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 qulitate 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

Ln 18 change "markers ions" to "marker ions"

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

Pg 10 Ln 11 please rephrase the sentence starting in "The ion…"

Figure 3 – please use a higher resolution image.

Figure 6 – reformat axis labels to be more readable

Pg 17 Ln 19 – remove "Error!..."

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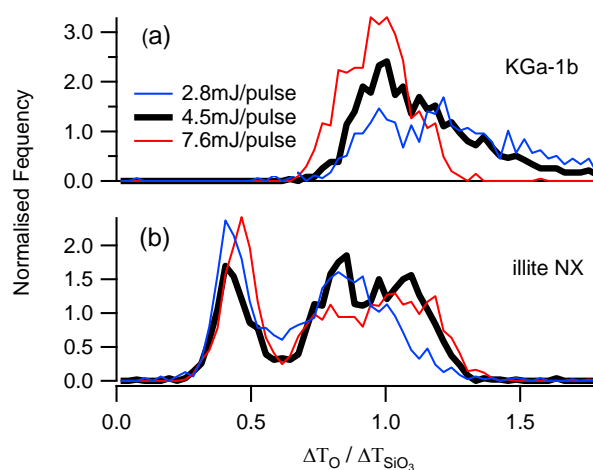
Figure 1. *Histograms of the ion arrival times shift ratio (τ) of the elemental ion O- and the molecular ion SiO_3- with different laser pulse energy settings.(a) kaolinite sample KGa-1b and (b) illite NX.*

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 4.5mJ. 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 τ > 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 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%
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 in 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 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 changed 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 leaser 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.