 0.5, and where the parameters are allowed to vary with time/spectra? This might actually reduce the shift in peak position in Figure 5. Both the mass scale and peak width dependence of the shift indicate failure of mass calibration. In other words, could one say that your study is in principle based on a failure of reproducible mass calibration in the LAAPTOF, and that you are using patterns of the failed mass calibration to infer mineral structure? What do your results signify for the mass calibration procedure in LAAPTOF in general?

Figure 6: Data points are based on how many spectra?

P. 18, l. 5/ Table 7: Table 7 indicates a negative correlation between the interlayer charge and τ – can you show it graphically? The table is presented in the manuscript without much of an interpretation of the result. More negative interlayer charges seem

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to increase “distortion” of spectra by reducing tau. Please elaborate further.

P. 19, l. 19 – 20: This paragraph would be easier to follow if you specified already here that you tried to classify the mineral samples, and that your results are number of particle per class.

P. 21, l. 6-12: The explanation of this part is too brief and should be expanded.

P. 22, l. 20: Can the authors say something about the influence of the size of ionization region on their results? If the plume expands in all directions, ions moving away from their respective extraction region of the bipolar TOF would presumably have a different flight time than ions moving towards their respective extraction region of the bipolar TOF, regardless of initial ion velocity.

P. 23, l. 1 – 19: It is not entirely clear in this paragraph if by “ion formation time” the authors here mean LDI, the time of particle-laser interaction, or specifically formation of individual ions within one specific particle. If they mean LDI, the shot-to-shot variation of LDI position based on particle flight time would influence ion formation time, and thus ion arrival time (which might be influenced non-linearly, depending on where ionization takes place, see comment above).

P. 24, l. 5-7: Is the shot-to-shot variation in energy delivered that large? The laser is presumably quite stable, and variation likely is more a question of how much energy is actually transferred to the particle, depending on when and where it is hit. This should be clarified.

Technical corrections

P. 2, l. 24: Closing bracket missing

P. 3, l. 10, and elsewhere: Physicochemical

P. 3, l.30: Typo, “because”

P. 4, l. 1: TOFMS is abbreviated TOF-MS in abstract

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P. 4, l. 19 and throughout manuscript: LAAPTOF no dash

P. 12, l. 13: Typo, 2x “in”

Figure 6 doesn't print well

P. 17, l.19: Reference error

P. 19, l.19: Reference error, and weird sentence structure

P. 23, l. 15: Sentence structure (“that” is too much)

P. 23, l.20: Typos/sentence structure

P. 25, l. 5-7: Sentence structure

Figure 10: Specify what grey and red are.

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