

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-paramter 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 $\tau > 1$.

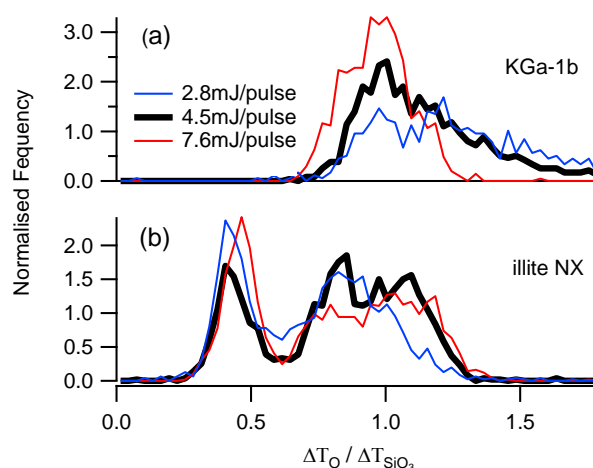


Figure 1. Histograms of the ion arrival times shift ratio (τ) of the elemental ion O^- and the molecular ion SiO_3^- , with different laser pulse energy settings. (a) kaolinite sample KGa-1b and (b) illite NX.

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 4.5 mJ. In addition, hit rate was much more sensitive to energy setting with KGa-1b than with illite NX. Increasing the laser energy from 2.8 mJ to 7.6 mJ 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 193 nm (Thomson et al., 1997). It is therefore reasonable to assume that the increase in the $\tau > 1$ fraction in illite NX at 7.6 mJ 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 7.6 mJ 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.

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 #2,

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 document.

Anonymous Referee #2

(Received and published: 12 September 2017)

The authors present a novel way to qualify minerals in single aerosol particles by type based on what seems to be reproducible matrix effects particular to the different mineral types. Although the manuscript could use a good proofread (see technical corrections below for some examples) it could also be expanded to note the reproducibility of these measurements. For instance it is unclear how sensitive the matrix effect is to various instrument parameters. Would the effects be particular to just the instrument in question or is it reproducible between instruments by the same manufacturer or between various aerosol mass spectrometric instruments. Without this information the applicability of this technique to the broader aerosol community is limited. However, if the method is indeed robust then this manuscript provides a step toward speciating aerosol particles by their mineral type.

Data that shows the reproducibility at different laser power settings has been added to the manuscript in Section 3.3 ‘The effect of laser power setting’ (See Major Correction A)

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. The transferability to other instrument models is now discussed towards the end of the Discussion section. The role of the co-axial geometry of the excimer laser and the field free extraction may be important design features.

Finally the authors must address the real world applicability of this technique by including data on ambient aerosol if possible from a well-defined source. Real world data tests the limits of any instrumental procedure and can reveal how changing temperature, humidity, organic aerosol coatings, and heterogeneity in aerosol type, could affect the qualitative analysis presented in this paper. Any data that speaks to dependence of results on environmental parameters should be mentioned. At the end of the day this is a good manuscript worthy of publication so that others can help determine the extent to which this technique might be practical in a real world setting.

The Discussion section has been extended to include 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 with reference to humidity and mixing state.

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

Other Major Corrections:

Pg 8 Ln 8-14. Can you speak to humidity effects on your measurements? does varying absolute humidity in the dust tower yield different results or matrix effects? Also the source of compressed air (company, and purity grade, water content) should be mentioned in the text

The humidity was not varied during the experiments.

The following line has been added to Section 2.2 Experimental Setup 'adjustable flow of dried, filtered and oil free compressed air (produced onsite using a compressor) introduced into the bottom of the tower'.

Pg 10 A couple of IGOR files/macros are mentioned however these seem to be homebuild analysis routines, The reader has no basis to judge the validity of these routines and thus they should be explained as to their function a bit more extensively, and/or code should be included in the supplemental if this hasn't already been done.

The peak fitting was carried out using a procedure (multipeak fit v2) in a commercially available software package igor v6.36. The only homebuilt part of this was used to apply this procedure to my data in batches. In our view it is not necessary to provide the code for this simple procedure in the supplement.

Pg 10 Define what is mean by "number of smoothes" and how the smoothing function works.

The number of smoothes is simply the data smoothing parameterisation in the commercially available software noted above.

Pg 12 Ln 3 Why are the resolution of the TOF around the same resolution as a quadrupole mass filter. I would expect resolution of TOF to be in the 4000-5000 range. Please comment on the lack of resolution for your instrument

The resolution produced by our instrument is typical in SPMS due to space focussing and energy focussing difficulties associated with this technique. See (Murphy, 2007) and references therein for further details.

Technical Corrections:

Pg 2 Ln 17 rephrase "The role of a mineral dust particle in the atmospheric processes..." to "The role of mineral dust particles in atmospheric processes"

corrected

Ln 20: remove "recently" as the articles cited are over 10 years old

corrected

Ln 24: need a closing parenthesis in the year 2010

corrected

Pg 3 Ln 9 define "NX" in "NX powder"

This is brand name for a product. The definition is unknown to the authors.

Pg 4 Ln 1 Be consistent with TOF-MS or TOFMS throughout the paper

corrected

Ln 18 change “markers ions” to “marker ions”

corrected

Pg 5 Ln 2 Be consistent with illite–smectite vs illite/smectite throughout the manuscript

Corrected to illite-smectite

Pg 10 Ln 11 please rephrase the sentence starting in “The ion...”

Corrected to ‘The configuration of the extraction optics in the LAAP-TOF is unusual in that the first extraction plate is grounded resulting in field free ionisation region.’

Figure 3 – please use a higher resolution image.

corrected

Figure 6 – reformat axis labels to be more readable

corrected

Pg 17 Ln 19 – remove “Error!...”

corrected

Pg 18 Ln 9 – remove extra space before the period.

Figure 9 – revise to clearly see the difference between the symbol types in part a. In part b there is a typo on the y-axis label. General quality of this figure needs to be improved upon.

Pg 23 Ln 20 revise for readability

corrected

References

Murphy, D. M.: The design of single particle laser mass spectrometers, *Mass Spectrom. Rev.*, 26, 150–165, doi:10.1002/mas, 2007.

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 $\tau > 1$.

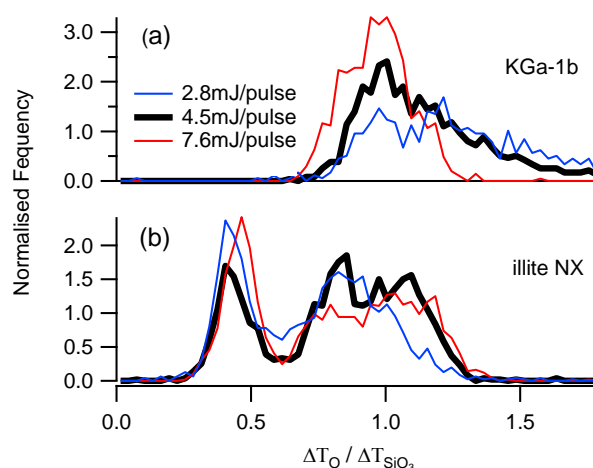


Figure 1. Histograms of the ion arrival times shift ratio (τ) of the elemental ion O^- and the molecular ion SiO_3^- , with different laser pulse energy settings. (a) kaolinite sample KGa-1b and (b) illite NX.

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 1**). The hit rate for illite NX was more than double that of KGa-1b at 4.5 mJ. In addition, hit rate was much more sensitive to energy setting with KGa-1b than with illite NX. Increasing the laser energy from 2.8 mJ to 7.6 mJ 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 193 nm (Thomson et al., 1997). It is therefore reasonable to assume that the increase in the $\tau > 1$ fraction in illite NX at 7.6 mJ 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 7.6 mJ was in a large part due to the acquisition of spectra showing a purer form of kaolinite as indicated by the titanium content (**Table 1**). 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 1. 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%
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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.

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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.

ON-LINE DIFFERENTIATION OF MINERAL PHASE IN AEROSOL PARTICLES BY ION FORMATION MECHANISM USING A LAAP- ~~ToF~~TOF SINGLE PARTICLE MASS SPECTROMETER

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Abstract. Mineralogy of silicate mineral dust has a strong influence on climate and eco-systems due to variation in ~~physicochemical~~physiochemical properties that result from differences in composition and crystal structure (mineral phase). Traditional off-line methods of analysing mineral phase are labour intensive and the temporal resolution of the data is much longer than many atmospheric processes. Single particle mass spectrometry (SPMS) is an established technique for the on-line size resolved measurement of particle composition by laser desorption ionisation (LDI) followed by time-of-flight mass spectrometry (~~ToF-MS~~TOFMS). Although non-quantitative, the technique is able to identify the presence of silicate minerals in airborne dust particles from markers of alkali metals and silicate molecular ions in the mass spectra. However, the differentiation of mineral phase in silicate particles by traditional mass spectral peak area measurements is not possible. This is because instrument function and matrix effects in the ionisation process result in variations in instrument response that are greater than the differences in composition between common mineral phases.

In this study, we introduce a novel technique ~~is introduced~~ that enables the differentiation of mineral phase in silicate mineral particles by ion formation mechanism measured from subtle changes in ion arrival times at the ~~ToF-MS~~TOFMS detector. Using a combination of peak area and peak centroid measurements, we show that the arrangement of the interstitial alkali metals in the crystal structure, an important property in silicate mineralogy, influences the ion arrival times of elemental and molecular ion species in the negative ion mass spectra. A classification scheme is presented that ~~allows~~allowed for the differentiation of illite/~~smectite~~, kaolinite and feldspar minerals on a single particle basis. On-line analysis of mineral dust aerosol generated from clay mineral standards produced mineral fractions that are in agreement with bulk measurements reported by traditional XRD analysis.

1 Introduction

Aerosol has a strong environmental impact by affecting climate, atmospheric processes, ecosystems, human health and visibility. Airborne mineral dust, which accounts for a large fraction of the global aerosol burden (Cakmur et al., 2006), influences climate by the direct radiative perturbation (Balkanski et al., 2007; Nousiainen et al., 2009; Tegen and Lacis, 1996), affecting cloud properties (DeMott, 2003; Rosenfeld et al., 2001) and atmospheric chemistry (Usher et al., 2003). In addition, mineral dust provides nutrients to land and ocean (Duce and Tindale, 1991; Jickells and Spokes, 2001), causes damage to human health through the inhalation of fine particulate matter (Prospero et al., 2008; Prospero and Mayol-Bracero, 2013; Samoli et al., 2011) and causes disruption to transport and economy with intense episodes of reduced visibility (Goudie and Middleton, 2006; Prospero, 1999).

Ambient measurement of mineral dust composition are important for validation of global dust cycle models and their incorporation into atmospheric models (Claquin et al., 1999; Nickovic et al., 2012; Perlwitz et al., 2015b). (Claquin et al., 1999; Nickovic et al., 2012; Perlwitz et al., 2015). Differentiation of mineral phase is particularly useful for the provenance of transported dust because distinct mass fraction ratios of mineral types, such as calcite content and illite/kaolinite ratio, can be used as signatures of potential source area (PSA) (Caquineau et al., 2002; Scheuven et al., 2013). However, the relative fraction of minerals evolves during transport, so that the mineralogical distribution close to source is different to that after long range transport. In general, measurements made within or close to PSAs show a relatively high proportion of large grains ($> 20 \mu\text{m}$) of quartz and feldspar that become depleted by gravitational settling and sorting during transport so that mineral dust populations measured far from PSAs are dominated by the clay fraction (Perlwitz et al., 2015a). The source variability and sorting during transport have important consequences for atmospheric processes and for fertilisation of the ocean such with phosphate and soluble Fe^{2+} (Journet et al., 2008).

The role of a mineral dust ~~particle~~particles in the atmospheric processes is a function of its physical and chemical properties which can be influenced by source and transport processes. Composition, external and internal mixing state, absolute aerosol mass concentration, particle size distribution and morphology/shape are important properties in many atmospheric processes (Formenti et al., 2011). Recently, the importance of chemical and mineralogical composition has been highlighted. Optical modelling of mineral dust aerosol has found that the radiative effects are very sensitive to internal and external mixing of mineral types, with iron oxide – clay mineral aggregates of particular importance (Lafon et al., 2006; Sokolik and Toon, 1999). The effective parameterisation of radiative transfer models requires the accurate representation of internal and external mineral combinations derived from laboratory and field measurements. For example, and in a radiative closure experiment McConnell et al. (2010) found that radiative closure experiments required accurate representation of aggregates of illite or kaolinite clay minerals with hematite or goethite (iron oxide minerals). McConnell et al. (2010) found that accurate representation of aggregates of illite and kaolinite clay minerals with hematite or goethite (iron oxide minerals) were required but the mineralogical combination had to be assumed due to the

inability of traditional X-ray diffraction techniques to accurately resolve the mineralogy on sparsely populated filter samples collected during airborne measurements.

Laboratory experiments have found a strong mineralogical dependence on the onset temperature of ice nucleation with respect to supersaturation, which have implications for modelling of cold and mixed phase clouds (Zimmerman 2008; Connolly 2009). For example, Atkinson et al. (2013) demonstrated that from a collection of common minerals, K-feldspar particles were the most efficient INP in the immersion mode using cold stage apparatus. ~~Radiative forcing due to change in cloud properties continues to be the biggest source of uncertainty in climate change prediction (Seinfeld et al., 2016), with the availability of ice nucleating particles (INP) in cold and mixed phase clouds a large source of this uncertainty.~~ Current climate models rely on simple parameterisation of INP number concentrations using properties such as surface area (Niemand et al., 2012) or particle size (DeMott et al., 2010, 2015), which assume all mineral dust behave in the same way regardless of chemical or mineralogical composition. ~~However, laboratory experiments have found a strong mineralogical dependence on the onset temperature of ice nucleation with respect to supersaturation, which have implications for modelling of cold and mixed phase clouds (Zimmerman 2008; Connolly 2009). For example, Atkinson et al. (2013) demonstrated that from a collection of common minerals, K-feldspar particles were the most efficient INP in the immersion mode using cold stage apparatus.~~

~~Heterogeneous ice nucleation in the natural environment can occur by multiple mechanisms that are difficult to recreate in the laboratory. Ice nucleation with particles in suspension using a variety of chamber techniques such as continuous flow diffusion chamber (CFDC), and controlled expansion cloud simulation chamber (CECC) create a realistic cold or mixed phase cloud simulation, but create difficulties in observing and measuring the actual INP in ice crystals as they must be extracted from the chamber as ice residue. In a comprehensive comparison of IN measurement techniques, Hiranuma et al., 2015 commented that differences in the IN efficiency of illite NX powder reported by a variety of techniques were not only a result of instrument function, but also differences in the physiochemical properties of the particles due to particle dispersion techniques and batch differences in the mineralogical composition of the sample. Representative samples of mineral dust aerosol for laboratory studies are difficult to source, and even nominally pure mineral samples can be heterogeneous in composition and contain substantial impurities that could be a significant source of INP. The ability to measure the mineralogy of a dust particle in real time would offer a huge advantage in the evaluation of both the starting material and the INP fraction in these types of studies.~~

In the field of atmospheric science, mineral dust is often collected in small volumes on microporous filters which are then analysed off-line by a variety of elemental, mineralogical and isotopic techniques. Typical techniques for elemental analysis include environmental scanning electron microscopy (ESEM), which reveals information on particle morphology, coupled with energy dispersive X-ray spectroscopy (EDS) e.g. (Reid et al., 2003; Young et al., 2016) or transition electron microscopy (TEM) e.g. (Kandler et al., 2007) for elemental analysis on a particle by particle basis. While elemental

composition is strongly correlated to mineralogical composition, the ~~accuracy of~~ quantitation required to differentiate common silicate mineral phase ~~distribution~~ in the bulk sample is rarely achieved. X-ray diffraction (XRD) is the established technique used to identify major mineral phases in many disciplines. However, this approach is considered semi-quantitative and is subject to comparatively large errors, particularly when dealing with clay minerals in the fine fraction ($< 2 \mu\text{m}$) (Moore and Reynolds, 1997), that require the preparation of textured samples. In addition, the XRD signal results only from the crystalline fraction so that the amorphous material is not counted leading to a discrepancy with the total dust mass (Formenti et al., 2008). The limit of detection of XRD analysis mean a mass loading of at least $800\mu\text{g}$ of aerosol dust- are typically required (Caquineau et al., 1997), making it unsuitable for the measurement of mineral dust particles with low number concentrations.

On-line measurements of aerosol properties are highly desirable ~~because~~because changes in properties can be linked to atmospheric processes and artefacts associated with off-line particle collection can be avoided. Single particle mass spectrometry (SPMS) is an on-line measurement technique that obtains size resolved composition of individual particles using laser desorption ionisation (LDI). In SPMS, aerosol is directly introduced into the instrument via an inlet and a high powered laser is used to ablate and ionise refractory and non-refractory particles in a particle beam. Ions produced in a low vacuum source by the LDI process are analysed by time-of-flight mass spectrometry (TOFMS). ~~The single particle nature of the technique is an advantage over bulk measurement because composition and mixing state of distinct particles can be obtained and directly correlated with other physiochemical properties such as particle size and density if used in tandem with other measurement techniques.~~ However, the composition measurement is considered non-quantitative on a single particle basis due to variation in instrument function and particle matrix effects that influence the ion formation process (Hinz and Spengler, 2007; Murphy, 2007; Zhou et al., 2007). ~~The origin of this matrix effect is not well understood, but systematic variation of ion signals in simple analogues of atmospheric aerosol suggest that ionisation potential, electron affinity and plume density are important factors (Reinard and Johnston, 2008).~~

Numerous studies of atmospheric aerosol using SPMS have identified a distinct silicate mineral class of particles in ambient aerosol (~~Dall'Osto et al., 2010; Middlebrook, 2003; Sullivan et al., 2007~~)(Dall'Osto et al., 2010; Middlebrook, 2003; Sullivan et al., 2007), and in ice residues extracted from mixed phase clouds (Baustian et al., 2012; Kamphus et al., 2010; Schmidt et al., 2016; Worringer et al., 2015). ~~Whilst this has proven useful in the investigation of internal and external mixing states of ambient aerosol population, identification of mineral types within the silicate class has remained elusive. Natural variation in composition between mineral phases is often smaller than the particle to particle variations in ion distribution recorded in the mass spectra due to instrument function and particle matrix effects. The origin of this strong matrix effect is not well understood, but systematic variation of ion signals in simple analogues of atmospheric aerosol suggest that ionisation potential, electron affinity and plume density~~Whilst this has proven useful in the investigation of internal and external mixing states of ambient aerosol population, identification of mineral types within the

silicate class has remained elusive with SMPS because natural variation in composition between mineral phases is often smaller than the particle to particle variations in ion distribution recorded in the mass spectra due to instrument function and particle matrix effects. ~~are important factors (Reinard and Johnston, 2008).~~

Ion formation processes in LDI can be studied by measuring initial ion velocities which are calculated by comparing the ion arrival time at the TOFMS detector of certain ion species after systematic variation in ion focussing (e.g Spengler & Kirsch 2003; Vera et al. 2005). In this paper we compare ion arrival times of key ~~markers~~marker ions in a variety of crystal structures in otherwise chemically similar particle types. Using a Laser Ablation Aerosol Particle Time-of-Flight (LAAP-TOF) single particle mass spectrometer (Aeromegt GmbH), we demonstrate that systematic variation in ion arrival times in laboratory-generated nominally pure mineral samples can be related to the ion formation mechanism and crystal structure of single particles. A method for the on-line differentiation of mineral phase in clay mineral standards is presented using spectral peak centroid as a measure of average ion arrival time in addition to traditional peak area analysis. The application of the method to analyse ambient dust particles will be presented in a separate publication (Marsden *et al.* manuscript in preparation, 2017).

2 Methods

2.1 Dust Samples

Laboratory studies of the physiochemical properties of mineral dust require an appropriate sample material that is representative and relevant to atmospheric processes. Field studies show that most dust in the atmosphere is dominated by varying quantities of quartz, k-feldspar, plagioclase, calcite, hematite, kaolinite, and the illite-/smectite group of clay minerals (Formenti et al., 2008; Jeong, 2008; Kandler et al., 2007, 2009, 2011; Kaufman et al., 2005; Kaufmann et al., 2016). At a single particle level, particle size dependence is observed with an abundance of quartz and feldspar grains in the coarse fraction and a fine fraction ($< 2 \mu\text{m}$) dominated by clay minerals. Detailed studies of the internal structures of Asian and Saharan dust have revealed complex internal structures of individual particles in terms of mineralogy and morphology. TEM analysis of sliced ~~particles has~~particle revealed that the most common sub- $5 \mu\text{m}$ particle type was clay-rich agglomerate, dominated by nano-thin platelets of illite-smectite series clay minerals (ISCM) with submicron grains of iron (hydr)oxides (goethite and hematite) commonly dispersed through the particles (Jeong et al., 2016; Jeong and Nousiainen, 2014).

In our laboratory study of silicate dust, clay mineral samples were chosen because they represent the most atmospherically relevant material in the size range of the LAAP-TOF transmission ($0.5\text{--}2.5 \mu\text{m}$). Samples of feldspar were compared to these clay samples because of the potential importance of K-feldspar as ice nuclei (Atkinson et al., 2013). In addition to aluminosilicates, $2.1 \mu\text{m}$ borosilicate glass spheres were used as an example of an amorphous silicate structure that

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contains abundant alkali and earth alkali metals that are not chemically bonded into a crystal structure. Carbon black (CB) (Elftex 124, Cabot Corp) was used as an example of a non-silicate particle that has a well characterised molecular structure. A summary of the samples used in this study is provided in **Table 1: Table 1.**

Table 1. Summary of the dust samples used in this study

Sample Name	Principal Mineral	Structure Type	Sub-Type	Origin
BSG	Borosilicate Glass	Amorphous	N/A	Duke Standards
Elftex124	Carbon Black	Sheet Graphite	N/A	Cabot
Ortho1	Orthoclase	Framework Silicate	Feldspar	Geo Supplies
Plag1	Plagioclase	Framework Silicate	Feldspar	Geo Supplies
KGa-1b	Kaolinite (low defect)	Sheet Silicate	1:1 Layer Clay	CMS
KGa-2	Kaolinite (high defect)	Sheet Silicate	1:1 Layer Clay	CMS
STx-1b	Ca-Montmorillonite	Sheet Silicate	2:1 Layer Clay	CMS
SWy-3	Na-Montmorillonite	Sheet Silicate	2:1 Layer Clay	CMS
IMt-2	Illite	Sheet Silicate	2:1 Layer Clay	CMS
ISCz-1	Illite-Smectite Mix	Sheet Silicate	Mixed Layer Clay	CMS
Illite NX	Illite	Sheet Silicate	2:1 Layer Clay	B+M Nottenkamper

Carbon black (CB) is distinct from the material commonly referred to as black carbon (BC) (Long et al., 2013; Watson and Valberg, 2001). CB has a characteristic particle morphology that consists of spherical primary particles fused into aciniform (grape-like) aggregates which cluster into larger-sized agglomerates. The primary particles are typically 10-500 nm in diameter and are composed of imperfect graphitic layers that are concentrically arranged around a growth center (Rivin, 1986). The spaces between the graphitic layers often accommodate cations such as potassium and sodium. Elftex 124 is a flame soot derived CB product comprised of > 95 % carbon (Wonaschutz et al. 2009).

Clay minerals have a sheet silicate structure in which silicate tetrahedra are two dimensionally polymerised to form structural layers that are separated by interlayer cations. The capacity of a clay mineral to accommodate interstitial cations (X-ions) in the interlayer spacing of clay mineral is related to the layer charge of the structural layer. The structural layers of clay minerals are composed of alternating tetrahedral and octahedral sheets in which the layer charge is created by isomorphous substitution of lower valency ions. Substitution of Si^{4+} for Al^{3+} ions in the tetrahedra produces tetrahedral charge while substitution of Al^{3+} for Mg^{2+} in the octohedra (Y-ions) produces octahedral charge. The composition of clay

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minerals is not fixed, but is determined by the varying degrees of cation replacement in the structural unit and interstitial complex. For example, the nominal chemical formula of illite is stated in the form $K_{1.5-1.0}Al_4[Si_{6.5-7.0}Al_{1.5-1.0}O_{20}](OH)_4$ to express the variability in composition that can exist within the illite member of the clay mineral group.

Source clays from the Clay Mineral Society (CMS) have been the subject of chemical, physical and thermodynamic analysis and therefore very well characterised. Average elemental composition of Si, Al, Fe(II), Fe(III), Mg, Ti, Mn, P, Ca, Na, K and H₂O of the bulk sample is available (Mermut and Cano, 2001) and enables the construction of the precise structural formula. The structural formulae for the source clay samples used in this study are given in a format that shows the average composition of the X-ions, Y-ions and tetrahedral layer in **Table 2**.

Table 2.

Kaolinite (samples KGa-1b and KGa-2) has a 1:1 layer structure in which each layer contains 1 tetrahedral layer and 1 octahedral layer. Kaolinite has no overall layer charge and hence a very low X-ion content. The remaining samples consist of the so called 2:1 layer clays in which one octahedral layer is sandwiched between two tetrahedral layers. The layer charge created by this 2:1 layer structure is balanced by a certain quantity of X-ions. Illite rich samples (IMT-2, ISCz-1) are characterised by very high quantities of K⁺ whereas the montmorillonite clays (STx-1b, SWy-3) are characterised by relatively high levels of Na⁺ and Ca²⁺.

Table 2. Structural formulae of source clays from the Clay Mineral Society calculated from elemental analysis (Mermut and Cano, 2001).

Sample	X-ion	Y-ion	Tetra	Anion
KGa-1b	Mg _{0.02} Ca _{0.01} Na _{0.01} K _{0.01}	Al _{3.86} Fe(III) _{0.02} Ti _{0.11} Mn _{Tr}	Si _{3.83} Al _{0.17}	O ₁₀ (OH) ₈
KGa-2	Ca _{Tr} K _{Tr}	Al _{3.66} Fe(III) _{0.07} Ti _{0.16} Mn _{Tr}	Si _{4.00}	O ₁₀ (OH) ₈
STx-1b	Ca _{0.27} Na _{0.04} K _{0.01}	Al _{2.41} Fe(III) _{0.09} Mg _{0.71} Ti _{0.03} Mn _{Tr}	Si _{8.00}	O ₂₀ (OH) ₄
SWy-3	Ca _{0.12} Na _{0.32} K _{0.05}	Al _{3.01} Fe(III) _{0.41} Mg _{0.54} Ti _{0.02} Mn _{0.01}	Si _{7.98} Al _{0.02}	O ₂₀ (OH) ₄
IMt-2	Mg _{0.09} Ca _{0.06} K _{1.37}	Al _{3.01} Fe(III) _{0.76} Fe(II) _{0.06} Mg _{0.43} Ti _{0.06} Mn _{Tr}	Si _{7.08} Al _{0.92}	O ₂₀ (OH) ₄
ISCz-1	Mg _{0.03} Ca _{0.10} Na _{0.09} K _{0.95}	Al _{3.39} Fe(III) _{0.12} Mg _{0.48} Ti _{Tr} Mn _{Tr}	Si _{7.19} Al _{0.81}	O ₂₀ (OH) ₄

Naturally occurring rock is rarely mono-mineralic. Mineralogical impurities in source clays have been previously quantified by X-ray diffraction analysis (~~Table 3~~)(Table 3) for the bulk sample (Chipera and Bish, 2001) and < 2 µm fraction (Vogt et al., 2002). For example, in natural environments montmorillonite is diagenetically altered to illite in the presence of K-feldspar (Garrels, 1984) so that clays often consist of fine interlayers of these two clay minerals. Sample ISCz-1 is an example of clay that consists of microscopic interlayers of illite and smectite clay minerals (ISCM). Recently, Broadley et al. (2012) suggested illite NX (B+M Nottenkamper, Munich, Germany) as a suitable representation of ambient mineral dust sampled at remote locations and it has been used in numerous ice nucleation studies (Hiranuma et al., 2015).

Illite NX is a clay rich nanopowder that contains significant mineralogical impurities. XRD analysis has shown significant variation in the impurity content that may represent significant batch differences in mineralogy (Table 4)-(Table 4).

Table 3. Mineralogical impurities in CMS clay as determined by X-ray diffraction.

Sample	Impurities (wt%)						Reference
	Quartz	Kaolinite	K-Feldspar	Plagioclase	Other	Total	
KGa_1b					Dickite 4.0	4	Chipera 2001
KGa-2					Dickite 4.0	4	Chipera 2001
PF1-1	1.7	1.7	5.8	2.5		11.7	Vogt 2002
STx-1b	30	2.1	0.9	0.6		33.6	Vogt 2002
SWy-3	5.2	1.3	ND	0.1	Pyroxene 5.8	12.4	Vogt 2002
IMt-2	3.3	0.7	4.6	1.5		10.1	Vogt 2002
ISCz-1	0.7	0.2	2.3	5.5	Chlorite 1.2	8.7	Vogt 2002

Table 4. Mineralogical impurities in illite NX as determined by X-ray diffraction. ND stands for not detected.

Study	Impurities (wt%)					
	Quartz	Kaolinite	K-Feldspar	Plagioclase	Other	Total
Manufacturer	4	10	ND	ND	ND	14
Hiranuma 2015	3	10	14	-ND	Calcite 3.0	30
Broadley <i>et al</i> 2012	7	7	10	-ND		24
Friedrich et al 2008	<1	5	4	1.1	Phlogopite 7.8, Anhydrite 1.4	20

In framework silicates such as feldspar, the silicate structure is formed from 3 dimensionally polymerised silicate tetrahedral. In contrast to the interlayer cation structure of clay minerals, a low valence cation is held in an interstitial cavity that balances the charge deficit created by substitution of Al^{3+} for Si^{4+} in the tetrahedral. Unlike clay minerals, the interstitial cations are fixed and not exchangeable during normal diagenetic processes. Most naturally occurring feldspars are not homogenous but contain separate potassium rich and sodium rich phases. Specimens of orthoclase (K-Feldspar) and plagioclase were purchased from Geo Supplies Ltd, and analysed by XRF analysis to determine the average elemental

composition. The average structural formula of the samples was then calculated from the relative proportions of the metal oxides (Table 5);(Table 5).

Table 5. Structural formulae of feldspar sample calculated from XRF analysis.

Sample	Interstitial X-ion	Tetra	Anion
Orthoclase	Ca _{0.01} Na _{0.25} K _{0.85}	Si _{2.95} Al _{1.02}	O ₈
Plagioclase	Ca _{0.16} Na _{0.76} K _{0.07}	Si _{2.83} Al _{1.17}	O ₈

2.2 Experimental Setup

Mineral dust aerosol was sampled by the LAAP-TOF after dry dispersion of powder in a home-made dust tower and transmission of the extracted aerosol through a centrifugal particle mass analyser (CPMA) (Cambustion, Ltd) (Olfert and Collings, 2005). Source clays, illite NX, borosilicate glass beads and CB were supplied in powder form or loose aggregate that was easily broken down into powder by gentle abrasion with a pestle and mortar. The feldspar samples were supplied as a large crystal that had to be reduced to powder in a timor mill prior to injection into the dust tower.

Powdered mineral dust was loaded into a modified sample vial and injected into the dust tower inlet using a short burst of compressed air from an air duster can. The mixing and suspension of mineral dust particles was achieved by turbulent flow, controlled with an adjustable flow of dried, filtered and oil free compressed air (produced onsite using a compressor) introduced into the bottom of the tower (Figure 1);(Fig. 1.). Aerosol was drawn out of the dust tower through the CPMA using a pumped sampling line throttled to a suitable flow rate (~1.6 L/min) using a needle valve. The flow was divided between the pumped line and the LAAP-TOF inlet (sampling at 0.078 L/min) using a `Y piece`.

The experiment was operated in two modes. In polydisperse mode, the CPMA was inactive so that the mass distribution of the aerosol analysed by the LAAP-TOF was determined by the transmission efficiency of the aerodynamic lens. In monodisperse mode, the CPMA was used in static mode so that only the selected particle mass was transferred to the LAAP-TOF.

2.3 LAAP-ToF Single particle mass spectrometer

The LAAP-TOF used in this study is a modified version of the commercially available single particle mass spectrometer manufactured by AeroMegt (GmbH) that features a modified optical detection system as described in detail by Marsden et al. (2016). Briefly, particle laden air enters the instrument via an aerodynamic lens inlet (Liu et al., 1995) which produces a narrow, but divergent particle beam along the instrument axis. A pulsed excimer laser interacts with a particle in the low vacuum pressure source region towards the back of the instrument (Figure 2);(Fig. 2). An optical particle detection stage,

located within the source region, is used for temporal alignment of the excimer laser pulse with the presence of a particle in the ion source. The option to measure aerodynamic particle size using an additional optical particle detection stage located upstream on the instrument axis was not used in this study.

The version of the instrument used in this study features an aerodynamic lens inlet (model LP2.5 Aeromegt GmbH) for transmission of particles approximately 0.07-2.5 μm in diameter that is similar in design to the high pressure lens (HPL) described by Williams et al. (2013). Divergence of the particle beam is size and shape dependent (Jayne et al., 2000), resulting in a morphological dependence on the fraction of particles that reach the ionisation region (Huffman et al., 2005), an effect that is particularly important for measurements of irregularly shaped platy mineral in polydisperse dust.

Laser desorption ionisation takes place in a high vacuum ($<1\text{e-}6$ mbar) region some 230 mm from the aerodynamic lens exit, where particles interact with a 8 ns pulse of 193 nm radiation that is fired co-axial but counter-propagate to the particle beam. The ablation laser, an ArF excimer (model EX5, GAM Laser Inc.), can be requested to produce 2-12 mJ per pulse via a setting in the software. The peak laser power actually encountered by a particle is unknown as the particle will transect the laser pulse at an unknown position in its Gaussian-profile due to particle divergence and temporal alignment. Consequently, particle to particle variations in the peak power and effective pulse duration can reduce the reproducibility of the measurement. A previous study with this instrument configuration has shown a sampling efficiency for ambient mineral dust of approximately 0.01 with a particle size dependent optical detection bias that favours the detection of particles with a mode of around 1.5 μm in diameter (Marsden et al., 2016). Sampling efficiency is important in SPMS as it influences the particle counting statistics of an aerosol population and can introduce a bias of compositional measurement towards a particular particle type (Zelenyuk et al., 2009).

The TOFMS used in the LAAP-TOF is a bipolar reflectron TOF analyser (BTOF, ToFwerks AG) for the simultaneous measurement of positive and negative ions. Ion arrival times at the multichannel plate (MCP) detectors, one for each ion mode, are recorded by a dual channel 14bit analogue to digital converter (model ADQ214, SP Devices) with a bin width of 2.5 ns. The ADQ clock is triggered by a signal that is synchronous with the firing of the ablation laser so that each spectrum represents the ions formed by a single particle ablation event. The ~~ion-configuration of the~~ extraction ~~condition~~optics in the LAAP-TOF ~~are~~is unusual in that ~~it utilises a field free extraction regime. The~~the first extraction lenses of the LAAP-TOF ion optics are grounded so that the evolution of the ion plume takes place in a field free region and only ions with the correct ion trajectories are extracted for analysis.

2.4 Mass spectral peak analysis

The aim of the peak analysis is to evaluate how composition and crystal structure of the particles affect ion arrival times at the multi-channel plate (MCP) detector by comparing the spectral characteristics of the samples of mineral dusts of known mineralogy. ~~TOF-MS~~TOFMS analysers focus a certain elemental or molecular ion species into a discrete packet of

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ions whose arrival times at the detector are represented by a Gaussian probability density function (PDF) which is represented as a spectral peak in the data. The average ion arrival time (T) of the ion packet at the detector is described by the peak centroid while the peak width (FWHM) describes the distribution around this average.

Peak centroid and peak width were extracted from the raw spectra using a peak fitting algorithm. Peak fitting within the spectra was problematic because of spectrum to spectrum variations in peak position, peak shape and interference from neighbouring peaks. To reduce the influence of these effects, a multipeak fitting procedure (~~multipeak~~Multipeak fit v2, igor v6.36) was performed on a portion of the mass spectrum which contained the peak of interest. Peak fitting parameters were set so that interfering signals were identified as separate peaks without comprising the integrity of the peak of interest. In most cases, the peak of interest was a well-defined Gaussian shape that was sufficiently separated from its neighbour, such as the example of SiO_3^- molecular ion (m/z -76) in [Figure 3a](#)([Fig. 3a](#)). Occasionally, especially in illite rich clay mineral samples, the molecular ion peak was much broader ([Figure 3b](#)([Fig. 3b](#))) therefore a number of data smooths were required to ensure satisfactory peak definition was obtained. A third peak morphology, featuring multiple modes was also encountered in illite rich clays samples that required careful consideration. Using a suitable peak fitting parameters (Number of Smooths 5, Number Fraction 0.1), the multimodal peak in [Figure 3e](#)([Fig. 3c](#)) was resolved into two peaks whose peak centres were approximately 1 Da (50 ns) apart. Note that further resolution of this multimodal peak using a fewer data smooths resulted in peaks that were separated by <0.5 Da (20ns) ([Figure 3d](#)([Fig. 3d](#))), which is an improbable solution in data that primary consists of singly charged ions. Consequently, peak fitting parameters were chosen that ensured peak centroid spacing of integer values (in mass) were produced from all fitting. The origin of the multimodal peak morphology will be discussed in more detail in the results section.

Prior to analysing the mineral dust samples, the ion optics were tuned for maximum resolution and symmetrical peak shape across the mass range for positive and negative ions using 700nm diameter PSL particles. The effect of particle type on ion arrival times was initially evaluated by comparing mass scale calibrations obtained from selected samples. 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. For the silicate, the same ion species were chosen in positive and negative ion modes for each sample. Changes in average arrival times of a certain ion species (i), apparent as a peak centroid shift ($\Delta T_{(i)}$) with respect to previously defined position, were examined in more detail by comparing the peak centroid with a nominal mass scale calibration and comparing $\Delta T_{(i)}$ with other ion species from within the spectrum (i.e. from the same ionisation event).

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3 Results

3.1 Tuning and calibration

Spectral resolution of the peaks in positive and negative spectra for PSL were typically 300 and 600 (FWHM at m/z 36) respectively, with unit mass resolution easily achieved over the mass range 10-100 Da. The optimum tune settings for the positive ion optics differed somewhat from those of the negative ion optics despite their identical geometry, indicating significant differences in the translational energies of the positive and negative ions produced in the same particle ionisation event.

Typical mass spectra of feldspar mineral dust (Figure 4a(Fig. 4a)) show elemental ions of alkali metals in positive ion mode and molecular fragment ions of silicate at m/z -60 (SiO₂) and m/z -76 (SiO₃) in negative ion mode which is in agreement with the mineral dust spectra observed by (Gallavardin et al. 2008a) who used a similar 193 nm excimer laser at approximately 10⁹ W/cm²cm⁻². Detector saturation was apparent on several positive ion peaks when Channel 1 signal amplifier line to the A/D was used (Figure 4a(Fig. 4a Top)). To avoid peak saturation, the Channel 2 signal amplifier with a greater attenuation was used for the subsequent peak analysis. The effect of changing the signal amplifier on the spectra is demonstrated in the typical mass spectra examples in Figure 4.Fig. 4. Detector saturation occurs at 1200 mV signal strength for the peaks at m/z 27, 39 and 44 with the signal channel 1. Saturation is avoided with signal channel 2 but comes at the expense of poor signal to noise ratio of ion species such as C⁺ (m/z 12) and CaO⁺ (m/z 56). Note the relative signal height between ion species is altered when the signal channel is changed, highlighting insufficient dynamic range of the ion detection system.

Mass scale calibration over a limited mass range (m/z 23-56) was possible in positive ion mode due to the limited number of peaks that were universally available in all spectra, whereas a mass scale calibration with a wider mass range (m/z 16-76) was possible in negative ion mode. Calibration coefficients obtained for PSL, Carbon Black, K-feldspar and borosilicate glass are shown in Table 6.Table 6. Note the increase in the intercept value for the K-feldspar and borosilicate glass samples, indicating an overall shift in the ion arrival times compared to the PSL.

Table 6. Mass calibration coefficients calculated from the mode peak position (ToF) of 3 ion species for each samples in each ion mode. The ions species used are m/z +24,+ 36 +48, -24, -60 and -72 in PSL and Carbon Black mass spectra and -m/z +27, +39, +44, -16, -60, and -76 in K-Feldspar mass spectra. Positive ion calibration of the borosilicate glass was not possible with the peaks selected. Calibration points are expressed in 2.5 ns bin widths.

	<i>a</i> (Pos)	<i>b</i> (Pos)	<i>a</i> (Neg)	<i>B</i> (Neg)
PSL	8.415	371.026	5.953	400.708
Carbon Black	16.1504	369.608	4.816	400.732
Feldspar	28.882	367.335	10.601	400.073
Borosilicate	N/A	N/A	34.125	397.435

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The average peak position and peak width (± 2 SD) of the Al^+ , K^+ and SiO^+ positive ion species and O^- , SiO_2^- and SiO_3^- negative ion species in the K-feldspar, Illite IMt-2 and borosilicate glass samples are displayed in ~~Figure 5~~-(Fig. 5). In positive ion mode, the peak position is often $> \pm 0.5$ Da of the K-feldspar calibrated mass position in all sample types. In negative ion mode, the average position of the SiO_2^- and SiO_3^- is significantly larger for the Illite IMt-2 than for K-Feldspar or Borosilicate glass. In addition to the peak analysis, average peak centroid and peak width are important for the creation of stick spectra used in routine cluster analysis techniques. The data ~~acquisition~~processing software provides an additional facility to ~~perform an accurate~~apply a unique 3 parameter fit calibration ~~correction by shifting selected peaks to the corresponding unit mass position on the mass scale~~each spectrum. However, for this calibration to be successful, the peak of interest must be located ± 0.5 Da from the average mass position which is not the case in a significant number of peaks in mineral dust spectra.

The mass scale dependence of the peak position shift suggests that the differences in calibrations do not arise from a simple linear shift in ion arrival times for all ion species in the mass spectra. This is further demonstrated by examining $\Delta T_{(i)}$ with respect to the negative ion calibration for borosilicate glass (~~Figure 6~~)-(Fig. 6). Carbon black has a clear mass dependence with respect to this calibration. Kaolinite does not have a strong mass dependence but is affected by a large kink in the mass scale between the SiO_2 and SiO_3 molecular ions (m/z 60 and 76 respectively), which is apparent with all the silicate minerals analysed.

3.2 Relative ~~Shift~~shift of elemental and molecular ions-ion ToF.

In this section we explore the relationship between the ion arrival times of O^- elemental ion (T_{O}) and the SiO_3^- molecular ion (T_{SiO_3}) within discrete ionisation events. In the case of borosilicate glass, an amorphous silicate material, a scatter plot of arrival times measured in individual mass spectra display an approximately linear distribution of data points with a gradient of 1 (~~Figure 7a~~-(Fig. 7a) indicating that $\Delta T_{\text{O}} \approx \Delta T_{\text{SiO}_3}$. In contrast, the non-silicate carbon black, a similar plot of elemental vs molecular carbon ions measured from C at m/z -12 and C_6 ion at m/z -60 respectively, gives a linear distribution of ion arrival times with a gradient of 0.35, indicating that generally $\Delta T_{\text{C}} \approx 0.35 \cdot \Delta T_{\text{C}_6}$.

Similar distributions of ion arrival times can be observed with the LDI of crystalline silicate mineral dust. The framework silicate orthoclase feldspar, has a distribution of ion arrival times that is similar to the borosilicate glass except the distribution is narrower (~~Figure 7b~~-(Fig. 7b), whereas illite IMt-2, a sheet silicate, has a large mode that is similar to the carbon black, with an additional mode of particles that is more similar to the borosilicate glass. The silicate mineral sample with the most variation in ion arrival times is the illite ~~nx~~NX where several distinct modes are apparent (~~Figure 7c~~-(Fig. 7c). The multimodal nature of this distribution was still apparent after the particles were mass selected with the CPMA before analysis with the LAAP-TOF. The ion arrival time distribution of mass selected 350 fg illite NX particle shows a smaller

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variation of up to 20ns whereas mass selected 700 fg illite NX particles have a distribution comparable to the polydisperse analysis.

In order to directly compare the ion arrival time distributions of different silicate minerals, the shift in arrival time ($\Delta T_{(i)}$) was calculated for each spectrum with respect to a set point on the time scale. For silicate containing particles, ΔT_O and ΔT_{SiO_3} were calculated with respect to the point where the mode distributions converge on the scatter plots at $T_O = 4010.2$ ns and $T_{SiO_3} = 8722.4$ ns respectively, which we will call the convergence point. The relative difference in the ion arrival times of the elemental and molecular ions in negative ion mode can then be expressed as a ratio (τ) for each particle analysed.

$$\tau = \frac{\Delta T_O}{\Delta T_{SiO_3}}$$

Histograms of τ values measured from the peak analysis in silicate mineral mass spectra are shown in [Figure 8](#). Potassium rich clay minerals illite NX and illite IMt-2 ([Figure 8a](#)) have a distinct mode around 0.3-0.5, that is aligned with the $\Delta T_O/\Delta T_{SiO_3}$ ratio derived from the peak analysis of carbon black. Other distinct modes can be seen in the illite IMt-2 sample at 0.79 and in the illite NX sample at 0.83 and 1.10 that is more similar to the distribution of τ values measured for borosilicate glass. The smectite and montmorillonite clays have modes in the distribution that range from 0.4 to 0.86 and the 1:1 layer clay kaolinite has the largest mode at 0.93 ([Figure 8b](#)).

Figure 8. Histograms

3.3 The effect of laser power setting

The laser power setting is important parameter in SPMS because, along with the ion arrival times shift ratio (τ) size of the elemental ion O focal point and pulse duration, the molecular ion SiO_3^- , (a) potassium rich illite samples and (b) Na and Ca rich samples amount of montmorillonite and 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, Borosilicate glass and carbon black are shown for reference. *Carbon black sample KGa-1b and illite NX is shown in Fig 9. 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 $\tau > 1$.

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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 7). 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 7). 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 7. 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 $\Delta T_c/\Delta T_{c_g}$ ratio, 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

3.4 The role of the interstitial complex

The main physiochemical difference between clay minerals is the nature of the interstitial X-ion that is accommodated between the silicate structural layers. For the source clays, the relative proportion of low valence interstitial cations (X-ion) present in the structure is discernible from the structural formulae provided by the clay mineral society (Table 2). These ion proportions are listed alongside the literature values for interlayer charge and value of τ of the principal mode derived from this study in Table 8. There is some negative correlation between τ and the layer charge, with the exception of the calcium rich montmorillonite STx-1. In calcium rich montmorillonite, the layer charge is balanced by abundant divalent ions of calcium, which has a first ionisation energy (589.8 kJ/mol), higher than the aluminium (577.5 kJ/mol) in the silicate structural layer. In contrast, SWy-1, ISCz-1 and

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IMt-2 samples have a layer charge that is principally balanced by sodium and potassium ions that have first ionisation energies that are lower than any component in the silicate structural layer (495.8 and 418.8 kJ/mol respectively).

Table 8. Measured values of τ compared to Interlayer charge and cation ratios from structural formulae derived from elemental analysis (Tr = Trace). Reference material from the clay mineral society.

Sample	InterLayer Charge	Interstitial Cation (X-ion)			Mode τ
		Ca	Na	K	
KGa-1b	-0.06	0.01	0.01	0.01	0.93
KGa-2	0.16	Tr	0	Tr	0.93
STx-1	-0.68	0.27	0.04	0.01	0.79
SWy-2	-0.55	0.12	0.32	0.05	0.47
ISCz-1	-1.29	0.10	0.09	0.95	0.37
IMt-2	-1.68	0.06	0	1.37	0.33

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3.3 The role of the interstitial complex

A comparison of the interstitial X-ion content derived from elemental analysis and the measured τ value for clay minerals and feldspars is given in Figure 9-Fig. 10. The combined sodium and potassium content, derived from the calculated structural formulae for source clays is plotted against the mode value of τ derived from the peak analysis. For clay samples that exhibit multi-modal τ distributions, only the lowest principal mode is represented in the data. Relatively high levels of sodium and potassium result in a low τ value for these modes. For feldspars, the cation content is measured from the positive ion mass spectra and plotted against τ on a single particle basis for orthoclase and plagioclase in Figure 9a Fig. 10a and Figure 9b Fig. 10b respectively. In contrast, higher sodium and potassium content in feldspars result in high τ values. The influence of the calcium ion on the τ value in plagioclase feldspar is demonstrated in the colour function in plot Figure 9b Fig. 10b. When Ca/Na ratios are high, the τ is >1 which is similar response as the kaolinite sample which is depleted in interstitial X-ions.

Mass selecting 700 fg orthoclase particles with the CPMA produces a similar distribution as polydisperse particles suggesting there is not particle size effect to the distribution. The low recorded potassium and sodium content in some feldspar particles may be a result of the crushing of the sample as this is known to cause collapse of the interstitial cavity (Garcia-guinea and Correcher, 2000) so that feldspar particles with low cation content may not be representative of natural occurring feldspar.

Distinctive clusters of data points are apparent in the illite NX sample when τ is plotted against alkali metal content derived from single particle mass spectra (Figure 9c)-(Fig. 10c). The concentration of particles in the region $\tau = 1.0$ -1.2 are

clearly distinguishable from particles in the $\tau = 0.6$ -1.0 region by the content of low valence potassium and sodium ions. These clusters of data points occupy similar areas of the plot as kaolinite and feldspars respectively. The large cluster of particles with $\tau < 0.64$ is congruent the principal mode in the Imt-2 and ISCz-1 samples, and is also characterised by relatively large peak width values. Multimodal peak shapes, as described in [Figure 3](#)~~Error! Reference source not found.~~, mainly occur with $\tau > 0.64$ in the illite NX sample but were never observed with feldspar where peak widths of the SiO_3 molecular ion were always < 15 ns. Broad (>15 ns), multimodal spectral peak morphologies were attributed to aggregated or mixed particles in which the ion formation process is not uniform.

3.4 Single particle differentiation of clay mineral standards

The dependence of ~~negative peak shift~~[the ion arrival times](#) on the nature of the cations in the interstitial complex gives rise to the possibility of using these measurements to classify the mineralogical contents of mineral dust samples: [on a single particle basis](#). Using published XRD analysis data as a guide, the ~~single particle~~ classification scheme outlined in ~~Error! Reference source not found.~~ [Table 8 Table 9](#) was used to quantify the particle number concentrations [of mineral types](#) in the clay rich mineral samples illite NX, IMt-2 and ISCz-1 (~~Figure 10~~)([Fig. 11](#)). The first class of particles is defined as the group of particles with $\tau < 0.64$ which only appear in samples rich in illite clays. This class is attributed to illite-smectite clay minerals (ISCM) because in natural clay samples, illite occurs in fine interlayers with smectite clays. The second class, is particularly well developed in the illite NX and IMt-2 samples and is defined by $\tau > 0.64$ and high potassium and sodium content that is typical of the orthoclase (K-feldspar) sample. The exception is particles within this group that exhibit broad multimodal peak morphology which are placed in a separate class of mixed particles (class 5). Kaolinite (class 3) has, by definition, very low potassium and sodium content and is also defined by high τ measured in the pure form of the mineral (KGa-1b above). The fourth mineral class assigns particles with intermediate values of τ and relatively low potassium and sodium content to montmorillonite or Na-Feldspar (plagioclase) because of the difficulty in distinguishing between these two minerals with the peak analysis. In cases where the peak analysis was unable to produce a result, mainly due to failure of the peak fitting, were allocated to a not classified particle class. [Examples of raw mass spectra of each particle class are presented in the supplement \(S2\) alongside example spectra for all other mineral samples used in this study.](#)

Table 9. Single particle mineral phase classification scheme based on τ , combined potassium and sodium content, and SiO_3 molecular ion peak width.

Class	Mineral Phase	$\Delta T_o/\Delta T_{\text{SiO}_3} (\tau)$	K + Na Peak Area	SiO_3 Peak Width
1	ISCM	< 0.64		
2	K-Feldspars	> 0.64	> 15000	< 15

3	Kaolinite	> 0.885	< 15000	
4	Montmorillonite/Plagioclase	0.64 – 0.885	< 15000	
5	Mixed	> 0.64		> 15
6	Not Classified (NC)			

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The differentiation of mineral phase by this classification method has some broad agreement with the XRD analysis. The relative particle number fraction of ISCM between the three samples is in agreement with the relative mass concentration of illite derived from XRD i.e. ISCz-1 is the most illite rich followed by IMt-2 and illite NX. A greater fraction of feldspar and kaolinite is also measured for illite NX than for the other samples in agreement with XRD analysis. The main difference in the mineral fraction reported by XRD analysis and this peak analysis technique is the relative fraction of ISCM minerals with non-ISCM minerals such as K feldspar and kaolinite mineral classes. The differences may arise from comparing a number counting technique with a mass fraction, and from hit-rate bias in the LAAP-TOF measurement which may discriminate against certain particle types due to morphology and composition as discussed in section 3.3 above. In addition, the XRD analysis technique does not report the unidentified fraction of such as amorphous glassy material that may contribute to the non-ISCM fraction in the peak analysis and the degree of homogeneity with regards to mineral fractions in the bulk samples is not well characterised and may result in sample to sample and batch to batch differences in the composition of a clay mineral standard.

The relatively poor resolution of the mineral differentiation makes the identification of the exact mineral phase difficult. Whilst the plots of τ vs K + Na content (Fig. 11, top panels) produces distinct particle clusters for illite NX and IMt-2, the corresponding plot for ISCz-1 is much less differentiated. It is not clear if this occurs because of the poor resolution of the method or because the natural variation in composition of the latter sample.

3.5 Relative shift of positive and negative ions

The ratio $\Delta T_K / \Delta T_O$ is plotted against $\Delta T_O / \Delta T_{SiO_3}$ (τ), in Figure 11-Fig. 12. In this plot, the distribution of data points for borosilicate glass and orthoclase feldspar suggest a positive correlation between these ratios, with the trends in the distributions converging towards a point where the magnitude of shift of all species is equal. In illite IMt-2 the ISCM mineral fraction, identified as class 1 in the classification scheme, does not show a correlation between positive alkali metals ion and negative silicate molecular ion arrival times which may indicate a de-coupling of the positive and negative ion formation process.

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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.

~~In Matrix Assisted Laser Desorption Ionisation (MALDI), the sample is introduced on a sample plate in a fixed position. This means that initial ion velocity distributions are considered to be the primary cause of mass spectral peak broadening (Colby et al., 1994). It is not possible to empirically derive starting position. 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.~~

~~Field free extraction may be a significant feature of the LAAP TOF because 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, the ion plume is allowed to evolve without the near instantaneous extraction of positive and negative ions that is a feature of systems using extraction by an electric field. One would expect a reduced plume density and therefore a reduction in space charge effects and collisions in the ion plume as it is free to expand in all directions.~~

~~The co axial geometry of the exeimer laser with the particle beam is likely to introduce shot-to-shot variation in the position in which LDI takes place within the ion source and the commencement of ion formation with respect to the firing of the laser pulse. The location on the instrument axis at which a particle encounters the threshold fluence for LDI will vary with particle trajectory and the absorbing properties of the material.~~

~~Ion species dependence of the shift in ion arrival times recorded in the mass spectra for minerals dusts by the LAAP-TOF 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 exeimer 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 but it is not possible to empirically derive 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.~~

~~Measurement of initial kinetic energy of ions~~ 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. ~~The equal shift in ion arrival times of elemental and molecular ions observed with borosilicate glass suggests that~~ 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 ~~that could result from a thermal ionisation mechanism or a charge transfer and cluster decay ionisation mechanism, as suggested by Spengler & Kirsch, (2003) as a cause of mass dependent initial ion velocity differences in MALDI TOF.~~ 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 in a 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 11); (Fig. 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 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 provenance~~
~~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, variation in 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 peak analysis. For example, one could 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. However, it is precisely this shot to shot variation in energy and how the substance responds that gives rise to the distinct distribution in ion arrival times observed.~~

~~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. ~~Regardless of the actual ionisation mechanism, careful calibration with a sample of known mineralogy, such as dry illite NX, will provide a suitable reference. The position of the convergence point, with respect to which the shift is measured, should be checked with illite NX after alignment of the excimer laser in the ion source.~~

~~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 4.5mJ/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.

5 Conclusions

A novel technique that uses peak centroid measurement in addition to peak areas to describe the mass spectral characteristics arising from the LDI of single particles of silicate mineral dust has been presented. To our knowledge, this is the first time that the properties of a material have been described by the relative changes in the ion arrival times of an ion species at a TOF-MS detector. Examination of the spectral patterns from dust samples reveals spectrum to spectrum variation in the relative peak position of the SiO_3^- molecular ion with respect to the O^- elemental ion that occurs in distinct modes. Comparison of these modes with the borosilicate glass and carbon black suggest that the mode preference is a result of particle crystal structure and elemental composition, the properties that define mineral phase.

Analysis of clay mineral standards and nominally pure feldspars suggest that the relative shift of the elemental and molecular ions is a function of the quantity and co-ordination of potassium and sodium cations in the interstitial complex. It is proposed that the mineral phase of the particle matrix influences the ion formation mechanism and produces variations

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in initial ion velocity and ion formation timing during the LDI of single particles. These effects are enhanced by the co-axial geometry of the excimer laser with the particle beam and are preserved in the field free extraction regime in the TOF-MS implemented in the LAAP-TOF. This may represent an important step in the understanding of how LDI proceeds in SPMS.

5 Analysis of multi-mineralic clay mineral standards reveals a multi-modal pattern in ion arrival times. A scheme that classifies single particles has been defined on the basis of the alkali metal peak areas and the relative difference in the shift in the ion arrival times of the O^- and SiO_3^- species with respect to a calibration, a parameter we call τ . Application of the scheme to clay mineral standards result in the single particle differentiation of illite-smectite clays mineral (ISCM), feldspars and kaolinite that is in agreement with bulk mineralogy reported in semi-quantitative XRD analysis.

10 The nature of the interstitial complex and its effect on crystal structure can be extremely varied even within a single grain or crystal so that complete reproducibility would not be expected from any single particle measurement of a natural mineral dust sample. ~~Most naturally occurring mineral dust particles are not homogenous in composition and it is expected that the result of the peak analysis to represent the principal matrix in clay sized particle ($< 2 \mu m$).~~ In circumstances in which the actual mineral phase cannot be determined, it is still expected that the ~~ions²ion~~ arrival time ratios will be a useful
15 parameter in describing differences in physiochemical properties of silicate particles ~~in time resolved measurements.~~ This represents an important step forward in the study of atmospheric processes where single particle mineral phase is important.

Data Availability

All laboratory acquired data presented in this manuscript is available by request from the corresponding author.

Author Contribution

The experiment was designed and performed by N.Marsden with the support of M.Flynn. The data analysis was developed and performed by N.Marsden. The manuscript was prepared by N.Marsden with contribution from H.Coe and J.Allan.

Competing Interests

The authors declare that they have no conflicts of interests.

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