

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.

Dear Anonymous Referee #3,

We sincerely appreciate the detail with which you have reviewed our manuscript and the constructive comments given. Our response to your comments is given below.

On behalf of the authors,
Nick Marsden

The response to the review is structured as follows: The original reviewer comments are given in black, followed by the author response in blue font colour.

Major corrections to the manuscript are reproduced in detail at the end of the this document.

Anonymous Referee #3

(Received and published: 8 August 2017)

General comments

The authors present a technique to analyze chemical composition and structure of airborne 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.

[Introduction has been streamlined. See tracked-change document for details.](#)

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

[Data was acquired at different excimer laser settings. This has been added to the manuscript as Section ‘3.3 The effect of laser power setting’ \(See Major correction A\). This data suggests that differences in the distribution with respect to laser power setting may arise due to differences in ionisation threshold of different materials.](#)

[The Discussion section has been reorganised and now contains a discussion on the validity and transferability of the results to other LAAP-TOF \(See Major Correction B\). The tuning of the TOF ion optic is likely to have a big impact on the transferability to other LAAP-Tof, therefore the tune settings used for these experiments have been added to the supplement.](#)

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.

The Discussion has been extended to a discussion of more complex particle such as desert dust and ambient sampling transported dust. The authors have analysed transported Saharan mineral dust which will be submitted for publication shortly, and is now referenced in the introduction and discussion sections (Marsden et al, manuscript in preparation, 2017). It is our intention that the current paper sets out the technical details of the method and the follow-up paper will demonstrate the application to ambient dust.

In addition, the ambient analysis is available in Chapter 8 of Nick Marsden's thesis, which will be available open access at the University of Manchester Library.

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?

The procedure is explained in the methods section 2.3. 'Calibration coefficients were calculated for each sample type by fitting the first order approximation of the time of flight equation (Eq. 1) to the averaged peak centroid of three ion species'

I have clarified this in the table 6 caption 'Table 1. Mass calibration coefficients calculated from the mode peak position (TOF) of 3 ion species for each samples in each ion mode.'

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.

The OEM Data analysis software gives the option to make a 3-parameter fit on each spectrum individually, which reduces the peak shift as long as the peak position in $\pm 0.5\text{Da}$ of the original calibration. Stick spectra are then created from the 3-parameter fit calibration.

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?

The mineral structure is inferred from the differences in the raw ion arrival times. Performing the mass calibration removes detail of the shot-to-shot variation. The first order calibration is performed to highlight the differences in behaviour of the samples and demonstrate the mass dependence on shifting. The impact of the mass scale calibration accuracy will be discussed in detail in the follow-up paper featuring ambient aerosol data.

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

800 spectra per sample. This has been added to the caption.

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

This is discussed in the first paragraph in section 3.4.

‘There is some negative correlation between τ and the layer charge, with the exception of the calcium rich montmorillonite STx-1.’

Because calcium montmorillonite is the exception, I have plotted Na + K fraction from table 7 against τ in figure 9 (now figure 10) instead of the layer charge. I have modified the caption in figure 10 to make this clearer

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.

This paragraph has been altered to make it clearer that we are classifying particle numbers.

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

This has been expanded to give a more detailed commentary of the results and more detailed discussion of the factors affecting the accuracy of the measurement.

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.

The first TOF extraction lens is grounded, and hence field free extraction. In such a there is no turn-around time associated with the TOF as only ions that have initial trajectories towards the respective positive and negative ion lenses are accepted. (as pointed out in the method section 2.3). The acceptance angle is not known to the authors but we expect the differences in TOF due to this is relatively small compared to the 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).

The ion formation time is a result of both processes suggested above. The following sentence has been added to this paragraph:

‘Changes in ion formation time will include differences in the timing of the initial particle-laser interaction, due to particle trajectory and the properties of the material, as well as the timing of ion species formation after the ablation process has commenced.’

In the following paragraph, the possibility of the de-coupling of the formation of K^+ and SiO_3^- in illite rich samples is suggested. This would be an example of both processes influencing the ion formation time. The possibility this occurs due to the co-axial geometry of the excimer laser is now mentioned in the final paragraph of the discussion.

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.

This line has been removed during the reworking of the discussion section.

Technical corrections

P. 2, l. 24: Closing bracket missing

corrected

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

corrected

P. 3, l.30: Typo, "because"

corrected

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

corrected

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

corrected

P. 12, l. 13: Typo, 2x "in"

corrected

Figure 6 doesnot print well

corrected

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)

corrected

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

corrected

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

corrected

Figure 10: Specify what grey and red are.

Now specified in the caption

Major Correction A

3.3 The effect of laser power setting

The laser power setting is important parameter in SPMS because, along with the size of the focal point and pulse duration, the amount of energy contained in each pulse defines the peak power density that occurs in the ionisation region. Differences in power density have been shown to affect the mass spectral patterns produced. For example, Reents and Schabel (2001) found that variation in peak power density, achieved by varying the 193 nm laser power setting, resulted in variations in the sodium fraction reported in the mass spectra of NaCl. The effect of different laser power setting on the distribution of τ values for kaolinite sample KGa-1b and illite NX is shown in **Figure 1**. For the kaolinite rich sample, increasing the pulse energy results in a narrowing of the distribution. The effect on the illite rich sample is somewhat different, in that increasing the pulse energy has the effect of increasing the number of particles in the mode $\tau > 1$.

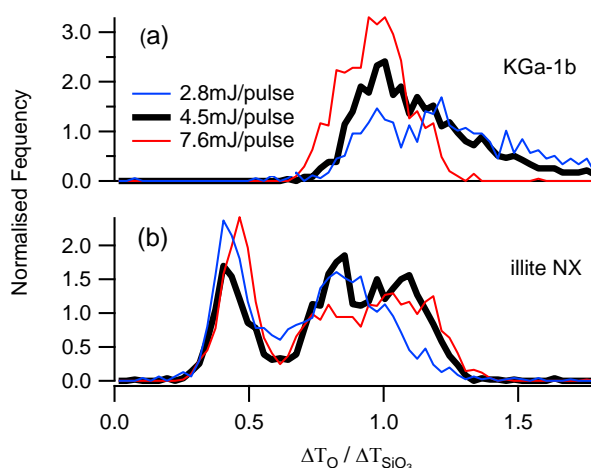


Figure 1. Histograms of the ion arrival times shift ratio (τ) of the elemental ion O⁻ and the molecular ion SiO₃⁻, with different laser pulse energy settings. (a) kaolinite sample KGa-1b and (b) illite NX.

An explanation for this behaviour may be found in the hit-rate efficiency, defined as the number of spectra acquired divided by the number of particles detected (**Table 2**). The hit rate for illite NX was more than double that of KGa-1b at 4.5mJ. In addition, hit rate was much more sensitive to energy setting with KGa-1b than with illite NX. Increasing the laser energy from 2.8mJ to 7.6mJ per pulse resulted in a hit rate increase of 42% for the KGa-1b sample. Species dependent hit rates are associated with the power density threshold required to initiate the ablation/ionisation process, which is related to the lattice energy and absorbing properties of the material at 193nm (Thomson et al., 1997). It is therefore reasonable to assume that the increase in the $\tau > 1$ fraction in illite NX at 7.6mJ per pulse is partly due to the presence of a material with a high power density threshold such as kaolinite. The increase in hit rate with KGa-1b at 7.6mJ was in a large part due to the acquisition of spectra showing a purer form of kaolinite as indicated by the titanium content (**Table 2**). It is not known if the titanium was present in these particles as a structural cation, therefore altering the crystal structure, or as free titanium impurity.

Table 2. The effect of the excimer pulse energy setting on the particle hit rate with illite NX and kaolinite sample KGa-1b. The number of particles that are low (<10% peak area) and high (>10% peak area) in titanium are given for the KGa-1b sample. The titanium content in the mass spectra was calculated from the combined peak area of the Ti⁺ (m/z 48) and TiO⁺ (m/z 64) and the total positive ion signal.

Sample	Excimer	Particles Detected	Spectra Acquired	Hit Rate	Ti < 10%	Ti > 10%
Illite NX	2.8mJ	7200	1901	0.26	n/a	n/a
	4.5mJ	7200	2106	0.29	n/a	n/a
	7.6mJ	7200	1825	0.25	n/a	n/a
KGa-b1	2.8mJ	7200	794	0.11	30	764
	4.5mJ	7200	994	0.14	86	908
	7.6mJ	7200	1397	0.19	673	724

Major Correction B

4 Discussion

In TOF-MS the principal limitations in resolving power of an instrument are attributed to the differences in initial ion velocity distribution (energy focussing) and differences in the initial starting positions (space focussing); it is not easy to decouple these effects (Guilhaus, 1995). In addition, ion formation time, ion trajectory through the ion optics, and temporal jitter of the timing electronics all contribute to differences in arrival times of a certain ion species at the TOF-MS detector. It is not possible to empirically derive starting position, initial ion velocity or ion formation times from the ion arrival times alone. However, the relative differences in ion arrival times may hold clues to the nature of the ion formation mechanism even if the actual ion velocities and ion formation times are not quantified.

Ion arrival times have been studied with the Matrix Assisted Laser Desorption Ionisation (MALDI) technique, where the sample is presented on a sample plate. With this method of sample introduction initial ion velocity distributions are considered to be the primary cause of mass spectral peak broadening (Colby et al., 1994) because the sample position is fixed, reducing the effects of space focussing. A measurement of initial kinetic energy of ions with MALDI indicated that the initial velocities of the matrix and analyte ions are identical, suggesting that the analyte molecule is entrained in to an expanding molecular jet of matrix ions and neutrals (Beavis and Chait, 1991; Pan and Cotter, 1992). In contrast, Spengler & Kirsch, (2003) observed a mass dependent initial ion velocity that could result from a thermal ionisation or a charge transfer and cluster decay ionisation mechanism.

In the case of SPMS, where the initial starting position is not fixed (due to particle beam divergence), space focussing is considered to be equally important as energy focussing in causing differences in ion arrival times. However, with the field free extraction featured in the LAAP-TOF, space focussing is reduced to a simple difference in the time it takes an ion to enter the extraction optics, which is likely to be small compared to the effects of different ion velocities. In addition, ion species dependence of the shift in ion arrival times recorded in the mass spectra indicate that the shot to shot differences in average flight times of the ions is not a result of a temporal offset of the firing of the excimer laser and/or starting of the A/D timing device as this would affect all ion species equally. This reasoning leaves changes in initial ion velocity and ion formation time as the primary candidates for the cause of the peaks shifting and peak broadening observed. Changes in ion formation time will include differences in the timing of the initial particle-laser interaction, due to particle trajectory and the properties of the material, as well as the timing of ion species formation after the ablation process has

commenced. The equal shift in ion arrival times of elemental and molecular ions observed with borosilicate glass suggests an equal addition to the scalar ion velocity and/or ion formation time, which can only be explained by shot to shot differences in ion formation time and initial ion velocities in a molecular jet. In contrast, the mass dependence to the negative ion peak shift for CB suggests a mass dependent velocity difference which suggests thermal ionisation or a charge transfer and cluster decay ionisation mechanism.

It is reasonable that decay of the crystal lattice would be a factor in the ablation of mineral particles whose crystalline mineral structures have typical lattice energy of $> 5000 \text{ kJmol}^{-1}$ (Jenkins et al., 2002), which far exceeds the energy available to a typical particle in a single laser pulse. Crystalline mineral structures could impose ion species dependence to the lattice decay and ion entrainment, such as that observed when comparing the average peak positions of the mineral dust with respect to the amorphous glass calibration. In clay minerals, the exchangeable interstitial cations that are weakly bonded layer provide an energy sink for the laser energy and could be desorbed before the negatively charged tetrahedral and octahedral layers which then disintegrate by lattice decay. In this scenario, the effective de-coupling of the positive and negative ion formation, as suggested in the comparison of positive and negative ion arrival times (Figure 12), may result from differences in ion formation time and initial velocities of the K^+ and SiO_3^- ions species. This process is not possible in feldspar mineral whose silicate structure must be broken in order to release the interstitial cation so that the K^+ and SiO_3^- ion species coexist in the ion plume, producing equal ion velocities due to coulombic forces and collisions. The provenance of the O^- elemental ion in the negative ion spectra is a source of uncertainty in the interpretation of a lattice decay mechanism. In pure feldspars, the O^- ion must be derived from the silica tetrahedra, but in clay minerals interstitial OH molecules or absorbed water in the particles are additional sources of oxygen. The presence of water may be of significance as it is known to affect the ionisation process in LDI (Neubauer et al., 1998) and warrants further investigation.

The weak interaction of the interstitial complex with the silicate tetrahedra controls the stability of minerals in natural rock forming processes (Hawthorne, 2015) and would appear to have an influence on relative ion arrival times in SPMS. The influence of the interstitial potassium and sodium ion content on the relative arrival times of the O^- and SiO_3^- species forms the basis of our classification of mineral phase. Measurement of the potassium and sodium content by peak area analysis is a potential source of uncertainty in the measurement due to particle matrix effects and the insufficient dynamic range of the TOF-MS detector. In addition, the amount of energy encountered by particles due to instrument function and laser power setting could be an important consideration for the accuracy and reproducibility of the analysis. The influence of laser power setting on the hit rate for kaolinite and illite demonstrate the potential for number fraction bias in the classification. Using the highest laser power setting would not be desirable for ambient sampling because of excessive fragmentation of non-silicate material such as internally and externally mixed organic material. One could also postulate that the same initial ion velocities would be reached by all ions if enough pulse energy is available to overcome the constraints of the lattice energy regardless of the crystal structure. In this study we found that 4.5 mJ/pulse was a suitable laser setting for differentiating particles types in illite NX.

The differentiation of mineral phases in this study was demonstrated with clay mineral standards with well characterised composition. The classification system was defined using the mineralogical composition from XRD analysis as a guide. Because of the huge variety in mineral phase that occurs in nature and the potential for mixing of phase within a single particle, the identification of specific mineral phases is expected to be more

difficult in complex natural samples such as desert dust, especially if XRD analysis of mineralogy is not available for reference. Even so, the distribution of τ values is expected to provide insight into the composition of clay sized fraction of a dust sample even if the exact mineral phase is not clearly identified. Analysis of the mineralogy of transported Saharan dust measured at Praia, Cape Verde Islands during the ICE-D campaign (August 2015) is presented in a separate publication (Marsden *et al*, manuscript in preparation, 2017)

Further work is required in development of this method. The tuning of the ion optics is of particularly important in determining the flight times of ions with respect to initial ion velocity. Modelling of the ion trajectories in a software package such as SIMION (Scientific Instrument Services, Inc.) may provide optimised tuning that further exploits the differences in ion focussing that arises from differences in particle composition. The transferability of the method to other LAAP-ToF instruments will also likely depend on the tuning of the ion optics. Tuning parameters used for this study are provided in the supplement (S1). Establishing the role of fixed instrument design features will indicate how transferable this method is to other designs of single particle mass spectrometers. For example, using extraction by an electric field one would expect an increased plume density and therefore an increase in space-charge effects and collisions as the ion plume is not free to expand in all directions. In addition, an orthogonal geometry of the excimer laser with the particle beam is likely to produce less variation in the position and timing in which a particle encounters the threshold power density for LDI compared to the co-axial geometry used in the LAAP-ToF.